

## REVIEW

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# Crystal facet and surface defect engineered low dimensional CeO<sub>2</sub> (0D, 1D, 2D) based photocatalytic materials towards energy generation and pollution abatement

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Surface defect engineering and crystal facet engineering are two important strategies which effectively enhance the efficiency of a photocatalyst by modulating its physiochemical properties. To date, surface defect and morphology dependent photoactivity has been explored by using different nanostructured photocatalysts. Among them CeO<sub>2</sub> based materials have recently received foremost interest, due to their easily tunable surface structure and low formation energy for surface defects. Therefore, in this review we have comprehensively summarized the recent achievements and progress in surface defect enriched low dimensional nanostructured CeO<sub>2</sub> and CeO<sub>2</sub> based heterostructure photocatalysts towards clean fuel generation reactions such as water splitting, CO<sub>2</sub> reduction, N<sub>2</sub> fixation and organic/inorganic environmental pollutant removal applications. The present review highlights the design of CeO<sub>2</sub> with particular crystal facets and morphology and the positive impact of the crystal facets on the construction of different CeO<sub>2</sub> based heterostructure materials (0D–2D, 0D–1D, 1D–2D, 2D–2D, 0D–3D, etc.) with other low dimensional photocatalysts. Next, the surface defects, crystal facets and heterojunctional interfaces responsible for improved photoactivity are briefly discussed with proper experimental evidence and the mechanism along with the theoretical concept is explained. Further, this review sheds light on the current challenges and future perspectives in this research area.

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## 1. Introduction

Energy shortage and environmental pollution are pressing concerns that adversely impact the sustainable development of our society. Hence, the development of green, sustainable and energy-efficient methods for energy production and pollutant detoxification is of utmost concern. With regard to this,

semiconductor photocatalysis has gained enormous popularity as it can convert solar energy into some useful energy feedstocks and also act as a boon for remediation of environmental pollutants.<sup>1–8</sup> However, a major difficulty faced in this area is the low efficiency of the photocatalyst. The efficacy of a photocatalytic system generally depends upon three mechanistic features such as appropriate excitation, bulk diffusion and surface charge transfer.<sup>9–12</sup> In order to achieve the higher efficiency of a photocatalyst, all these three properties have to be controlled in a single platform. With the development of modern technology and advanced characterization techniques,

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the terminologies surface defect engineering and crystal facet engineering have come to light very recently.<sup>13–15</sup> It is found that either of these two approaches is a game changing entity for enhancing the reactivity and selectivity of a photocatalyst by modulating its physical and chemical properties.

Crystal facet engineering can efficiently modify the kinetic parameters responsible for the improved charge pair transfer and separation parameter and reaction rates of a photocatalytic reaction. In brief, morphologies with different exposed facets have different atomic rearrangement and co-ordination, and hence different morphologies exhibit different surface electronic structures (band gap, band edge potential, *etc.*), electrical conductivity, surface built-in electric field, reaction centers and reactant adsorption sites.<sup>16–19</sup> By simply changing an exposed plane to another one, there is a drastic change in the photoactivity and selectivity of a photocatalyst for a photocatalytic reaction<sup>15</sup>, so there is an increased interest in morphology tuning and crystal facet engineering. While considering a multicomponent system, crystal facet engineering in nanostructured hybrids is quite complicated, as a heterostructural interface is evolved between the individual components. Those hybrids possess individual components with their own crystal planes of different orientation as well as a distinct interface with different band energy alignment. In most of the cases, proper band alignment at the interface between two individual components is found to be very crucial for interfacial charge transfer and separation. Hence the rational design of photocatalytic systems with active surface planes and suitable interfaces is very challenging.<sup>20–26</sup> The Arienzo group prepared TiO<sub>2</sub> with (001) and (101) exposed facets by using a morphology directing agent. Both theoretically and experimentally, they proved that the 001 surface is more active for photocatalytic oxidation reaction while the exposed 101 surface is a reductive surface, as it

didn't directly assist the oxidative process.<sup>22</sup> In another example, Bomio *et al.* prepared a PbMoO<sub>4</sub> photocatalyst with predominant 111, 100, 011 and 110 facets by using a template directing agent. They found that the 001 surface exhibited the lowest activity for RhB photodegradation as the surface acts as a recombination centre of photogenerated electrons and holes.<sup>23</sup> Further, Zhu *et al.* prepared 010 and 011 facet exposed BiVO<sub>4</sub>. They found that the morphology and the distinct facets play a vital role in the anisotropic charge distribution at the photocatalyst surface. For the 011 facet the surface photovoltage signal was 70 times higher than that on the 010 facet; hence the former could be a better photocatalyst.<sup>24</sup> Further, Naresh *et al.* explained the interaction of two exposed facets of two individual components in a heterostructure. They reported that 110 exposed Cu<sub>2</sub>O (rhombohedral dodecahedra) was a more active photocatalyst towards MO degradation than 111 exposed Cu<sub>2</sub>O (octahedral), while cubic 100 exposed facet Cu<sub>2</sub>O is photocatalytically inactive. But when these are made into heterostructures with 200 exposed ZnS, Cu<sub>2</sub>O(111)/ZnS(200) performed well in comparison to Cu<sub>2</sub>O(110)/ZnS(200). The reason was attributed to the unfavourable band alignment within Cu<sub>2</sub>O(110) and ZnS(200), showing the lowest charge separation efficiency.<sup>25</sup> Hence photocatalytic activity is also strongly related to the exposed facet as well as their interfacial interaction.

Surface defects are another interesting feature which has a positive role in enhancing the photoactivity of a photocatalyst; hence defect engineering is catching more scientific significance for modifying the properties of a photocatalyst. In general, defects are created in a slightly reductive environment where the periodic arrangement is broken with little lattice distortion, and this can change intrinsic semiconductor properties such as orbital hybridization, conductivity, atom coordination number, and light absorption ability and can also change the electron density around the Fermi level.<sup>27–30</sup> Basically there are two types of defects, *i.e.* bulk defects and surface defects, and among these two, surface defects enhance the charge separation efficiency of a photocatalyst while bulk defects act as a recombination center for photogenerated charge carriers.<sup>31,32</sup> The surface defects are again classified into many divisions on the basis of dimension such as point defects, line defects, planar defects and volume defects. Surface anion vacancies (oxygen, sulphur and nitrogen) are regarded as the most explored type of vacancy which are employed in photocatalysis to modify the activity of the photocatalyst by enhancing its light absorption ability and charge transfer and separation efficiency and drive the surface reactions.<sup>33,34</sup> Moreover, in a multicomponent nanohybrid, additional defects, *i.e.* interfacial defects, are found which enhance the photoactivity by accelerating the interfacial charge pair separation.<sup>35</sup> However the controlled design of desirable vacancies in single and multicomponent photocatalysts without complete lattice distortion is very demanding. Hence, many studies have been concentrated on the design of a photocatalytic system with the combination of both surface defects and exposed crystal facets. For example, Li *et al.* prepared an oxygen vacancy enriched BiOBr(001) nanosheet and tested its effectivity towards the photocatalytic nitrogen reduction reaction. They found that the

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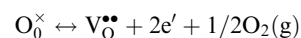


oxygen vacancy centres successfully activated the adsorbed nitrogen on BiOBr by  $\pi$ -back donation and significantly promoted the interfacial electron transfer from BiOBr to the activated nitrogen.<sup>36</sup> In another report, Zhang *et al.* designed a defect enriched WO<sub>3</sub> nanosheet and found that the as-prepared photocatalyst efficiently coupled sunlight into aerobic coupling of amines to the corresponding imines with excellent stability and enhanced the kinetic rate 6 times compared with defect deficient WO<sub>3</sub>. They deduced that defect engineering can serve as a versatile approach to refine the photocatalyst.<sup>37</sup> Apart from the surface defects, interfacial defects in a heterojunction photocatalyst also play a vital role in photocatalysis. Zhang *et al.* successfully prepared a heterostructure between MoS<sub>2</sub> QDs and ZnIn<sub>2</sub>S<sub>4</sub> in a 2-D architecture with interfacial S-vacancies. The vacancies acted as electron traps and avoided the vertical transmission of electrons.<sup>38</sup> Hence the heterostructure exhibited a high photocatalytic hydrogen evolution rate, which was higher than that of neat systems without vacancies.

Rare earth cerium oxide (CeO<sub>2</sub>) is considered as one of the most attractive metal oxides which can easily be tuned into different shapes with desired exposed facets. Further, another feature, *i.e.* surface defects, can easily be formed with very slight energy expense at the CeO<sub>2</sub> surface. Due to these special features, it is often used as a catalyst in various catalytic applications such as solid oxide fuel cells (SOFCs), ultraviolet adsorbents, glass polishing materials, water gas shift reaction, PROX (CO oxidation), oxygen sensors, selective organic transformation, photocatalytic water oxidation and pollutant degradation.<sup>27,39–43</sup> In addition to this, CeO<sub>2</sub> has other special features such as cost-effectiveness, high stability, low toxicity and specific physical and chemical characteristics, such as high oxygen storage capacity (OSC), oxygen ion conductivity and fast shuttling of oxidation state (Ce<sup>3+</sup> → Ce<sup>4+</sup>), which makes it an ideal candidate for photocatalysis.<sup>44–59</sup> In brief, the rare earth CeO<sub>2</sub> has a crystal structure of triclinic, tetragonal or cubic phase. However, mostly CeO<sub>2</sub> crystallizes in the cubic fluorite structure with a space group of *Fm*3*m* (*a* = 0.541134 nm) over the temperature range extending from room temperature to its melting point.<sup>48</sup> The fluorite structure consists of a face centred cubic unit cell of Ce<sup>4+</sup> while eight oxygen anions occupy the tetrahedral interstitial sites. As a result, each Ce<sup>4+</sup> is octahedrally coordinated by eight oxygen anions while each oxygen ion is tetrahedrally coordinated by four Ce<sup>4+</sup> cations forming a CeO<sub>8</sub> cluster as the basic unit. In cubic CeO<sub>2</sub>, mainly three exposed planes (111), (110) and (100) are observed, but due to thermodynamic restrictions, CeO<sub>2</sub> predominantly exposes the (111) plane, as it is very stable and requires low surface energy. The (111) surface plane is terminated by three-fold co-ordinated oxygen atoms, while the polar (100) surface is terminated by two-fold co-ordinated oxygen atoms. The (110) surface is terminated by a CeO<sub>2</sub> plane with three-fold co-ordinated oxygen and six-fold co-ordinated cerium atoms.<sup>29</sup>

Surface defects especially oxygen vacancies are termed as the most important feature of CeO<sub>2</sub>, which regulates all its properties. In a slightly reductive environment or at a low partial pressure of oxygen, surface defects (oxygen vacancies, interstitial metal defects) are generated on CeO<sub>2</sub>, as they require low formation energy.

In brief, surface defects in CeO<sub>2</sub> are generally created when the on plane oxygen is released from the lattice yielding a CeO<sub>7</sub> type cluster with the concomitant oxygen vacancy formed in the crystal lattice. Further, these vacancies are accompanied by localization of the electrons left behind in the Ce 4f state leading to the formation of two Ce<sup>3+</sup> ions. Hence, altogether oxygen vacancies and Ce<sup>3+</sup> are termed as surface defects on CeO<sub>2</sub> as shown in Fig. 1(a).<sup>50,51</sup> The reaction of defect formation is as follows,<sup>51</sup> where O<sub>0</sub><sup>x</sup> is the oxide ion in the lattice, V<sub>O</sub><sup>••</sup> is the charged oxygen vacancy and e' represents the electrons in the conduction band:



In addition to the doubly charged oxygen vacancy, singly charged and neutral vacancies are also present in the defective CeO<sub>2</sub> lattice.<sup>54</sup> Huang *et al.* reported a neutral oxygen vacancy (V<sub>O</sub><sup>0</sup>) centre in CeO<sub>2</sub> with very low formation energy in an oxygen-deficient environment. It acts as a deep donor with negative U (repulsive potential) behaviour leading to excellent photoactivity. In addition to this, easy shuttling of Ce<sup>3+ ↔ 4+</sup> helps to generate an anion Frankel defect which enhances oxygen storage as well as release capability.<sup>52</sup> Further, to know the structure and geometry of oxygen vacancies, Esch *et al.* thoroughly studied the defect formation and nature of defects from STM images and DFT calculations. They found that two types of oxygen vacancies are predominantly formed: the first type is the simple one oxygen vacancy which appears as a depression surrounded by three lobes, shown by the magenta triangle in Fig. 1(b), and the second type, which is called the subsurface vacancy, appears as triple protrusions centred on third layer oxygen sites (shown by the cyan triangle in Fig. 1(b)). The delocalization of the electron left behind determines which type of vacancy can be formed on CeO<sub>2</sub>. Hence, a permutation and combination of single and subsurface oxygen vacancies creates different dimeric and trimeric vacancy clusters with different orientation, which causes a major structural rearrangement in the crystal lattice of CeO<sub>2</sub>.<sup>57</sup>

Next is the optical property of CeO<sub>2</sub>. Theoretically the optical band gap of CeO<sub>2</sub> is 6–8 eV because of the transition between O 2p and Ce 5d states.<sup>49</sup> And, the experimental result reveals a bandgap of around 3 eV due to the charge transfer spectra of Ce(IV)–O(II), while the band gap may vary from 3.2 to 2.8–2.7 eV. The drastic change in the band gap and in the colour from yellow to blue-black arises only due to the presence of surface defects in CeO<sub>2</sub>.<sup>53</sup> The change is due to the oxygen vacancy, which creates a Ce<sup>3+</sup> state; thus the energy of the 4f orbitals shifts towards lower potential and hence shortens the bandgap. The density of state (DOS) of Ce 4f for Ce(III) is larger than that of Ce(IV) in the positive energy range, which indicates that Ce(III) can be more easily excited than Ce(IV) under light irradiation, which suggests that the oxygen vacancy enhances visible light absorption.<sup>55</sup> In addition to the optical property, the oxygen vacancy of CeO<sub>2</sub> also has a profound effect on the electrical as well as magnetic character. With the increase in oxygen vacancy concentration, the movement of the oxygen atom becomes





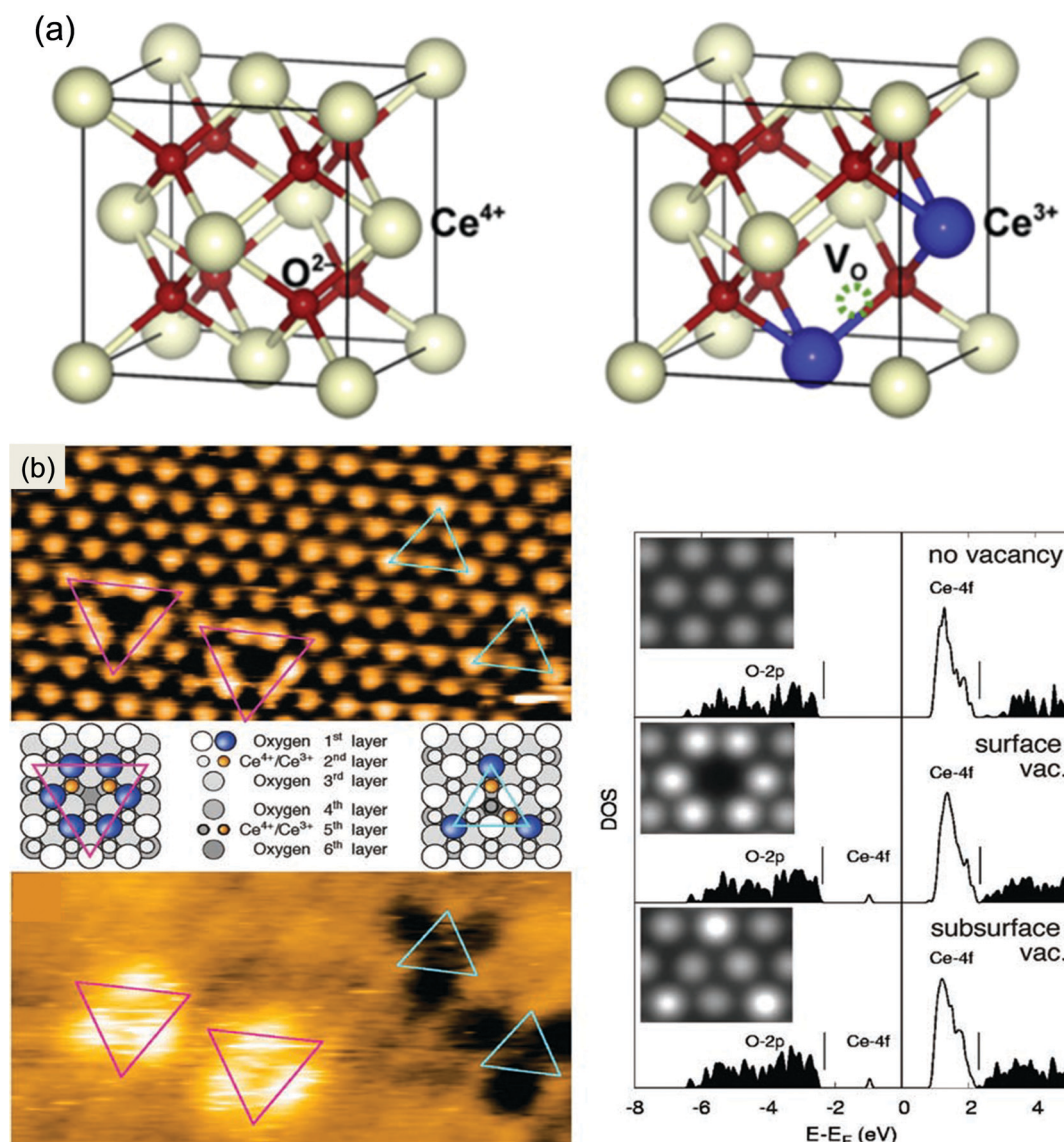


Fig. 1 (a) Crystal structure of  $\text{CeO}_2$  with the formed oxygen vacancy. Reprinted from ref. 50 with permission from Elsevier. (b) Filled-state and empty-state STM images of single and subsurface vacancies and related structural models and calculated density of states (DOS) and simulated filled-state STM images. Reproduced from ref. 57 with permission from Science.

easier in the crystal, as the vacancy easily migrates throughout the lattice *via* a vacancy hopping mechanism at an elevated temperature, and hence the crystal has a high electrical conductivity.<sup>56–58</sup> This increased diffusion rate in the lattice is a probable cause of the increase in catalytic activity.<sup>58</sup> Chen *et al.* reported that the intrinsic surface defects also have a direct relationship with the magnetic behaviour of  $\text{CeO}_2$ . They found that an increase in the local oxygen vacancies and  $\text{Ce}^{3+}$  concentration directly increases the magnetism of  $\text{CeO}_2$  nanoparticles. However, after a certain concentration of  $\text{Ce}^{3+}$  the magnetic properties gradually decrease and vanish completely. The reduction of magnetic moments may be due to ion pair formation by oxygen vacancies which favours antiferromagnetism. Further, from the X-ray magnetic circular dichroism measurement and theoretical analysis, they found that the electrons in Ce bear

magnetic moments and show magnetism *via* bound magnetic polarons which are constituted by oxygen vacancies and an oxygen mediated super-exchange framework ( $\text{Ce}^{3+}\text{--O--Ce}^{3+}$ ).<sup>5</sup> Therefore it is confirmed that oxygen defects and shuttling of oxidation states in  $\text{CeO}_2$  lead to some peculiar changes in optoelectronic, electrical as well as magnetic properties.

Another interesting feature of ceria is its morphology variation; ceria can be easily tailored to different morphologies such as nanorods, nanotubes, nanocubes, nanopolyhedra, and nanosheets with exposed active facets. Moreover, particle size and morphology have a prominent effect on the intrinsic surface defect formation in  $\text{CeO}_2$ . From the literature survey, it was found that the smaller the particle size is, the higher the surface to volume ratio will be, and hence the more defects there will be. Additionally, designing a particular shape or exposure of a specific plane in  $\text{CeO}_2$  decides



the formation and concentration of defects. Based on the DFT calculation, the (100) plane exhibits the lowest energy for vacancy formation, while the (111) crystal plane requires more energy. So based on this, nanostructures of (100) and (110) exposed facets contain more surface defects than (111) oriented surface structures.<sup>60–64</sup> Wu's group evaluated the surface defects and their relationship with the photoactivity of different exposed planes of three types of CeO<sub>2</sub> nanostructures such as nanorods, nanocubes and nano-octahedra. *Via* UV-Raman spectroscopy and O<sub>2</sub> adsorption analysis, they found that both oxidized and reduced CeO<sub>2</sub> of nanorod morphology ((110) + (100)) has the most intrinsic defects followed by nanocubes (100) and nano-octahedra (111). Furthermore, the team observed that some defects are of one electron containing singly charged species while some are two electrons containing doubly charged.<sup>63</sup> Recently by combining experimental and theoretical results, Oliveira and his group concluded that CeO<sub>2</sub> consisting of the (111) exposed plane contains only one vacancy, due to the presence of the [CeO<sub>7</sub>-V<sub>o</sub><sup>•</sup>] cluster, while (100) and (110) crystal planes exhibit two vacancies, because of the presence of the [CeO<sub>6</sub>-2V<sub>o</sub><sup>•</sup>] cluster. In the samples consisting of (100) and (110) facets with two vacancies, there is a resonance between the vacancies which stabilizes the interaction between electrons and holes. Moreover, the one vacancy containing facet shows higher stability for the formed holes only, which reduces the electrical resistance to some extent. Hence the morphology containing (100) and (110) planes shows higher photoactivity and lower electrical resistance than the (111) plane containing morphology.<sup>54</sup> In most cases, surface defects, exposed planes and morphology of CeO<sub>2</sub> are the key factors that decide the enhancement in catalytic as well as photocatalytic activity.<sup>62–64</sup> However, the vacancies can easily be healed in an oxidative environment (O-rich) and sometimes act as hole trapping centers which retards photo-efficiency. Importantly, designing a specific facet exposed system is very challenging. So fabricating CeO<sub>2</sub> based nanomaterials with controlled surface defects and a well compatible merged facet interface is getting more attention and interest.

Therefore more emphasis has been given to the construction of hybrid/heterostructure based photocatalytic systems for

potential application in the photocatalysis field. So far many such CeO<sub>2</sub> based photocatalytic systems have been made and from the recent studies it was found that the construction of heterostructure photocatalysts of different morphologies, with other visible light semiconductors, is a feasible and effective method to improve the photogenerated electron-hole separation which ultimately improves the photocatalytic efficiency under visible light. In this approach, a wide bandgap metal-oxide semiconductor, *i.e.* CeO<sub>2</sub>, is often combined with a narrow bandgap semiconductor such as other metal oxides, sulphides, phosphides, and selenides to form a heterostructure oriented system.<sup>45–48</sup> Further, the *in situ* generation of surface defects helps to minimize the hole-electron recombination and provides a strong interfacial surface for reactant binding and the corresponding dissociation, resulting in improved photoefficiency. Regarding this concept, several articles corresponding to the CeO<sub>2</sub> based photocatalytic systems have been published in the field of solar fuel generation and pollutant removal, which we have discussed in the application section.

Nanostructured CeO<sub>2</sub> has witnessed numerous possible scientific advancements and has always been the centre of attraction in photocatalysis, as summarized in Fig. 2. Currently, extensive studies have been made towards developing efficient CeO<sub>2</sub> based photocatalytic systems by adopting different advanced strategies such as surface interface tuning and defect engineering. Hence, there are several reviews on CeO<sub>2</sub> covering areas such as its properties, synthesis, nanostructure and catalytic application.<sup>27,39,45–48</sup> However, a systematic review on the current progress and growth trend of exposed facet and defect mediated CeO<sub>2</sub> based materials is highly needed to update the scientific society with regard to photocatalysis. So in this review, we have specifically discussed the strategic updates and the latest progress in exposed facet, morphology dependent CeO<sub>2</sub> with defect engineering and then CeO<sub>2</sub> based heterostructured materials towards various photocatalytic applications. In brief, the review elaborates the basic concepts and the design strategy of lower dimension (2D, 0D, 1D, 3D) CeO<sub>2</sub> with particular crystal facets and broadly summarizes the synthetic strategy involving CeO<sub>2</sub> based materials with a distinct

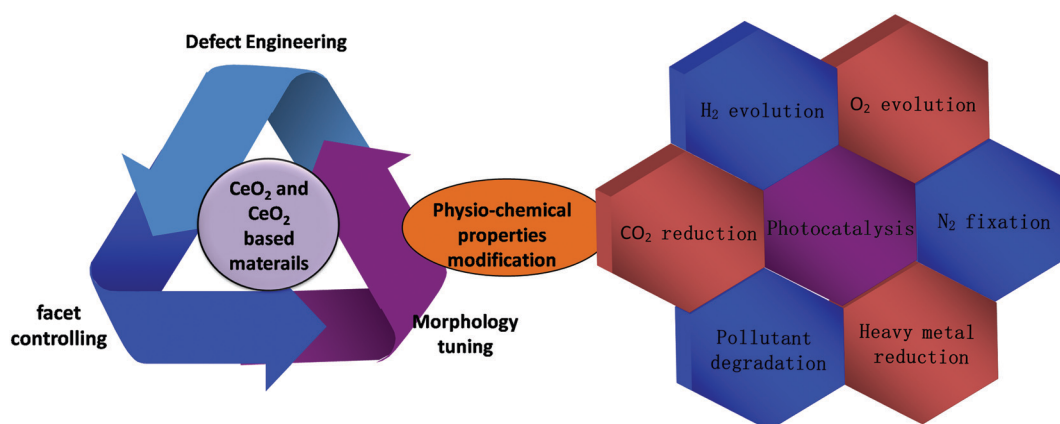


Fig. 2 Complete schematic illustration of CeO<sub>2</sub> based materials' property tuning and applications.



morphological interface such as 0D–2D, 0D–1D, 1D–2D, 2D–2D, 0D–3D, *etc.* Further, it also narrates the detailed defect chemistry of such heterointerface systems in different photocatalytic applications such as water splitting ( $\text{H}_2$  and  $\text{O}_2$  evolution),  $\text{CO}_2$  reduction,  $\text{N}_2$  reduction, and pollutant removal (dyes, phenolic derivatives, antibiotics and heavy metals) along with elucidation of morphology dependent activity correlations. At last, we throw some light on the challenges encountered and provide future direction for improvement of  $\text{CeO}_2$  based materials to achieve benchmark efficiency.

## 2. Crystal facet engineering and defect designing

During the last two decades, several synthetic methods have been reported for the preparation of nanostructured  $\text{CeO}_2$ . Generally the methods used for the synthesis of shape and size selective  $\text{CeO}_2$  with appropriate exposed active planes are precipitation, hydrothermal treatment, surfactant/capping agent-assisted solvothermal method, thermal decomposition, sol–gel combustion, template-directed synthesis, sonochemical method, microemulsion technique, electrochemical deposition and many more.<sup>65–91</sup> More often two or more methods are combined to prepare facet orientated  $\text{CeO}_2$  as summarized in Fig. 3(a). Sun *et al.*, Zhang *et al.* and Wang *et al.* have thoroughly explained the hidden mechanism and the science behind the adopted strategy toward designing different shape-selective nanostructured  $\text{CeO}_2$ .<sup>39,45,46</sup> Hence, in this section, we have briefly summarized some of the essential points for the synthesis of lower-dimensional facet oriented  $\text{CeO}_2$  and cited some latest examples of the corresponding synthesis.

The controlled nucleation and growth rate of  $\text{CeO}_2$  crystals determines the formation possibility of a particular facet, size and shape. Hence, appropriate additives such as precipitating agents/mineralisers [ $\text{NaOH}$ , urea, HMT, ammonia, *etc.*], template

[soft, hard and self], surfactant/capping agent, organic ligands, polymers, *etc.*, are often used to manage the exposed plane, shape and size of nanostructured  $\text{CeO}_2$ . For example, the commonly used solutions to obtain facet oriented  $\text{CeO}_2$  are  $\text{NaOH}$  solution (cubes, rods, wire (110)),  $\text{PO}_4^{3-}$  (octahedral, rod), and  $\text{NH}_3\cdot\text{H}_2\text{O}$  (nanowires). In addition to these, the concentration of precipitants and the reaction temperature and time are also important for obtaining different exposed facets.<sup>65–96</sup> Oliveria *et al.* prepared  $\text{CeO}_2$  of different morphology by simply varying the synthesis time *via* microwave-assisted hydrothermal synthesis. They found that when using cerium nitrate and  $\text{NaOH}$ , at first they obtained sheet like morphology, and after a certain time these sheets were elongated to form nanorods while after some time polyhedron type morphology was obtained followed by nanocubes.<sup>54</sup> Further, it was reported that anions like  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  mainly coming from the cerium precursor and the added precipitants have also influenced the morphology and the properties of  $\text{CeO}_2$ . For example, Jiang *et al.* prepared  $\text{CeO}_2$  nanocubes and nanorods by using two different cerium precursors; for nanocubes, they used cerium chloride while for nanorods they used cerium nitrate. After the hydrothermal treatment at  $110^\circ\text{C}$  for only 24 h, from both cerium precursors in  $\text{NaOH}$  solution, they got rod like morphology, while a further higher temperature treatment ( $180^\circ\text{C}$ ) yielded nanocube type morphology with only the chloride containing precursor.<sup>15</sup> In another report by Zhu *et al.*, 110 exposed facet nanorods were prepared from cerium chloride and  $\text{NaOH}$  *via* hydrothermal treatment at  $140^\circ\text{C}$  for 18 h, while 100 exposed nanocubes were prepared from the same concentration of  $\text{NaOH}$  with cerium nitrate precursor at  $180^\circ\text{C}$  for 24 h.<sup>95</sup> The controlled design of one kind of exposed facets requires more complicated reactions; hence in most of the cases nanostructured ceria is prepared by controlling the most active plane while other facets are also present but in a dormant form. Therefore a number of systematic studies on morphology oriented low dimensional nanostructured ceria with one (in some cases more than one) active facet have been carried out. From the conclusive research

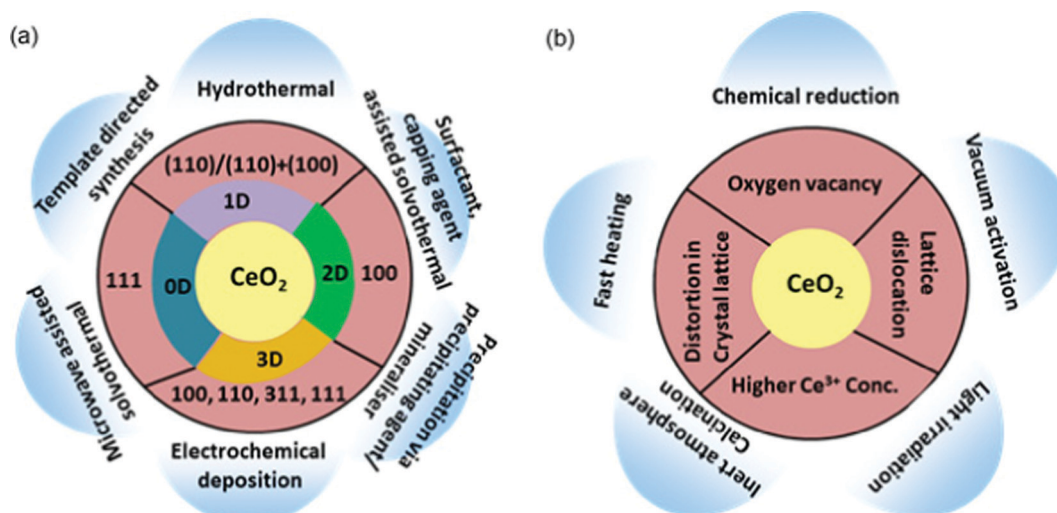


Fig. 3 (a and b) Strategy for crystal facet designing and defect engineering.



experiments it was found that by controlling the dimension of nanostructured CeO<sub>2</sub> the desired active crystal facets can be controlled simultaneously. For example, by making 1-D nanorods or nanowires, 110 + 100 exposed facets are controlled wisely, while high surface to volume ratio 100 planes are controlled by making 2-D nanosheet and 3D-nanocube like structures.<sup>81,97,98</sup> For example, Imagawa and Lin *et al.* prepared 100 exposed facet CeO<sub>2</sub> nanoplates by using oleic acid and oleylamine, while Hao *et al.* prepared monodispersed 100 exposed ceria nanocubes by a simple hydrothermal method by using decanoic acid as an organic surfactant.<sup>99</sup> In another report, a 200 exposed crystal facet CeO<sub>2</sub> nanocube was prepared by Yang *et al.* using *tert*-butyl amine as the facet directing agent.<sup>100</sup> Next, Liu *et al.* reported another CeO<sub>2</sub> morphology, *i.e.* an octahedron with a predominant 111 exposed facet, *via* a hydrothermal method followed by high pressure.<sup>101</sup> Hence, the synthesis of lower-dimensional CeO<sub>2</sub> with controlled exposed facets requires conceptual designing and experimental evidence, which we have briefly discussed in the below segments.

In addition to crystal facet engineering, surface defect designing is another crucial strategy for remodifying the photocatalyst property. Doping is considered as an effective strategy to generate defects in CeO<sub>2</sub>; however, dopants form deep impurity levels within the forbidden band of semiconductors, where they act as recombination centres and impair photocatalytic activity.<sup>102</sup> So in this review we have excluded the doping concepts and their impact on CeO<sub>2</sub> based materials. Further, a number of synthetic methods such as chemical reduction, light irradiation, vacuum activation, inert atmosphere (N<sub>2</sub>, Ar, H<sub>2</sub>) calcination, *etc.* are often combined with the general nanostructured CeO<sub>2</sub> preparation methods to achieve higher defect density at the surface as schematically presented in Fig. 3(b).<sup>28,103–106</sup> Moreover, the different exposed facets exhibited different energy for vacancy formation. In general it is found that the 110 and 100 planes exhibited higher energy for surface vacancy formation while the 111 plane required a minimum energy. Among 110 and 100, 110 CeO<sub>2</sub> has lower energy for vacancy formation than 100 CeO<sub>2</sub>. So *via* controlling the facets one can control the defects in CeO<sub>2</sub>. To further enhance the vacancy concentration, additional treatments as mentioned above are considered. For example Zhang *et al.* prepared oxygen vacancy enriched CeO<sub>2</sub> nanorods by a one step hydrothermal method followed by *in situ* reduction treatment. Briefly, they used the cerium precursor and NaOH along with NaBH<sub>4</sub> and treated the solution hydrothermally. NaBH<sub>4</sub> here acts as a reducing agent and *in situ* generates oxygen vacancies during the growth of nanorods.<sup>103</sup> And in some cases NaBH<sub>4</sub> treatment was carried out after the complete preparation of CeO<sub>2</sub> to increase the surface defect concentration.<sup>104</sup> Next, Zhao *et al.* prepared defective CeO<sub>2</sub> NRs by a simple hydrothermal method followed by calcination in different atmospheres (such as argon, a mixture of argon and hydrogen gas and air atmosphere) at 800 °C. *Via* systematic analysis through XPS, they found that in an Ar-H<sub>2</sub> atmosphere maximum surface vacancies were produced, due to the reducing nature of hydrogen gas.<sup>69</sup> Further, Aslam *et al.* synthesized nanosized CeO<sub>2</sub> by using Triton X-100 as a surfactant *via* a solution combustion method followed by 500 °C calcination.

They found that when the as-prepared CeO<sub>2</sub> was additionally treated with direct sunlight, some CeO<sub>2-x</sub> was formed on the CeO<sub>2</sub> surface. This defective CeO<sub>2</sub> exhibited enhanced absorption in the visible region and its band gap reduced from 2.9 to 2.6 eV.<sup>105</sup> Hezam *et al.* reported another O<sub>v</sub> enriched CeO<sub>2</sub> *via* a sunlight assisted combustion method. They found that more defects are present in CeO<sub>2</sub> prepared by the sunlight assisted combustion method compared to that by the conventional solution combustion method.<sup>106</sup>

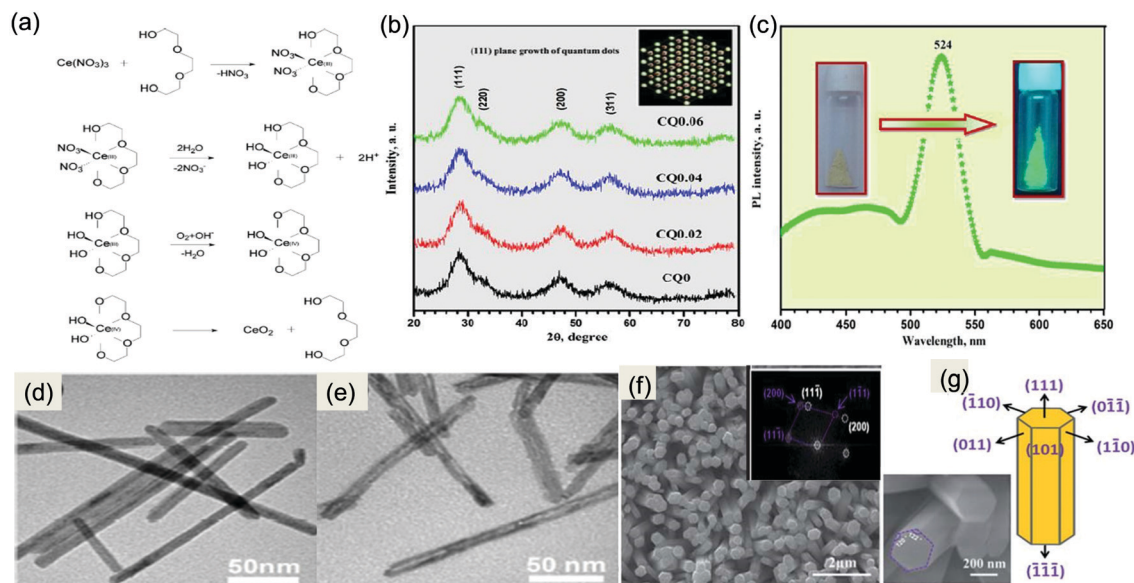
### 3. Synthesis of nanostructured CeO<sub>2</sub> and CeO<sub>2</sub> based materials

#### 3.1 Zero-dimensional CeO<sub>2</sub>

In recent years 0D quantum dots (QDs) have attracted great attention due to their size-derived properties which keep them one step ahead of their corresponding normal nanoparticles. The quantum confinement effect modulated extraordinary optoelectronic properties and prominent active sites make zero-dimensional materials promising candidates in a variety of applications including photocatalysis, electrocatalysis and biocatalysis.<sup>107</sup> Different synthesis methods like non-hydrolytic sol-gel, hydrothermal, microwave-assisted solvothermal methods, *etc.*<sup>65–68</sup> with suitable capping agents have been reported for the synthesis of CeO<sub>2</sub> QDs. In this context, Xin *et al.* proposed a synthetic route to prepare monodisperse CeO<sub>2</sub> QDs by heating a cerium precursor in triethylene glycol (TEG). In short, they obtained uniform monodisperse 5 nm QDs *via* a facile low cost, polyol condensation route which is based on the hydrolysis of the cerium alkoxide complex at an elevated temperature in the presence of an organic solvent (TEG) as shown in Fig. 4(a). The prepared CeO<sub>2</sub> QDs show good redispersion ability and a high specific surface area.<sup>65</sup> Further, Hassan and co-workers suggested two methodologies for the preparation of different size CeO<sub>2</sub> QDs. In the typical hydrothermal process, they used a mixed solution of cerium precursor along with a particular molar concentration of bases (NaOH, NH<sub>4</sub>OH) and obtained 7 nm size QDs. While in the next strategy, they obtained 3 nm QDs *via* the non-hydrolytic sol-gel method by using the cerium precursor in polyamine and then adding the organic capping agent diphenyl ether to control the size of the nanoparticles.<sup>66</sup> Moreover, in the above processes, more than one metal precursor was used in addition to the surfactant/capping agents which is quite essential for restricting the growth of QDs. In light of this, Lehne *et al.* used a single metal-organic precursor, *i.e.* a heteroleptic alkoxide complex of cerium, to obtain highly crystalline CeO<sub>2</sub> QDs with a narrow size distribution *via* the microwave-assisted solvothermal synthesis in *N*-methyl pyrrolidine.<sup>67</sup> Adding more to the text, for the biomedical application of quantum dots, their synthesis, storage and self-agglomeration were considered as serious parameters for their effective utilization. Hence incorporation of a suitable capping agent or organic moiety over the surface of QDs is an apparent solution. Arumugam's group synthesized 2.4 nm CeO<sub>2</sub> QDs capped with the anionic group 2-amino-3-chloro-5-trifluoromethyl pyridine (ACTP). From XRD it







**Fig. 4** (a) Proposed mechanism for Ce chelated complex formation with the corresponding decomposition to quantum dots. Reprinted from ref. 65 with permission from Wiley. (b) and (c) XRD pattern of plane and ACTP capped  $\text{CeO}_2$  QDs; (inset) schematic (111) plane growth of QDs and PL spectrum of  $\text{CeO}_2$  QDs, exhibiting strong green emission at 524 nm. Reprinted with permission from ref. 68, copyright 2016 American Chemical Society. (d) and (e) TEM micrographs of  $\text{CeO}_2$  nanorods and nanotubes. Reprinted from ref. 70 with permission from Springer Nature. (f) SEM images and FFT pattern showing the single-crystalline nature. (g) Schematic diagram of facet oriented  $\text{CeO}_2$  NRs and its resemblance with the FESEM image (inset).<sup>76</sup> Reproduced by permission of The Royal Society of Chemistry.

was observed that capped as well as uncapped QDs exhibited a dominant (111) plane as shown in Fig. 4(b), and the QDs' orientation was along the 110 direction. Further, they found another interesting fact, *i.e.* the synthesized QDs exhibited strong green emission at 295 nm (Fig. 4(c)), which confirms that the synthesized sample was in the quantum range with particle size  $\sim 2.4$  nm that is below its Bohr radius of 7–9 nm. Furthermore, it was found that due to the dielectric confinement effect the band gap energy values of QDs gradually decreased with the increasing amount of the capping agent, which is a good sign for photocatalysis.<sup>68</sup>

### 3.2 One-dimensional $\text{CeO}_2$

One-dimensional (1D) nanostructures (nanowires, nanorods and nanotubes) have been intensively researched due to their fascinating physical and structural behaviour along with high chemical reactivity. Because of their high aspect ratio, they are beneficial for many potential technological applications.<sup>108</sup> Different mediators such as mineralizers, organic solvents, and surfactants are used to kinetically control the 1D anisotropic crystal growth and other parameters like temperature, pH, concentration, *etc.* are also optimized for obtaining a thermodynamically favoured 1D structure.<sup>69–77,104</sup> Zhao *et al.* prepared single-crystalline nanorods *via* the hydrothermal method (140 °C for 56 h) by using  $\text{NH}_3\cdot\text{H}_2\text{O}$  as an alkaline agent without the use of any surfactant or capping agent followed by calcination.<sup>69</sup> The study showed that the additional use of a capping agent/surfactant increases the probability of one-dimensional growth at lower temperature and consumes less time.<sup>54–60</sup> Further, Cao *et al.* reported an interesting

methodology (etching–dissolution–deposition) for the preparation of hollow nanotubes at low temperature. In this procedure, they first prepared  $\text{CeO}_2$  nanorods hydrothermally by using NaOH as a precipitating agent, and then they added a Ce salt precursor to the prepared  $\text{CeO}_2$  nanorod suspension under heating to obtain  $\text{CeO}_2$  nanotubes. They proposed that the surface  $\text{Ce}^{3+}$  underwent hydrolysis and further dissolution at the tips of the nanorods resulting in nanotube formation. Further, the redeposition and crystallization on the outer sides of the nanorods yielded  $\text{CeO}_2$  nanotubes of an average diameter of 11.8 nm, as shown in Fig. 4(d and e).<sup>70</sup> In another work, Kuiry *et al.* prepared  $\text{CeO}_2$  nanotubes of diameter 40 nm and length 250 nm by using bis(2-ethylhexyl)sulfosuccinate sodium salt (AOT) as a surfactant in toluene–water solvent through the micro-emulsion technique.<sup>72</sup> Besides, 1D  $\text{CeO}_2$  has been synthesized by using some hard templates such as AAO, ZnO,  $\text{K}_x\text{Mn}_y\text{O}_z$ , *etc.* as these substrates encourage 1D nucleation.<sup>73–75</sup> For example, Wu's team first prepared  $\text{K}_{1.33}\text{Mn}_8\text{O}_{16}$  nanowires through the hydrothermal technique and then deposited  $\text{CeO}_2$  over them by a second hydrothermal treatment. The  $\text{K}_{1.33}\text{Mn}_8\text{O}_{16}$  nanowire template was instantaneously removed due to the release of an excess of  $\text{HNO}_3$  during the precipitation of  $\text{CeO}_2$  in the second hydrothermal treatment, leaving behind  $\text{CeO}_2$  nanotubes with a diameter of  $90 \pm 10$  nm which fits with the diameter of  $\text{K}_{1.33}\text{Mn}_8\text{O}_{16}$  nanowires.<sup>75</sup> Furthermore, the electrochemical deposition technique is now more popular for the growth of 1D nanostructures like nanorods and nanotubes over a conductive substrate.<sup>76,77</sup> Lu *et al.* reported hexagonal  $\text{CeO}_2$  nanorods with prominent (110) exposed planes by a facile cathodic electro-deposition technique over a Ti substrate using  $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ , and KCl chemicals at a current density of  $0.5 \text{ mA cm}^{-2}$ .



They found that the average diameter of the grown nanorods was about 200–400 nm and the length was up to 800 nm as shown in Fig. 4(f and g), while two sets of diffraction spots in the FFT pattern as shown in the inset of Fig. 4(f) confirmed the single crystalline nature with some defects.<sup>76</sup> And Zhang *et al.* fabricated nanorod and nanowire CeO<sub>2</sub> over a Cu substrate by using the same nitrate precursor at a current density of 0.44 mA cm<sup>-2</sup> and 0.88 mA cm<sup>-2</sup> respectively for 2 h at 70 °C. They found well-aligned CeO<sub>2</sub> nanorods with an average diameter of about 200 nm while the diameter of nanowires was about 80 nm.<sup>77</sup>

### 3.3 Two-dimensional CeO<sub>2</sub>

Recently 2D materials have attracted a lot of interest because of their size-derived special properties such as high conductivity, high mobility, high mechanical strength and large spin diffusion length. Their excellent properties make them an outstanding material for many catalytic and energy applications.<sup>109</sup> Metal oxide semiconductors, *i.e.* CeO<sub>2</sub>, with a cubic crystal structure have no intrinsic driving force for 2D anisotropic growth.<sup>78</sup> So, the synthesis of 2D CeO<sub>2</sub> is generally carried out by using a template/surfactant/mineraliser for controlling the crystal growth

along two or more facets.<sup>78–83</sup> Yu *et al.* synthesized CeO<sub>2</sub> nanosheets *via* a two-step hydrothermal treatment. At first, the inorganic–organic Ce–EDA hybrid nanorods were prepared by using a hydrothermal reaction at 150 °C between 1,2-ethanediamine (EDA) and Ce(OAc)<sub>3</sub>. Then, the hybrid nanorods were again hydrothermally treated at 280 °C to form single-crystal-like CeOH(CO)<sub>3</sub> nanosheets which were further calcined to obtain 2.4 nm thick ultrathin mesoporous CeO<sub>2</sub> nanosheets as schematically represented in Fig. 5(a).<sup>79</sup> Further, Yu and his research team described the synthesis of ultrathin ceria nanosheets by using a single surfactant/stabilizer (6-amino hexanoic acid) only. They found that the thickness of the nanosheet was approximately 2.2 nm and the lateral dimension was up to 4 μm as shown in Fig. 5(b and c). In the preparation procedure, at first small ceria nanocrystals stabilized by AHA were formed, and later these crystals were organized into ultrathin nanosheets through 2D self-assembly, followed by an *in situ* re-crystallization process.<sup>78</sup> Huang *et al.* prepared 2D CeO<sub>2</sub> nanosheets through electrochemical anodic deposition methods (0.2 mA cm<sup>-2</sup> for 60 min at 70 °C) over a substrate by using cerous nitrate and NH<sub>4</sub>NO<sub>3</sub>.<sup>80</sup> Likewise, Wang *et al.* reported ultrathin ceria nanoplates *via* a simple and robust solution-phase synthesis method where a soft

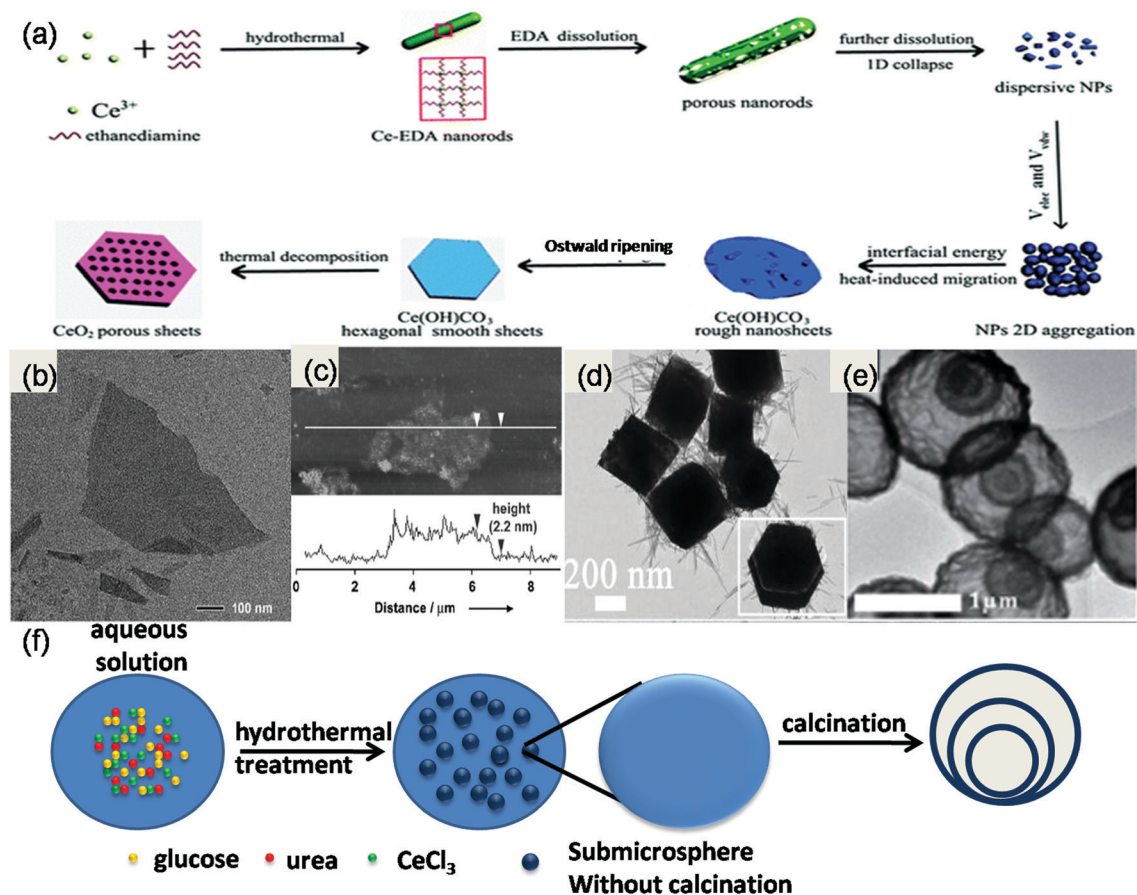


Fig. 5 (a) Structure evolution mechanism of porous CeO<sub>2</sub> sheets.<sup>79</sup> Reproduced by permission of The Royal Society of Chemistry. (b) and (c) Ultrathin CeO<sub>2</sub> nanosheets with AFM showing the single-crystalline nature. Reprinted from ref. 78 with permission from Wiley. (d) TEM micrographs of hexahedron prism anchored octahedral CeO<sub>2</sub>. Reprinted with permission from ref. 84, copyright 2015 American Chemical Society. (e) TEM micrographs of multishell CeO<sub>2</sub> and (f) complete synthetic route for preparation of this.<sup>91</sup> Reproduced by permission of The Royal Society of Chemistry.



surfactant (oleic acid or oleylamine) was used in the presence of a mineraliser (sodium diphosphate or sodium oleate) to prepare highly efficient ceria nanoplates. They concluded that thickness and morphology solely depend upon the reaction time. And the nanoplates possessed a high surface to volume ratio and the desirable high OSC(100) plane.<sup>81</sup>

### 3.4 Three dimensional CeO<sub>2</sub>

The three-dimensional nanoarchitecture with a large aspect ratio, high porosity, high surface area and high oxygen storage capacity has emerged as a promising candidate for different types of catalytic oxidation reactions.<sup>110</sup> Generally, template or surfactant-assisted methods are applied to synthesize 3D (prism, octahedron, ordered mesoporous, sphere, hollow architecture, *etc.*) CeO<sub>2</sub> materials.<sup>84–91</sup> Li *et al.* synthesized hexahedron prism anchored octahedral 3D CeO<sub>2</sub> by using phosphate ions as a mineraliser through a simple hydrothermal method, where the nanorods emerged out from the tintured octahedra as shown in Fig. 5(d). The unique hierarchical 3D structure provides selected redox facets and spatial charge separation sites, which are quite effective in enhancing the photocatalytic activity.<sup>84</sup> A pillow like CeO<sub>2</sub> microstructure of 10  $\mu\text{m}$  length and 4  $\mu\text{m}$  width was prepared by Han and co-workers by a facile solvothermal method by using a cerium salt and ammonium nitrate as starting materials at pH 10. The obtained CeO<sub>2</sub> pillows have a BET surface area of 191  $\text{m}^2 \text{g}^{-1}$  and a pore diameter ranging from 2 to 10 nm.<sup>85</sup> Through a novel hydrothermal method followed by a controlled calcination method, Sun *et al.* prepared monodisperse flowerlike CeO<sub>2</sub> microspheres containing a micro/nanostructure. Because of the simultaneous polymerization–precipitation process open three-dimensional (3D) porous and hollow structures were formed consisting of nanosheets as the petals with an average thickness of about 20 nm.<sup>86–88</sup> Besides, mesoporous ceria attracts a lot of attention as a versatile catalyst and support specimen because of its high surface area and porosity, because of which it can increase the dispersion of active secondary components. Adding more to it, Ji *et al.* reported an ordered mesoporous (OM) CeO<sub>2</sub> by using cubic Ia3d mesoporous MCM-48 silica where the obtained OM structure CeO<sub>2</sub> achieved very high efficiency towards photocatalytic dye degradation.<sup>89</sup> Further, hollow core–shell 3D structures are also investigated due to their peculiar advantageous properties. In this direction, Fang *et al.* communicated a variety of hollow 3D structures of CeO<sub>2</sub> like cubic, polyhedral and spherical through the template-engaged (Cu<sub>2</sub>O) coordinating etching technique.<sup>90</sup> However, template-free synthesis is more convenient and easy nowadays. Qi and team prepared multi-shelled CeO<sub>2</sub> hollow microspheres (Fig. 5(e)) by a simple hydrothermal method followed by calcination without using any hard or soft template. Firstly, the reaction precursor glucose was subjected to a condensation and polymerization process under hydrothermal conditions resulting in carbon microspheres. Subsequently, Ce<sup>3+</sup> ions got attached to the deprotonated functional groups inside the carbon microspheres in an alkaline environment. Finally, the as-formed carbon microspheres were used as sacrificial

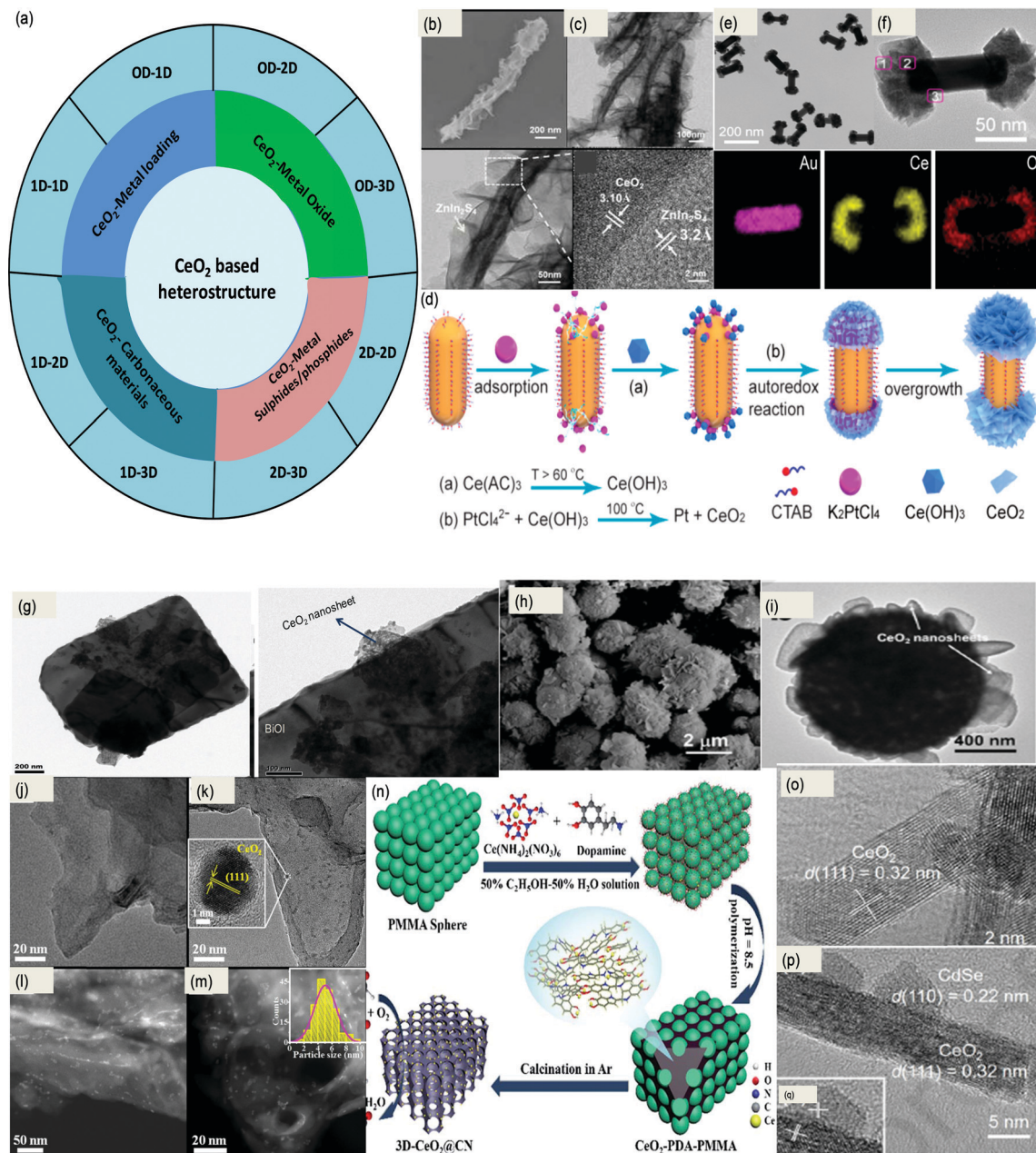
templates to obtain triple-shelled CeO<sub>2</sub> hollow microspheres *via* calcination in air as shown in Fig. 5(f).<sup>91</sup>

### 3.5 Nanostructured CeO<sub>2</sub> based materials

Considering the popularity of nanostructured CeO<sub>2</sub> in different photocatalytic applications, a wide variety of facet based CeO<sub>2</sub> heterojunctional systems such as CeO<sub>2</sub>–metal oxide, CeO<sub>2</sub>–metal sulphide/selenide, CeO<sub>2</sub>–metal phosphide, CeO<sub>2</sub>–carbonaceous materials, CeO<sub>2</sub>–metals,<sup>111–133</sup> *etc.* have been synthesized and utilized in different energy and environmental applications thoroughly. More importantly, manipulation of the morphology of non-CeO<sub>2</sub> based components is very essential regarding the design of efficient interfaced nanostructured CeO<sub>2</sub> based composite photocatalysts. This is because the dimensionality of the other units and interfacial contact between them mainly determine the activity of the composites.<sup>134</sup> On the basis of dimensionality and size, CeO<sub>2</sub> based composite materials are classified into 0D–2D, 0D–1D, 1D–2D, 2D–2D, 0D–3D, *etc.* as schematically represented in Fig. 6(a). Their synthetic procedure follows either *in situ* growth methods or *ex situ* assembly approaches or the one-pot method. But most often two or more methods are combined in these multistep reaction procedures to prepare different nanostructured CeO<sub>2</sub> based materials. For example, small-sized 2D nanosheets can grow vertically or wrap on the surface of relatively large 1D CeO<sub>2</sub>NRs. Du *et al.* reported small MnO<sub>2</sub> nanosheets decorated over CeO<sub>2</sub> nanowires *via* an *in situ* growth method. They reported a two-step hydrothermal method in which first CeO<sub>2</sub> nanowires were synthesized from Ce(OH)<sub>3</sub> nuclei, and then these nanowires were dispersed in KMnO<sub>4</sub> solution to obtain the 2D–1D heterostructure.<sup>111</sup> In another method reported by Jiang *et al.*, CeO<sub>2</sub> nanorods were derived from the Ce-MOF precursor. As shown in Fig. 6(b and c), ZnIn<sub>2</sub>S<sub>4</sub> nanosheets were beautifully anchored on top of CeO<sub>2</sub> nanorods. They carried out the beautiful 2D–1D heterostructure synthesis *via* a low-temperature solvothermal procedure. As shown in the HRTEM image, a beautiful interface is formed between the 111 plane of CeO<sub>2</sub> and the 102 plane of ZnIn<sub>2</sub>S<sub>4</sub> forming a facet merged interface.<sup>112</sup> Additionally, CeO<sub>2</sub> nanosheets decorated over Au nanorods were reported by Jia *et al.*, where simple site-selective growth of crystalline CeO<sub>2</sub> nanosheets on the end of AuNRs was observed resulting in the formation of a 2D–1D heterostructure. The AuNR capped CeO<sub>2</sub> heterostructure was prepared as follows: at first the AuNRs were prepared by using CTAB as a surfactant. Then the nanorods were re-dispersed again in CTAB solution and K<sub>2</sub>PtCl<sub>4</sub> was subsequently added to the above solution followed by the addition of a cerium precursor at moderate temperature. The design of the site-selective heterostructure was based on the following points: (i) the AuNRs have a different crystal structure and curvature difference (at the side and the end), so the less dense molecular chains of CTAB at the ends offer less steric hindrance for the other species to reach the AuNR than those of the sides, and hence PtCl<sub>4</sub><sup>2–</sup> ions preferentially adsorb at the two ends of AuNRs as shown in Fig. 6(d), (ii) further the ceria precursor is rapidly hydrolyzed into Ce(OH)<sub>3</sub> at elevated temperature and is easily oxidized by the pre-adsorbed PtCl<sub>4</sub><sup>2–</sup> to produce the nuclei for the further growth of CeO<sub>2</sub>. The preferential adsorption of PtCl<sub>4</sub><sup>2–</sup> and the autoredox







**Fig. 6** (a) Schematic representation of different types of CeO<sub>2</sub> based heterostructure. (b) and (c) FESEM and TEM (HRTEM) images of the CeO<sub>2</sub>-ZnIn<sub>2</sub>S<sub>4</sub> heterostructure showing the 2D-1D interface between 111 (CeO<sub>2</sub>) and 102 (ZnIn<sub>2</sub>S<sub>4</sub>) planes. Reprinted from ref. 112 with permission from Elsevier. (d) Schematic illustration of the synthesis process of a Au/end-CeO<sub>2</sub> nanostructure. (e) and (f) TEM, HAADF-STEM and the corresponding elemental map images of the Au/end-CeO<sub>2</sub> nanostructures. Reprinted with permission from ref. 113. (g) TEM images showing the face-to-face BiOI and CeO<sub>2</sub> 2D-2D heterostructure. Reprinted with permission from ref. 117, copyright 2019, 2018 American Chemical Society. (h) and (i) SEM and TEM images of the 3D-2D heterostructure consisting of Bi<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. Reprinted from ref. 119 with permission from Elsevier. (j) and (k) TEM and HRTEM images showing the uniform distribution of CeO<sub>2</sub> QDs over g-C<sub>3</sub>N<sub>4</sub> and (l) and (m) corresponding HAADF images and particle size distribution. Reprinted from ref. 123 with permission from Wiley. (n) Schematic representation of the synthesis procedure of 0D-3D CeO<sub>2</sub>@CN.<sup>128</sup> Reproduced by permission of The Royal Society of Chemistry. (o-q) TEM and HRTEM images showing the CdSe QD decorated CeO<sub>2</sub> NRs with lattice fringes and a clear interface. Reprinted from ref. 131 with permission from Elsevier.

reaction between  $\text{PtCl}_4^{2-}$  and  $\text{Ce}(\text{OH})_3$  result in site-selective nucleation and growth of CeO<sub>2</sub> nanosheets at the end of the Au nanorod heteronanostructure as shown in the TEM images in Fig. 6(e and f).<sup>113</sup> Further, Feng and co-workers prepared a FeOOH/CeO<sub>2</sub> heterolayered nanotube (1D-1D) over Ni foam through the electrodeposition technique by using ZnO as a hard template.

First, they deposited the CeO<sub>2</sub> layer over the ZnO NRs placed vertically over the nickel foam substrate, and then they deposited the FeOOH layer over the top of CeO<sub>2</sub> followed by removal of the ZnO template to yield a core-shell type 1D-1D heterostructure.<sup>114</sup>

Compared to other heterostructures, 2D-2D materials possess maximum hetero-interfaces and strong physical and electronic



coupling effects, which further facilitate the anti-recombination process and thus contribute to high photocatalytic performance. For example Wen *et al.* reported a face to face heterostructure, where they first prepared CeO<sub>2</sub> microplates *via* a sol-gel auto-combustion method and then BiOBr nanosheets were loaded onto the surface of CeO<sub>2</sub> with the assistance of ethylene glycol by a facile deposition-precipitation technique.<sup>116</sup> Further, Parida and co-workers prepared a series of 2D/2D-BiOI/CeO<sub>2</sub> nanocomposites through a simple precipitation technique followed by *ex situ* coupling. Initially, they prepared a CeO<sub>2</sub> nanosheet coupled with a dodecyl sulphide ion layer and then sonicated it in formamide solution. In this process the CeO<sub>2</sub> nanosheet got free and rectangular BiOI microplates were introduced onto this resulting in a beautiful face to face 2D-2D heterostructure as shown in Fig. 6(g).<sup>117</sup> Moreover, Zhang *et al.* delineated a one-pot synthetic strategy to produce vertical 2D-2D Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> nanosheets over Ti mesh *via* the hydrothermal method; then the samples were further selectively calcined in the presence of sodium hypophosphite to produce an efficient CoP-CeO<sub>2</sub>/Ti hybrid.<sup>118</sup> Furthermore, Yang *et al.* prepared a 3D-2D core-shell type Bi<sub>2</sub>O<sub>3</sub>@CeO<sub>2</sub> heterostructure through a simple two-step hydrothermal process followed by high-temperature calcination. They observed that the high-temperature treatment facilitates the outward diffusion of the interior Bi<sub>2</sub>O<sub>3</sub> leading to the formation of a more prominent 3D-2D heterojunction effective for photocatalysis. As shown in Fig. 6(h and i) 2D CeO<sub>2</sub> nanosheets are very beautifully attached to the Bi<sub>2</sub>O<sub>3</sub> sphere leading to an efficient heterostructure.<sup>119</sup> Gong *et al.* prepared a CeO<sub>2</sub>@MoS<sub>2</sub> (3D-2D) hybrid heterostructure *via* a facile two-step wet chemistry strategy. At first, they prepared CeO<sub>2</sub> hollow spheres by a template-assisted method and then few-layered ultrathin MoS<sub>2</sub> nanosheets were deposited on the hollow CeO<sub>2</sub> spheres through a hydrothermal process.<sup>120</sup>

Furthermore, CeO<sub>2</sub> QDs are in the limelight because of their outstanding size-derived properties and visible light absorbing nature; however, the associated drawbacks like self-aggregation and high charge carrier recombination restrict their photoactivity. So CeO<sub>2</sub> QDs are often combined with 1D nanorods,<sup>121,122</sup> 2D nanosheets<sup>123-126</sup> and also with 3D<sup>127-129</sup> structured materials to improve their catalytic activity. Li *et al.* prepared a 0D-1D heterostructure where CeO<sub>2</sub> QDs were decorated over sulphur doped carbon nitride nanotubes through an *in situ* deposition-precipitation technique without using any surfactant or template. They found that the CeO<sub>2</sub> QDs are distributed inside as well as outside of S-CN nanotubes.<sup>121</sup> Likewise, Xia and the group proposed a strategy for the preparation of CeO<sub>2</sub> QDs on a template. They prepared quantum sized nanoceria on to the surface of polymeric carbon nitride nanosheets (PCN) without using for growth inhibitor essential for QDs preparation. The synthetic strategy they reported is as follows: the cerium precursor was mixed with the suspension of PCN; here Ce ions adsorbed on the surface of PCN because a strong coulomb interaction existed between the positively charged Ce ion and the lone pair electron of nitrogen atoms. Upon further heating, the adsorbed Ce ions hydrolyzed with water in the presence of DMF and further calcination yielded QDs of CeO<sub>2</sub> uniformly decorated over PCN as shown

in Fig. 6(j and k). It was observed from HAADF-TEM images as shown in Fig. 6(l and m) that 5 nm sized CeO<sub>2</sub> QDs are uniformly anchored over PCN nanosheets producing a 0D-2D heterojunction.<sup>123</sup> Again, Zhang *et al.* reported a 0D-2D heterostructure between 10 nm CeO<sub>2</sub> nanoparticles and ZnIn<sub>2</sub>S<sub>4</sub> nanosheets. At first, through a simple solvothermal method, the ZnIn<sub>2</sub>S<sub>4</sub> nanosheet was prepared and the Ce<sup>3+</sup> precursor was added into the alcohol-water mixed solution containing ZnIn<sub>2</sub>S<sub>4</sub> to obtain the heterostructure. They termed the 0D CeO<sub>2</sub> nanoparticle on the 2D ZnIn<sub>2</sub>S<sub>4</sub> nanosheets as a “chess piece” on the “checkerboard” type morphology of CeO<sub>2</sub>.<sup>124</sup> Further, Luo *et al.* reported an interesting synthesis procedure for the *in situ* generation of CeO<sub>2</sub> QDs within the pores of 3D-nitrogen doped porous carbon. In the first step, self-assembled PMMA colloidal spheres were prepared and the voids were filled with ceric ammonium nitrate and dopamine solution. At pH 8.5, dopamine underwent self-polymerization and got adhered to the PMMA scaffold and in the meantime the cerium precursor was chelated by the same as shown in Fig. 6(n). Further, upon calcination the hard template (PMMA) was removed to generate the 0D-3D heterostructure.<sup>128</sup>

Besides these, 0D QD decorated CeO<sub>2</sub> nanostructures have gained a huge positive response; for example, quantum sized particles are decorated over nanorods, nanosheets, and nanoflowers of CeO<sub>2</sub> giving rise to various heterointerfaces with noticeable performance.<sup>130-133</sup> In this direction, Ma *et al.* reported a 0D-1D heterostructure containing CdS QDs over CeO<sub>2</sub> NRs through a solvothermal technique.<sup>130</sup> In addition to this work, the team also studied a 0D-1D CdSe QDs-CeO<sub>2</sub> nanorod heterostructure as shown in Fig. 6(o) through a wet chemistry method (details discussed below). They first dispersed CeO<sub>2</sub> nanorods and then added a Cd salt precursor and a capping agent, *i.e.* L-cysteine, followed by dropwise addition of a Se precursor to obtain the heterostructure. From the TEM micrographs (Fig. 6(p and q)) a clear interface between 0D CdSe QDs(110) with 1D CeO<sub>2</sub>(111) nanorods is seen.<sup>131</sup> Further Ma *et al.* also reported another heterostructure, *i.e.* CdS QD decorated Fe-CeO<sub>2</sub> based nanoflowers (3D), through a simple solvothermal method in the presence of dodecanethiol and oleylamine.<sup>133</sup>

In the past decade, nanostructured CeO<sub>2</sub> and CeO<sub>2</sub> based materials have received increasing attention as photocatalysts for pollutant degradation and solar fuel generation because of the unique properties such as biocompatibility, chemical inertness, strong oxidizing capability, higher charge separation and transportation efficiency and most importantly absorption of more photonic energy. So in the following section, we have summarized different photocatalytic applications of CeO<sub>2</sub> and CeO<sub>2</sub> based materials, with a thorough description of the theoretical concept along with some examples.

## 4. Photocatalytic water reduction and oxidation

Water splitting is a process of breaking water into its elemental constituents such as di-hydrogen and oxygen. It is a very promising approach but the process is a multielectron, endothermic uphill



reaction that requires a high positive Gibb's free energy. Thus specific energy such as solar light is required to cleave a high energy HOH bond. Generally, 2.458 eV energy is required to split one water molecule to generate one hydrogen molecule, which works under 1.23 V potential difference for the displacement of two electrons. So a photocatalyst that has the ability to decrease the overpotential required to carry out the reaction is the need of the hour.<sup>135–140</sup>

#### 4.1 Hydrogen evolution

The hydrogen evolution reaction is a major half-reaction of water splitting which generates sustainable clean H<sub>2</sub> energy. To replace fossil fuels, different fuels have been investigated recently, among which hydrogen has emerged as an appealing clean and green energy resource for future generation energy systems. It has a high energy density as compared to other hydrocarbon fuels and doesn't release any harmful toxic gases into the environment after its use. Thus, it can minimize pollution as well as reduce greenhouse gas emissions. Currently, most of the H<sub>2</sub> is prepared from either the hydrocarbon steam reforming process or the coal gasification process, which are high energy-consuming processes and require very high temperature processing. So its generation by utilising solar

energy through water splitting is the most suitable and promising approach.<sup>135–157</sup> In this regard CeO<sub>2</sub> and CeO<sub>2</sub> based materials are explored both theoretically and practically towards the photocatalytic H<sub>2</sub> evolution reaction as summarized in Table 1.

Water splitting over ceria includes 2 major steps: the first is water hydroxylation and the second is H<sub>2</sub> formation. First water molecularly adsorbs by the oxygen atom on the top of the Ce atom of CeO<sub>2</sub>(111), while water adsorbs dissociatively near the oxygen vacancy of defect enriched CeO<sub>2</sub>(111) and in both cases one H of water bonds with the surface oxygen atom. Then water dissociation into hydroxyl takes place and the surface vacancies facilitate the water dissociation step. And finally hydroxyl decomposition occurs and liberates H<sub>2</sub> through an asymmetric process, which involves oxidation of Ce<sup>3+</sup> to Ce<sup>4+</sup>.<sup>158–160</sup> Further, in the case of excessive hydroxylated CeO<sub>2</sub>, water hydroxylation and liberation of H<sub>2</sub> might involve a new intermediate, *i.e.* Ce–H. It is found that the OH species plays a very important role in water splitting and its formation and H<sub>2</sub> liberation mainly depend upon the surface vacancy.<sup>160</sup> Further Mullins *et al.* did theoretical calculations over both planes of reduced CeO<sub>2</sub>(100) and CeO<sub>2</sub>(111). They found that dissociation is much more favorable on CeO<sub>2</sub>(100) than on CeO<sub>2</sub>(111); however, in the reduced state H<sub>2</sub> generation occurs much more on CeO<sub>2</sub>(111)

**Table 1** Complete results of the H<sub>2</sub> evolution performance of CeO<sub>2</sub> and CeO<sub>2</sub> based heterostructures

Materials	Light source	Experimental conditions	Activity	Ref.
Defective CeO <sub>2</sub> NRs	300 W Xe lamp	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	5.020 μmol h <sup>−1</sup> g <sup>−1</sup>	71
Single crystalline hexagonal CeO <sub>2</sub> NRs(110)	300 W Xe lamp	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	741 μmol h <sup>−1</sup> g <sup>−1</sup>	76
Au@CeO <sub>2</sub>	50 W Xe lamp	Methanol sacrificial agent, Pt co-catalyst	8.7 μmol h <sup>−1</sup> mg <sup>−1</sup>	162
Au@CeO <sub>2</sub>	300 W Xe lamp (λ > 420 nm)	Methanol sacrificial agent	4.05 μmol mg <sup>−1</sup> h <sup>−1</sup>	163
CdS QDs/CeO <sub>2</sub> NRs	300 W Xe lamp (λ > 300 nm)	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	101.12 μmol h <sup>−1</sup> g <sup>−1</sup>	130
CdSe QDs/CeO <sub>2</sub> NRs 111 facet	300 W Xe lamp (λ > 300 nm)	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	283.32 μmol h <sup>−1</sup> g <sup>−1</sup>	131
CdS/CeO <sub>2</sub>	300 W Xe lamp (λ > 420 nm)	Lactic acid	8.4 mmol h <sup>−1</sup> g <sup>−1</sup>	165
Mn <sub>0.2</sub> Cd <sub>0.8</sub> S QDs/2D CeO <sub>2</sub>	Xenon lamp with a power of 5 W, λ > 400 nm	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	8.73 mmol g <sup>−1</sup> h <sup>−1</sup>	166
MoS <sub>2</sub> (2 wt%)-CeO <sub>2</sub>	150 W Xe lamp	Methanol sacrificial agent	2.542 mmol h <sup>−1</sup> g <sup>−1</sup>	167
1D/2D-CeO <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp AM 1.5G filter	50 μL of BA was dispersed in 5 mL of acetonitrile	1496.6 μmol g <sub>cat</sub> <sup>−1</sup> h <sup>−1</sup>	112
0D/2D CeO <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp (λ > 420 nm)	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	847.42 μmol h <sup>−1</sup> g <sup>−1</sup>	124
SnS <sub>2</sub> -Ce <sub>2</sub> S <sub>3</sub> -CeO <sub>2</sub>	300 W Xe lamp AM 1.5G filter	TEOA	240 μmol g <sup>−1</sup> h <sup>−1</sup>	168
CeO <sub>2</sub> /ZnS-CuS	300 W Xe lamp	Methanol sacrificial agent	13.47 mmol g <sup>−1</sup> h <sup>−1</sup>	169
CeO <sub>2</sub> QDs/carbon	300 W Xe lamp	Methanol sacrificial agent	582 μmol g <sup>−1</sup> h <sup>−1</sup>	129
CeO <sub>2</sub> @N,S-C	300 W Xe lamp	TEOA	555 μmol h <sup>−1</sup> g <sup>−1</sup>	170
CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp (λ > 420 nm)	TEOA, 1.5 wt% Pt	0.83 mmol h <sup>−1</sup> g <sup>−1</sup>	171
c-CeO <sub>2</sub> (100) and g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp (λ > 420 nm)	TEOA, 3 wt% Pt	860 μmol h <sup>−1</sup> g <sup>−1</sup>	173
rCN{110} > cCN{100} > oCN{111}	300 W Xe lamp (λ > 420 nm)	TEOA, 3 wt% Pt	rCN – 1100 μmol h <sup>−1</sup> g <sup>−1</sup>	174
CeO <sub>2</sub> QD-S-doped g-C <sub>3</sub> N <sub>4</sub> NR	300 W Xe lamp (λ > 420 nm)	TEOA, 1 wt% Pt	2923.8 μmol h <sup>−1</sup> g <sup>−1</sup>	121
CeO <sub>2</sub> /ZnONTs FTO	300 W Xe lamp	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	2.7 μmol cm <sup>−2</sup> h <sup>−1</sup>	175
CeO <sub>2</sub> -ZrO <sub>2</sub>	300 W Xe lamp	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	≈ 4 μmol g <sup>−1</sup> h <sup>−1</sup>	176
W <sub>18</sub> O <sub>49</sub> /CeO <sub>2</sub>	300 W Xe lamp (λ > 400 nm)	TEOA	0.2061 mmol g <sup>−1</sup> h <sup>−1</sup>	177
MOF-derived NiO/CeO <sub>2</sub>	300 W Xe lamp	Methanol sacrificial agent	29.6 μmol h <sup>−1</sup> g <sup>−1</sup>	178
CeO <sub>2</sub> /CeVO <sub>4</sub> /V <sub>2</sub> O <sub>5</sub>	300 W Xe lamp	MB aqueous solution (50 mg L <sup>−1</sup> )	47.42 μmol g <sup>−1</sup> h <sup>−1</sup>	179
CeO <sub>2</sub> -MoS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> as 0D/2D	UV light emitting diodes (UV-LEDs) (λ > 420 nm)	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	1308 μmol g <sup>−1</sup> h <sup>−1</sup>	139
(110) CeO <sub>2</sub> -IT/2HMoS <sub>2</sub>	UV-light emitting diodes	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	73.1 μmol h <sup>−1</sup>	180
CeO <sub>2</sub> -CuO QDs/graphene	300 W Xe lamp	Methanol sacrificial agent	2481 μmol g <sup>−1</sup> h <sup>−1</sup>	181
3DOM Ag/CeO <sub>2</sub> -ZrO <sub>2</sub>	300 W Xe lamp	Na <sub>2</sub> S–Na <sub>2</sub> SO <sub>3</sub> sacrificial agent	6.62 μmol h <sup>−1</sup>	182
Ag-ZnO-CeO <sub>2</sub>	300 W Xe lamp	Glycerol	18 345 μmol g <sup>−1</sup> h <sup>−1</sup>	183
Rod-rod	AM 1.5G filter	—	—	—
MoS <sub>2</sub> /CeO <sub>2</sub> -Co <sub>3</sub> O <sub>4</sub>	5 W LED lamp (λ > 420 nm)	TEOA	221 μmol in 3 h	184
Ni-P/CeO <sub>2</sub> -TiO <sub>2</sub>	Solar simulator (1 sun)	—	1300 μmol/5 h	185





than on the former due to the different adsorption sites. On reduced  $\text{CeO}_{2-x}$ (111) the dissociated water easily reoxidizes the ceria substrate, liberating  $\text{H}_2$ .<sup>161</sup> In accordance with the above prediction different  $\text{CeO}_2$  based materials were explored in the water splitting reaction as follows. Lu *et al.* synthesized single crystalline hexagonal  $\text{CeO}_2$  NRs, directly grown on Ti substrates with highly exposed (110) planes, which showed significant photocatalytic activity for hydrogen evolution ( $741 \mu\text{mol g}^{-1}$ ) in  $\text{Na}_2\text{S}$ – $\text{Na}_2\text{SO}_3$  solution. They also tested the hydrogen evolution activity in methanol as a scavenger, where  $\text{CeO}_2$  NRs exhibited a higher activity than commercial  $\text{CeO}_2$ , CdS as well as P25 due to the presence of exposed 110 active planes; however the yield rate was one fourth of that obtained with the sodium sulphide/sulphite scavenger because of the special redox capacity of the latter. Moreover, they observed a red shift in the absorption edge of  $\text{CeO}_2$  NRs due to the presence of  $\text{Ce}^{3+}$  defects, hence harvesting more visible light which may be another cause of enhanced activity, and in addition the presence of  $\text{Ce}^{3+}$  acted as an intermediate medium which accelerated the hole consumption of the sacrificial agent, hence enhancing the availability of reducing electrons for the water reduction reaction.<sup>76</sup> Further, Dong *et al.* reported another defective  $\text{CeO}_2$  NR towards photocatalytic hydrogen evolution. They prepared high surface area ( $65.26 \text{ m}^2 \text{ g}^{-1}$ )  $\text{CeO}_2$  NRs by a simple hydrothermal method with a higher percentage of  $\text{Ce}^{3+}$  (22.53%) and oxygen vacancies (0.74).<sup>71</sup> The as-prepared nanorods displayed hydrogen production at a rate of  $5.020 \text{ mmol g}^{-1} \text{ h}^{-1}$  under solar light irradiation, and the enhanced activity was attributed to the favourable band structure, which enabled the effective photonic energy absorption along with the redox shuttle of  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$ , which retarded the charge recombination.

However nanostructured  $\text{CeO}_2$  alone doesn't give appreciable results as compared to others, because of its high recombination rate of photogenerated excitons and the low ability for solar light absorption. Hence,  $\text{CeO}_2$  is often combined with noble metals<sup>162,163</sup> or other photocatalysts/co-catalysts.<sup>164–169</sup> Dao *et al.* developed a novel route for the synthesis of the  $\text{Au@CeO}_2$  core-shell functionalized with Pt. The  $\text{Au@CeO}_2$  nanostructure photocatalyst was further tested for the  $\text{H}_2$  evolution reaction under visible light and it exhibited  $\text{H}_2$  production efficiency at a rate of  $8.7 \mu\text{mol h}^{-1} \text{ mg}^{-1}$ . The enhanced activity was attributed to the SPR effect of Au, which was helpful for visible light absorption and the corresponding charge carrier generation. Further, the photogenerated hot electrons travel *via* direct injection and cross tunnelling into the conduction band of  $\text{CeO}_2$ , where they travel to the Pt co-catalyst and reduce the adsorbed  $\text{H}^+$ .<sup>162</sup> Further, a number of modified nanostructured  $\text{CeO}_2$  materials in combination with other low bandgap materials such as metal sulphides<sup>112,124,130,131,164–169</sup> have been reported compared to neat  $\text{CeO}_2$ . You *et al.* synthesized a type II heterojunction composite between CdS NPs and  $\text{CeO}_2$  NRs and tested its photocatalytic activity towards the hydrogen evolution reaction. Under visible-light irradiation ( $\lambda > 420 \text{ nm}$ ) the as-prepared 1:1 ratio CdS/ $\text{CeO}_2$  achieved an optimum  $\text{H}_2$  evolution rate of  $8.4 \text{ mmol h}^{-1} \text{ g}^{-1}$ , with a high apparent quantum yield (AQY) around 11.2%. The enhanced activity

can be attributed to the promoted lifetime and separation efficiency at the heterojunction interface.<sup>165</sup> Recently, Ma *et al.* reported the  $\text{H}_2$  evolution activity of CdS QD decorated  $\text{CeO}_2$  NRs and observed an optimum rate of  $\text{H}_2$  production, *i.e.*  $101.12 \mu\text{mol h}^{-1} \text{ g}^{-1}$  (3 atm% CdS) which was 45 times higher than that of neat  $\text{CeO}_2$  NRs under light irradiation (300 W Xe lamp  $\lambda > 300 \text{ nm}$ ) as shown in Fig. 7(a). The enhanced photoactivity for a prolonged period of 60 h was mainly attributed to higher light absorption ability, enhanced charge transfer and separation efficiency and greater lifetime of photogenerated charge carriers due to the presence of the CdS component. The efficient charge transfer mechanism was found to be of the Z-scheme type instead of the heterojunction type charge transfer mechanism as shown in Fig. 7(b) where higher reducible electrons resided at the conduction band of CdS while higher oxidizable holes were quenched by the sulphide/sulphite scavenger over the  $\text{CeO}_2$  surface. They represented solid evidence of the Z-scheme, where the catalyst responds to both hydroxyl and superoxide radicals in the spin trapping ESR experiment as shown in Fig. 7(c and d) despite the incapability of neat CdS for hydroxyl radical generation, thereby proving that the photogenerated charge separation occurred through the Z-scheme rather than the conventional double charge transfer mechanism.<sup>130</sup> Moreover, in addition to CdS, Ma *et al.* reported CdSe QD decorated  $\text{CeO}_2$  NRs for photocatalytic hydrogen evolution and they found a rate of  $283.32 \mu\text{mol h}^{-1} \text{ g}^{-1}$ , which is higher than that of the neat component. Further through DFT analysis they found that the 111 exposed facet interwined heterostructure increases the water adsorption ability and creates a lower energy barrier for water dissociation, while the same Z-scheme mechanism was followed by this heterostructure also.<sup>131</sup> Wang *et al.* reported another 0D–2D heterostructure where  $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$  quantum dots were decorated over a 2D  $\text{CeO}_2$  building block and gave rise to a perfect 0D(101)–2D(111) interface. They used different types of scavengers such as methanol, lactic acid and the sulphide + sulphite mixture and observed that the catalytic efficiency was continuously decreased in methanol and lactic acid solution, while the activity was retained in the sulphide+ sulphite solution. As the photocatalyst contains metal sulphide, upon light irradiation the metal sulphide corrodes down which retards its long term activity in the methanol scavenger solution. Hence, they observed that  $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$ – $\text{CeO}_2$  exhibited a maximum hydrogen production rate of  $8.73 \text{ mmol g}^{-1} \text{ h}^{-1}$  in the sulphite/sulphide scavenger solution with an apparent quantum efficiency greater than 2 at 400 nm. The introduction of  $\text{CeO}_2$  prolonged the lifetime of the photogenerated charge pair through the Z-scheme, and thereby increased the charge separation efficiency and lowered the charge transfer resistance.<sup>166</sup> Recently, 1D/2D and 0D/2D heterostructures between  $\text{CeO}_2$  and  $\text{ZnIn}_2\text{S}_4$  have gathered attention, as  $\text{ZnIn}_2\text{S}_4$  can easily be tuned to two dimensional nanosheet materials.<sup>112,124</sup> Jiang *et al.* prepared  $\text{ZnIn}_2\text{S}_4$  nanosheets which were grown *in situ* on the surfaces of  $\text{CeO}_2$  nanorods. The 2D/1D composites exhibited a hydrogen production yield of  $1496.6 \mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$  in tandem with the selective oxidation of aromatic alcohol, due to the synergistic advantage of both  $\text{CeO}_2$  and  $\text{ZnIn}_2\text{S}_4$ . The combined effect of both the moieties especially that of the excellent  $\text{ZnIn}_2\text{S}_4$  nanosheets is



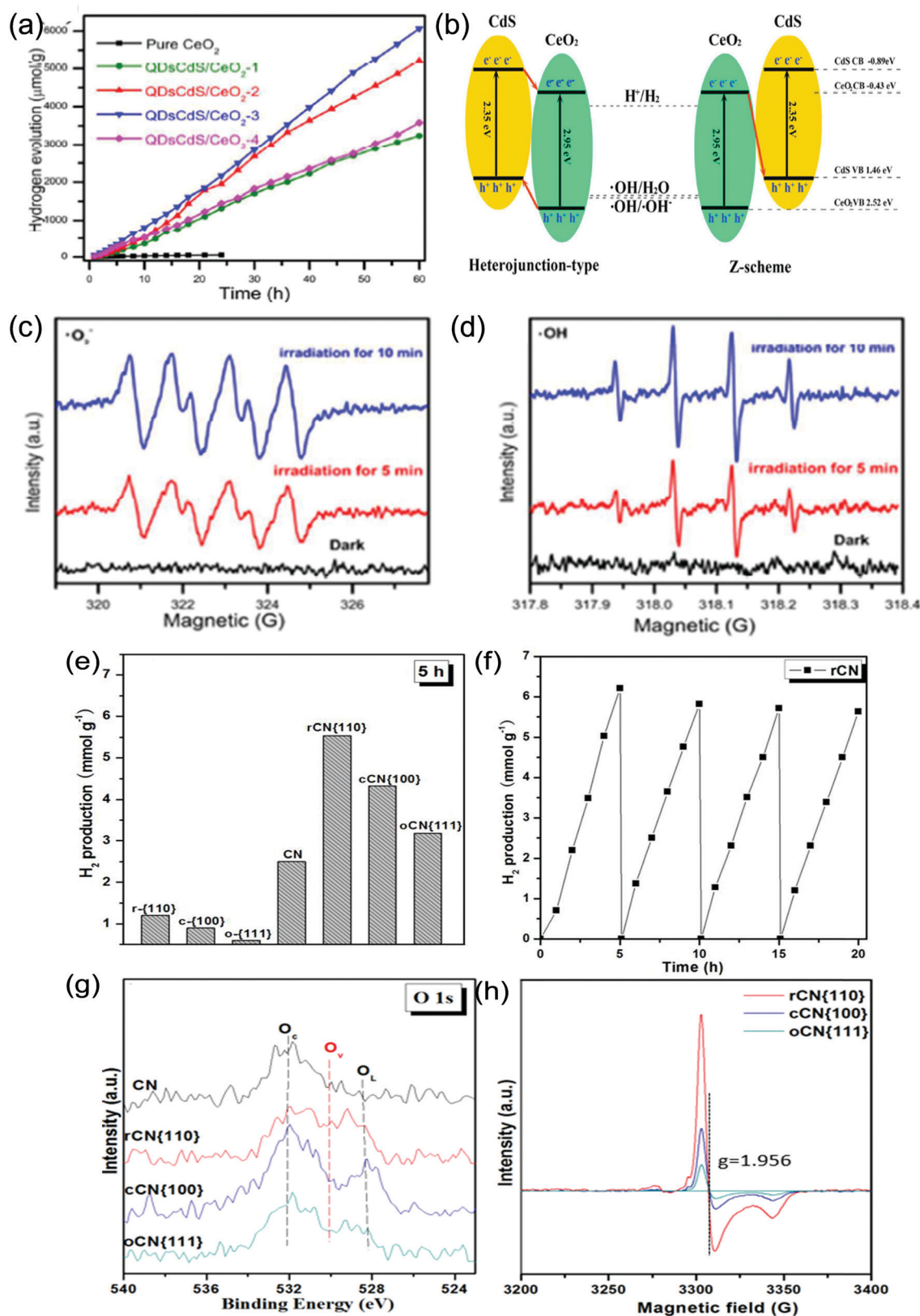


Fig. 7 (a) Photocatalytic hydrogen evolution over CeO<sub>2</sub> nanorods and CdS QD decorated CeO<sub>2</sub> in 60 h. (b) The possible photocatalytic mechanism exploration of the heterojunction-type and Z-scheme over the CdS QDs/CeO<sub>2</sub> nanorod 0D/1D heterostructures. (c and d) The DMPO spin-trapping ESR spectra of CdS QDs/CeO<sub>2</sub>-3 composites. Reprinted with permission from ref. 130, copyright 2018 American Chemical Society. (e) H<sub>2</sub> production of CeO<sub>2</sub> nanorods, cubes, octahedra, CN, rCN, cCN, and oCN composites under visible light irradiation after 5 h. (f) Reusability test of the rCN composite. (g) O 1s XPS spectra of CN, rCN, cCN, and oCN. (h) ESR results of rCN, cCN, and oCN. Reprinted from ref. 174 with permission from Elsevier.



helpful for visible-light absorption and CeO<sub>2</sub> nanorod enabled one directional charge transport contributes to higher efficiency of the composite. Moreover, intimate interfacial contacts are formed in the solid Z-scheme heterostructures, which accelerate the charge transfer and separation while retaining the strong reducibility of electrons in the CB of ZnIn<sub>2</sub>S<sub>4</sub> nanosheets and the oxidizability of holes in the VB of CeO<sub>2</sub> nanorods.<sup>112</sup> Moreover, *in situ*-MOF derived CeO<sub>2</sub> based materials have also come to light.<sup>169,170</sup> With respect to this, Wang *et al.* prepared a CeO<sub>2</sub>-ZnO nanoheterostructure from a Ce-doped ZIF-8 MOF as the precursor. Further through an *in situ* vulcanization process the above heterostructure was converted to CeO<sub>2</sub>-ZnS, which showed the best photocatalytic hydrogen production performance. However, further loading of the CuS co-catalyst *via* an *in situ* cation exchange method led to a hydrogen production rate of 13.47 mmol g<sup>-1</sup> h<sup>-1</sup> which was about 1.4 times that of CeO<sub>2</sub>/ZnS.<sup>169</sup>

Nanostructured CeO<sub>2</sub> has also been modified with carbon-based materials such as carbon, graphene, and g-C<sub>3</sub>N<sub>4</sub>,<sup>121,129,171-174</sup> and it was found to show better photocatalytic activity than neat CeO<sub>2</sub>. For example, recently Qian *et al.* reported a new biotemplate oriented synthetic strategy for the synthesis of zero dimensional CeO<sub>2</sub> QDs embedded in a porous carbon tube. The biotemplate carbonization process provided a layer matrix and a small amount of oxygen for QD deposition and growth. The obtained 3D porous CeO<sub>2</sub> QDs/carbon exhibited the highest H<sub>2</sub> evolution rate which was 5.5 times higher than that of the bulk CeO<sub>2</sub> due to the presence of defective CeO<sub>2</sub> along with its quantum dot property. Upon visible light irradiation, the photogenerated electrons and holes were produced at the CeO<sub>2</sub> surface, where the electrons drifted towards the carbon skeleton *via* the Ce-C bond, thereby accelerating charge pair separation as well as effective utilization of these energetic electrons towards the water reduction reaction.<sup>129</sup> Next, Zou *et al.* synthesized CeO<sub>2</sub> nanocubes decorated over g-C<sub>3</sub>N<sub>4</sub> nanosheets and described the interaction through hydrogen bonds and a p- $\pi$  hybrid between c-CeO<sub>2</sub>(100) and g-C<sub>3</sub>N<sub>4</sub>. Further, the H<sub>2</sub> evolution activity was determined to be 4300  $\mu$ mol g<sup>-1</sup> for 5 h illumination, which was higher than that of pristine CeO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub> and irregular CeO<sub>2</sub> nanoparticles/g-C<sub>3</sub>N<sub>4</sub>. The same group performed another extensive study and compared the hydrogen evolution activity of morphology dependent (cube, rod and octahedral) CeO<sub>2</sub> coupled g-C<sub>3</sub>N<sub>4</sub>. They found that the CeO<sub>2</sub> nanorod with an exposed 110 facet when combined with the g-C<sub>3</sub>N<sub>4</sub> nanosheet gave a much higher hydrogen production value than the others because of the stronger built-in interface. In brief, they prepared morphology tunable CeO<sub>2</sub> with (110), (100), and (111) exposed planes and found that the crystal planes of CeO<sub>2</sub> greatly alter some of the characteristics in the CeO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> heterostructure. They observed that 110 exposed CeO<sub>2</sub> nanorod modified g-C<sub>3</sub>N<sub>4</sub> exhibited higher photocatalytic hydrogen production efficiency than other CeO<sub>2</sub> modified samples as shown in Fig. 7(e) and the order was found to be CeO<sub>2</sub> NR(110)/g-C<sub>3</sub>N<sub>4</sub> > CeO<sub>2</sub> Cube(100)/g-C<sub>3</sub>N<sub>4</sub> > CeO<sub>2</sub> octahedron (111)/g-C<sub>3</sub>N<sub>4</sub> > g-C<sub>3</sub>N<sub>4</sub>. And also the optimally prepared catalyst retained its photoactivity in more than one cycle for up to 20 h (Fig. 7(f)). Furthermore, as shown in Fig. 7(g and h), from the XPS and ESR analysis it was found that the 110 rod shaped CeO<sub>2</sub> possesses more oxygen vacancies and higher Ce<sup>3+</sup> concentration. Hence, the surface oxygen vacancies

played a major role in determining the photoactivity. Further from DFT analysis, it was found that nanorod decorated g-C<sub>3</sub>N<sub>4</sub> showed significant charge transport and separation at the interface, as the charge was increased in the C and N of g-C<sub>3</sub>N<sub>4</sub> while it was decreased in the Ce atom of CeO<sub>2</sub>, which led to better charge separation under light illumination than in the other materials.<sup>173,174</sup>

Further, other metal oxide combined CeO<sub>2</sub> nanostructures have also been explored in the field of the photocatalytic hydrogen evolution reaction.<sup>175-179</sup> For example, Zeng *et al.* reported a CeO<sub>2</sub>/ZnONTs FTO heterojunction through a two-step electrodeposition technique and tested its photocatalytic H<sub>2</sub> evolution activity which was found to be 2.7  $\mu$ mol cm<sup>-2</sup> h<sup>-1</sup>. The higher photocatalytic activity was attributed to a larger surface area, more active sites and effective electron-hole separation at the interface between two metal oxides.<sup>175</sup> Recently Shen *et al.* prepared a novel heterojunction photocatalyst W<sub>18</sub>O<sub>49</sub>/CeO<sub>2</sub> *via* a hydrothermal strategy. Under visible light irradiation, the oxygen vacancy enriched heterostructure exhibited the highest hydrogen production efficiency of about 0.2061 mmol g<sup>-1</sup> h<sup>-1</sup> which was 1.93 times higher than that of pure CeO<sub>2</sub>. According to the DFT calculations, the authors claimed that between CeO<sub>2</sub> and W<sub>18</sub>O<sub>49</sub>, the Z-scheme charge transfer mechanism occurred, which retarded the efficient charge recombination, and hence electrons accumulated over the CeO<sub>2</sub> surface and reacted with H<sup>+</sup> to yield H<sub>2</sub>.<sup>177</sup> Apart from all of these, nanostructured CeO<sub>2</sub> is also combined with more than one photocatalyst or co-catalyst towards the productive hydrogen evolution reaction.<sup>180-185</sup>

## 4.2 Oxygen evolution

The oxygen evolution reaction is another half reaction of water splitting, where water is oxidized to generate oxygen gas in the presence of a catalyst. It is a core process of many energy storage and conversion systems, such as solar cells, fuel cells, metal-air batteries, *etc.*<sup>186-197</sup> And for the water electrolysis to produce sustainable H<sub>2</sub> energy, water oxidation is a preliminary reaction. It is a multi-electron and multi-proton reaction, and is therefore kinetically as well as energetically a difficult/sluggish process. This is because for the generation of one molecule of O<sub>2</sub>, four protons and four electrons are required. In order to oxidize two water molecules simultaneously, the catalyst must be able to store four electrons-holes close together.<sup>197</sup> So a catalyst which can absorb water and simultaneously oxidize two water molecules is a promising one. Since CeO<sub>2</sub> has the ability to carry out water oxidation smoothly, a number of CeO<sub>2</sub> based materials have been explored in this field which are summarized below.

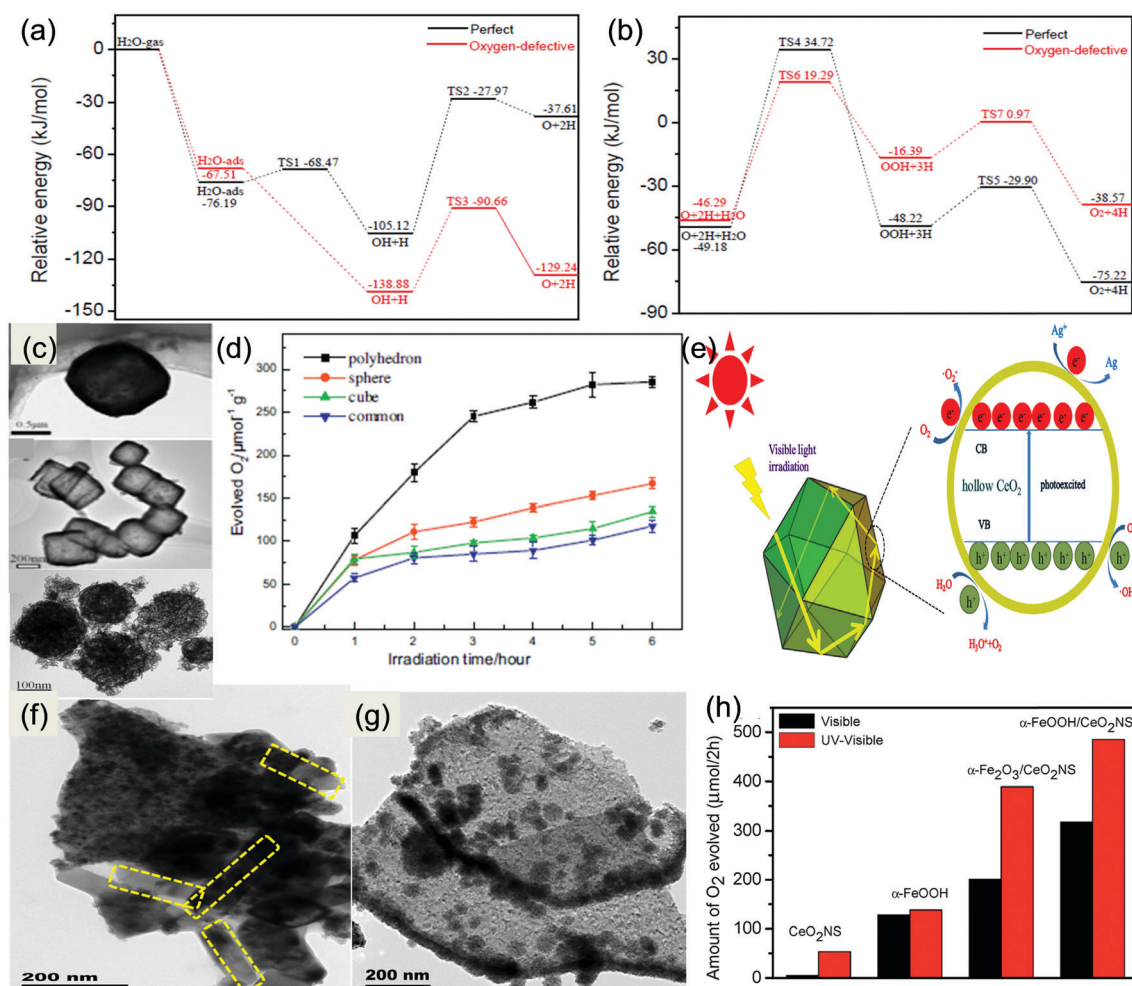
In general water oxidation over CeO<sub>2</sub> involves two major steps as confirmed from DFT studies. The first step is the sequential dehydrogenation of water, *i.e.* H<sub>2</sub>O  $\rightarrow$  OH + H  $\rightarrow$  O + 2H. In particular, on CeO<sub>2</sub>(110), H<sub>2</sub>O is adsorbed on the top Ce site and the adsorbed H<sub>2</sub>O dehydrogenates to OH and H. Then the formed OH group dissociates into O and H, as the H migrates to the neighbouring top O site. Further, the formation of O<sub>2</sub> requires an additional step, in which an additional H<sub>2</sub>O further dehydrogenates to form the second OH and H. The second OH





then combines with the O from the first H<sub>2</sub>O molecule to form OOH. The formed OOH species binds to the Ce site in the final state. Meanwhile, O<sub>2</sub> is generated by the dehydrogenation of OOH *via* O–H bond scission.<sup>103</sup> Zhang *et al.* studied the theoretical concept behind the water oxidation process involving normal and defective CeO<sub>2</sub>(110) nanorods. According to DFT, they found that the presence of oxygen vacancies on CeO<sub>2</sub>(110) effectively modulates the electronic structure which enhances the charge transfer required for water dehydrogenation and also narrows the band gap. In brief, as shown in Fig. 8(a) the energy profile of defective CeO<sub>2</sub> for water dehydrogenation to O is very similar to that of perfect CeO<sub>2</sub>, but is easier. Moreover, the dissociation of OH is unfortunately very difficult in perfect CeO<sub>2</sub> as the formed O and H tend to combine with each other producing OH again. But in the case of defective CeO<sub>2</sub>, OH dehydrogenation is much easier as the reverse reaction is very slow. Further, the presence of oxygen vacancies on CeO<sub>2</sub>(110) significantly reduces the activation energy of the rate limiting

step (O–O bond formation) of water oxidation, due to the decreased O binding strength. Moreover, the distance between O and the second OH is shortened in the defective CeO<sub>2</sub> compared to that of the perfect one, which indicates that lower activation energy is required for the formation of O<sub>2</sub> *via* the OOH pathway in the defective CeO<sub>2</sub> as shown in Fig. 8(b). They found that normally in CeO<sub>2</sub>, the HOOH pathway is not favoured because of its high activation barrier, but the OOH pathway is favoured as described above. In addition to this, defective CeO<sub>2</sub>(110) possesses a higher rate constant for the rate limiting step which is about 2–3 orders of magnitude higher compared to that of the perfect CeO<sub>2</sub>(110). They also studied the photocatalytic oxygen generation under visible light of the above materials and found that the NaBH<sub>4</sub> reduced CeO<sub>2</sub>, *i.e.* defective CeO<sub>2</sub> NRs, exhibited the highest photocatalytic activity with the highest oxygen evolution rate (137.7 μmol g<sup>−1</sup> h<sup>−1</sup>) than the pristine. For the first time, they reported how to control the defects by varying the NaBH<sub>4</sub> amount. They found that on adding a particular amount of NaBH<sub>4</sub>, the vacancy concentration



**Fig. 8** Potential energy profiles for (a) water dehydrogenation to O and (b) O–O bond formation. Reprinted from ref. 103 with permission from Elsevier. (c) TEM micrographs of polyhedron, cube and sphere shaped CeO<sub>2</sub> (d) and their corresponding photocatalytic O<sub>2</sub> evolution curves under visible light irradiation. (e) The schematic illustration of the photocatalytic O<sub>2</sub> evolution mechanism over CeO<sub>2</sub> hollow structures under visible light irradiation. Reprinted from ref. 90 with permission from Elsevier. (f and g) TEM micrographs of FeOOH/CeO<sub>2</sub>NS and Fe<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>NS. (h) Oxygen evolution bar graph showing Fe modified CeO<sub>2</sub>.<sup>200</sup> Reproduced by permission of The Royal Society of Chemistry.

is optimized, and a further increase in the  $\text{NaBH}_4$  amount decreases the vacancy density, which strongly affects the photocatalytic hydrogen evolution activity.<sup>103</sup>

Jiang *et al.* reported on the effect of crystal facets on the photocatalytic water oxidation reaction. They prepared  $\text{CeO}_2$  of two different shapes, *i.e.* cube (100) and rod (110 + 100), *via* a simple hydrothermal method, where for the rod morphology two different types of precursors (nitrate and chloride) were used. Under 5 sun illumination,  $\text{CeO}_2$  NRs prepared from the chloride precursor exhibited the highest oxygen evolution rate of  $1.70 \mu\text{mol h}^{-1}$ , which might be due to the presence of surface bound hydroxyl group at the defect sites and two active planes, *i.e.* 100 and 110, which retarded the photogenerated charge recombination ability.<sup>15</sup> Further, Zhao *et al.* developed another nanostructured  $\text{CeO}_2$ , *i.e.*  $\text{CeO}_2$  NRs, by hydrothermal synthesis followed by post-calcination under different atmosphere conditions. They found that Ar- $\text{H}_2$ -800 possesses more active oxygen (24.16%) which is directly related to  $\text{Ce}^{3+}$ , and hence it emerged as a better water oxidation catalyst. They concluded that  $\text{CeO}_2$  NRs prepared under mixed  $\text{H}_2$  and Ar gas at  $800^\circ\text{C}$  exhibit higher photocatalytic water oxidation ability at a yield rate of  $707.73 \mu\text{mol g}^{-1}$ , which was 10 times higher than that of  $\text{CeO}_2$  NRs calcined under air at  $800^\circ\text{C}$ . The origin of the enhancement in the activity is mainly due to the increased content of surface oxygen vacancies and paramagnetic  $\text{Ce}^{3+}$  species under the reduced atmosphere which is helpful for reduction of the energy barrier for water adsorption and the corresponding photooxidation.<sup>69</sup> Next, Qi *et al.* synthesized a multi-shell hollow microsphere through a general self-templating method and tested its activity towards photocatalytic water oxidation in the presence of  $\text{AgNO}_3$  solution ( $\text{e}^-$  scavenger). They found that the triple shelled  $\text{CeO}_2$  hollow microsphere exhibited the highest  $\text{O}_2$  evolution activity of  $78 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$  which was higher than that of the commercial  $\text{CeO}_2$  NPs. This outstanding performance of the catalyst was attributed to the hollow structure which absorbs more incident light because of the multiple reflections by the multi-shell and possesses a larger surface area with more active sites for water oxidation.<sup>91</sup> Further Fang and co-workers synthesized different morphology oriented  $\text{CeO}_2$  such as polyhedral, cubic and sphere-shaped nanocages through the template ( $\text{Cu}_2\text{O}$ ) assisted method as shown in Fig. 8(c). A very interesting observation was made, *i.e.* polyhedral  $\text{CeO}_2$  ( $47.5 \mu\text{mol g}^{-1} \text{ h}^{-1}$ ) nanocages possessed higher photocatalytic  $\text{O}_2$  evolution activity than cubic nanocages ( $22.4 \mu\text{mol g}^{-1} \text{ h}^{-1}$ ) and sphere-shaped nanocages ( $27.8 \mu\text{mol g}^{-1} \text{ h}^{-1}$ ) as shown in Fig. 8(d).<sup>90</sup> As shown in Fig. 8(e), under light irradiation the  $\text{CeO}_2$  hollow structure absorbs photons and excites electron-hole pairs; then the photogenerated holes react with water to give molecular oxygen while the generated electrons are quenched by  $\text{AgNO}_3$ . The activity improvement was ascribed to the polyhedral nanocage containing more active sites, a higher surface area and efficient photogenerated charge transport and separation. Additionally, the light absorption ability is enhanced in this particular nanostructure because of its inner shell which reflects the light properly. Primo *et al.* decorated gold particulate over quantum sized  $\text{CeO}_2$  for activity improvement and efficient light absorption. It was found

that 1 wt% gold loaded  $\text{CeO}_2$  nanoparticles exhibited the highest oxygen evolution rate, *i.e.*  $105 \mu\text{mol h}^{-1}$ , which was much more than that of the standard  $\text{WO}_3$  photocatalyst ( $1.7 \mu\text{mol h}^{-1}$ ). This remarkable photocatalytic activity was mainly due to the small size (5 nm)  $\text{CeO}_2$ , where they controlled the particle size of ceria (5 nm) by means of electrostatic binding of Ce 4p to alginate gel, subsequent supercritical  $\text{CO}_2$  drying, and calcination.<sup>198</sup>

Other than nanostructured  $\text{CeO}_2$ , very limited work on modified  $\text{CeO}_2$  based materials has come into existence.<sup>199–201</sup> For example, Fang *et al.* fabricated  $\text{CoO}_x$  decorated  $\text{CeO}_2$  hollow nanocages for improved water oxidation. With an appropriate amount of  $\text{CoO}_x$  loading, the  $\text{CeO}_2$  based hollow structure not only possessed a higher ability for light absorption but also showed a high  $\text{O}_2$  evolution rate, *i.e.*  $200 \mu\text{mol g}^{-1} \text{ h}^{-1}$ , under visible-light irradiation with excellent durability.<sup>199</sup> Further, Parida and co-workers attempted to exploit new visible light self-healing 1D–2D  $\text{FeOOH}$  nanorods/ $\text{CeO}_2\text{NS}$  and 3D–2D  $\text{Fe}_2\text{O}_3/\text{CeO}_2\text{NS}$  hybrids in 2-dimensional nanosheet architecture photocatalysts as shown in Fig. 8(f and g) by a facile hydrothermal method and evaluated their photocatalytic performance towards the oxygen evolution reaction under UV-visible light. The optimised  $\text{FeOOH}/\text{CeO}_2\text{NS}$  and  $\text{Fe}_2\text{O}_3/\text{CeO}_2\text{NS}$  systems exhibit unprecedented photocatalytic activity towards  $\text{O}_2$  evolution, *i.e.*  $485 \mu\text{mol}/2 \text{ h}$  and  $389 \mu\text{mol}/2 \text{ h}$  respectively (Fig. 8(h)). The enhanced performance of  $\text{Fe}/\text{CeO}_2$  is attributed to the 2D structure of  $\text{CeO}_2$  which provides the perfect site for growth of iron materials and extends the charge separation process throughout the nanohybrid. Additionally, the formation of a n–n junction across the heterointerface modifies the charge separation and transportation process. Further, the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox cycle acts as an activator which healed photocorrode  $\text{Fe}^{2+}$  and regenerating the structural damage caused by irradiation.<sup>200</sup> Recently, Meng *et al.* synthesized a new type of molecular catalyst (MC) combined semiconductor heterostructure, *i.e.* a  $\text{CoTCPP}@ \text{CeO}_2$  nanotube heterostructure. The optimized  $\text{CoTCPP}@ \text{CeO}_2$  nanocomposite exhibited  $\text{O}_2$  evolution at a rate of  $30 \mu\text{mol g}^{-1} \text{ h}^{-1}$  with long term durability and was found to be superior to other MC combined  $\text{CeO}_2$ , for example  $\text{H}_2\text{TCPP}@ \text{CeO}_2$  NTs,  $\text{Co}_3\text{O}_4@ \text{CeO}_2$  NTs and  $\text{TCPP}@ \text{Co}_3\text{O}_4@ \text{CeO}_2$  NTs, under the same conditions. They proposed that initially,  $\text{CoTCPP}$  acts as a charge transporter to propel photoexcited electrons to  $\text{CeO}_2$  by d–f electron coupling, which effectively suppresses the photo-generated charge recombination. In addition to this, the interfacial charge transfer results in *in situ* generation of surface oxygen vacancies and  $\text{CoOOH}$  species, which are found to be the major sites for enhancing water oxidation.<sup>201</sup>

## 5. $\text{CO}_2$ reduction reaction

The continuous rise in the atmospheric carbon dioxide level and depletion of fossil resources is a pressing concern that is directly threatening the balance of earth's ecosystems and sustainability of life for future generations. Among various on-going research activities for protection and remediation of the environment and solving the energy crisis, carbon dioxide



**Table 2** Complete results of the CO<sub>2</sub> photoreduction performance of CeO<sub>2</sub> and CeO<sub>2</sub> based heterostructures

Catalyst	Light source	Reaction conditions	Activity	Ref.
CeO <sub>2</sub> (100)/CeO <sub>2</sub> (110)	300 W Xe lamp	Water, CO <sub>2</sub> gas	CH <sub>4</sub> 0.86 μmol h <sup>-1</sup> g <sup>-1</sup> 1.12 μmol h <sup>-1</sup> g <sup>-1</sup>	84
Defective CeO <sub>2</sub> NRs	500 W Xe lamp	Pt/MnO <sub>x</sub>	(Pt, MnO <sub>x</sub> co-catalyst)	104
CeO <sub>2</sub> -SAC (defective)	300 W Xe lamp	CO <sub>2</sub> gas phase reduction	CO 24–28 μmol g <sup>-1</sup> in 6 h	106
CeO <sub>2</sub> -CSC		NaHCO <sub>3</sub>	CH <sub>3</sub> OH – 0.702 μmol h <sup>-1</sup> g <sup>-1</sup>	
r-CeO <sub>2</sub> (110)	300 W Xe lamp	Water, CO <sub>2</sub> gas	0.397 μmol h <sup>-1</sup> g <sup>-1</sup>	206
c-CeO <sub>2</sub> (100)			CO 0.203 μmol h <sup>-1</sup> g <sup>-1</sup>	
Ordered mesoporous CeO <sub>2</sub> -TiO <sub>2</sub>	300 W Xe arc lamp	Water, CO <sub>2</sub> gas	CO 0.130 μmol h <sup>-1</sup> g <sup>-1</sup>	207
3D ordered macroporous TiO <sub>2</sub> -CeO <sub>2</sub>	300 W Xe lamp (λ > 420 nm)	Water, CO <sub>2</sub> gas	CH <sub>4</sub> – nearly 12 mmol g <sup>-1</sup> in 325 min and CO – nearly 70 mmol g <sup>-1</sup> in 325 min	208
ZnO-CeO <sub>2</sub>	300 W Xe lamp	Water, CO <sub>2</sub> gas	CO – 0.52 μmol h <sup>-1</sup> g <sup>-1</sup> and CH <sub>4</sub> – 0.06 μmol h <sup>-1</sup> g <sup>-1</sup>	209
Vacancy Cu <sub>2</sub> O/CeO <sub>2</sub>	300 W Xe lamp	Water, CO <sub>2</sub> gas	CO nearly 1.2 μmol g <sup>-1</sup> in 8 h	210
CeO <sub>2</sub> /Bi <sub>2</sub> MoO <sub>6</sub>	300 W Xe arc lamp (λ > 420 nm)	Water, CO <sub>2</sub> gas	CH <sub>3</sub> OH – 32.5 μmol h <sup>-1</sup> g <sup>-1</sup> and C <sub>2</sub> H <sub>5</sub> OH – 25.9 μmol h <sup>-1</sup> g <sup>-1</sup> in 4 h	211
CdS@CeO <sub>2</sub> core/shell	300 W Xe lamp (λ > 420 nm)	Water, CO <sub>2</sub> gas	CH <sub>3</sub> OH – nearly 1100 μmol g <sup>-1</sup> in 8 h	212
ZnIn <sub>2</sub> S <sub>4</sub> flower/CeO <sub>2</sub>	300 W Xe lamp (λ > 420 nm)	NaHCO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub>	CH <sub>4</sub> – nearly 7 μmol g <sup>-1</sup> in 8 h	213
Defect rich g-C <sub>3</sub> N <sub>4</sub> @CeO <sub>2</sub>	300 W Xe lamp (λ > 420 nm)	Water, CO <sub>2</sub> gas	CH <sub>3</sub> OH 0.542 μmol h <sup>-1</sup> g <sup>-1</sup>	214
m-CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	300 W Xe arc lamp	Water, CO <sub>2</sub> gas	CH <sub>4</sub> – 3.5 μmol g <sup>-1</sup> , CH <sub>3</sub> OH – 5.2 μmol g <sup>-1</sup> and CO – 16.8 μmol g <sup>-1</sup> in 3 h	215
CeO <sub>2</sub> -3D-gC <sub>3</sub> N <sub>4</sub>	UV light	NaOH, TEOA, CO <sub>2</sub> gas	CO – 0.590 μmol/50 mg/6 h and CH <sub>4</sub> – 0.694 μmol/50 mg/6 h	216
CeO <sub>2</sub> -N-doped graphene-Cu <sup>2+</sup>	250 W Xe lamp	Pt-cocatalyst	CO 4.69 μmol h <sup>-1</sup> g <sup>-1</sup> and CH <sub>4</sub> 3.03 μmol h <sup>-1</sup> g <sup>-1</sup>	217
CeO <sub>2</sub> MOF	300 W Xe lamp	NaHCO <sub>3</sub> , Na <sub>2</sub> SO <sub>3</sub> , CO <sub>2</sub> gas	CH <sub>3</sub> OH 507.3 μmol h <sup>-1</sup> g <sup>-1</sup>	218
		Water, CO <sub>2</sub> gas	CO 1.68 μmol h <sup>-1</sup> g <sup>-1</sup>	

capture and subsequent conversion into high liquid fuels including value-added chemicals is regarded as a potential strategy to slow down the alarming climate change and sustainably address the upcoming energy crises. Photocatalytic conversion of CO<sub>2</sub> to renewable fuel using solar energy has attracted more attention in the past 3 to 4 decades. Since then, various nanostructured metal oxide photocatalysts have been examined for the reduction of CO<sub>2</sub>, and great achievements have been made. However, the rational design and synthesis of photocatalysts with high activity and selectivity towards the reduction of CO<sub>2</sub> is highly challenging.<sup>202,203</sup> CeO<sub>2</sub> has been widely used as the catalyst for CO<sub>2</sub> reduction, so both theoretical and experimental studies have eventually surfaced in this field, as summarized in Table 2.<sup>204–217</sup>

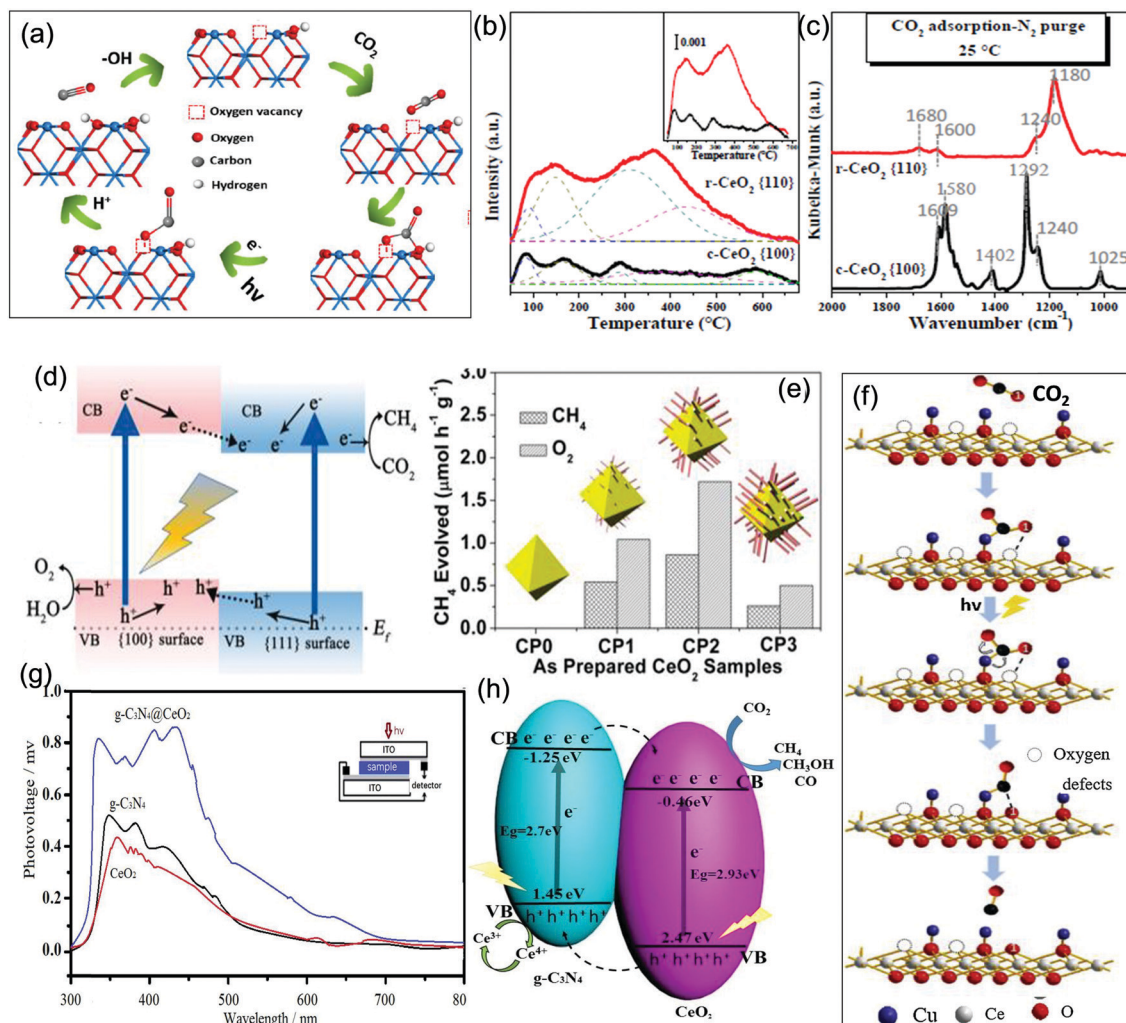
The theoretical concept of CO<sub>2</sub> adsorption, activation and subsequent reduction over the CeO<sub>2</sub> surface is as follows: at first, the CO<sub>2</sub> molecule is adsorbed in a horizontal configuration where the O atoms sit on top of the surface of Ce while the C atom sits on the four-fold hollow site of the top layer CeO<sub>2</sub>. Then the adsorbed CO<sub>2</sub> is reduced to either a formate or carboxyl intermediate in the presence of adsorbed hydrogen, while in the absence of any adsorbed hydrogen, the CO<sub>2</sub> directly forms carboxylate species. Further, the formed intermediate (formate/carboxyl) undergoes dissociation to form CO species. However in defective CeO<sub>2</sub>, CO<sub>2</sub> is directly dissociated into CO by donating its one oxygen to the oxygen vacancy. On CO<sub>2</sub> activation, the oxygen atom is directly incorporated into the vacant site *via* a redox mechanism and neutralizes the vacancy to generate the CO intermediate. Both the carboxyl and formate intermediates can produce CO while only the carboxyl intermediate will on further hydrogenation produce methanol on the ceria surface.

The carboxylate pathway is more favourable for hydrogenation due to the presence of surface vacancies. Hence, the theoretical calculation gives full proof evidence for the effective CO<sub>2</sub> reduction in both oxidized and reduced CeO<sub>2</sub>.<sup>204,205</sup> In this regard, there are a number of experimental reports on CO<sub>2</sub> photoreduction over CeO<sub>2</sub> based materials with eye-catching results. For example, Dong and coworkers analyzed the CO<sub>2</sub> reduction over (110) and (100) surfaces through both experimental and theoretical investigations and proposed a mechanism of CO<sub>2</sub> photoreduction over defective CeO<sub>2</sub> as shown in Fig. 9(a). They observed that the synergistic effect of both Lewis acid sites (oxygen vacancy) and Lewis base sites (hydroxyl group) was responsible for CO<sub>2</sub> activation and its subsequent reduction. Combining the results of CO<sub>2</sub>-TPD, CO<sub>2</sub>-adsorption, DRIFTS and DFT studies (Fig. 9(b and c)), the authors concluded that the CeO<sub>2</sub>(100) plane possesses more hydroxyl species than the CeO<sub>2</sub>(110) plane, which are beneficial for the adsorption and subsequent activation of CO<sub>2</sub>. Additionally, they illustrated the CO<sub>2</sub> reduction mechanism as follows (shown in Fig. 9(a)): the O atom of the surface hydroxyl group of CeO<sub>2</sub> donated electrons to the C atom of CO<sub>2</sub> and eventually, the O atom of the CO<sub>2</sub> reactant gave its p electrons to the oxygen vacancy of CeO<sub>2</sub>, resulting in the formation of HCO<sub>3</sub><sup>-</sup> species. Next, the carboxylate (\*CO<sub>2</sub><sup>-</sup>) radical ion intermediate was formed when the photoexcited electron transferred to the surface HCO<sub>3</sub><sup>-</sup> species which was further confirmed by *in situ* ESR analysis. Finally, with the formation of OH, the CO gas was produced from the intermediate carboxylate species. Therefore, the synergistic interactions between the Lewis acidic and basic group are beneficial for CO<sub>2</sub> photoreduction.<sup>95</sup>

Additionally, Jiang *et al.* prepared defective CeO<sub>2</sub> nanorods for the photocatalytic gas-phase CO<sub>2</sub> reduction reaction and *via*







**Fig. 9** (a) The possible CO<sub>2</sub> photoreduction mechanism on the oxygen-defective CeO<sub>2</sub>(110) surface. (b) and (c) CO<sub>2</sub>-TPD and CO<sub>2</sub> adsorption DRIFTS of the CeO<sub>2</sub>(110) nanorod and the CeO<sub>2</sub>(100) nanocube. (d) Schematic illustration of the photogenerated charge transfer mechanism between two exposed planes within prism anchored octahedral CeO<sub>2</sub>. (e) CO<sub>2</sub> photoreduction efficiency showing the best prism anchored octahedron. Reprinted with permission from ref. 84 and 95, copyright 2020, 2015 American Chemical Society. (f) Proposed mechanism of CO<sub>2</sub> photoreduction on CuO decorated CeO<sub>2</sub>. Reprinted from ref. 210 with permission from Elsevier. (g) Photocatalytic CO<sub>2</sub> reduction profile of CeO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub> and a series of g-C<sub>3</sub>N<sub>4</sub>@CeO<sub>2</sub> heterostructures. (h) Plausible photogenerated charge pair separation and transfer and CO<sub>2</sub> photoreduction mechanism over the g-C<sub>3</sub>N<sub>4</sub>@CeO<sub>2</sub> heterostructure. Reprinted from ref. 214 with permission from Elsevier.

a systematic TEM and HRTEM study they confirmed the lattice distortion and dislocation type surface defects. Further, they found that the prepared CeO<sub>2</sub> can generate CO with nearly 100% selectivity with a yield of 24–28  $\mu\text{mol g}_{\text{cat}}^{-1}$  after 6 hours of irradiation, which was like a milestone for neat CeO<sub>2</sub>. However, after the prolonged irradiation (more than 20 h), the photoreduction activity was slowed down, as initially the local strain and oxygen vacancy help to activate adsorbed CO<sub>2</sub>, but after a certain time, these vacancies were gradually consumed leaving behind massive electrophilic oxygen species over the CeO<sub>2</sub> surface which restricts the further photoreduction, thereby slowing down the formation yield of CO. They further found that the activity was recovered when the exhausted CeO<sub>2</sub> was again treated with NaBH<sub>4</sub> solution resulting in the subsequent defect formation.<sup>104</sup> Further, Li *et al.* reported the first kind of nano-

structured CeO<sub>2</sub>, *i.e.* hexahedron prism anchored octahedron, towards photocatalytic CO<sub>2</sub> reduction. According to the DOS study, there is a slight energy difference between the CB and VB of the (100) plane of the hexahedron prism and the (111) plane exposed octahedron which forms a homojunction between them. This homojunction is mainly responsible for the effective charge pair separation and transfer, where the electrons flow from the higher Fermi level of the hexahedron prism with exposed (100) facets to the (111) octahedron surface and catalyze the adsorbed CO<sub>2</sub> as shown in Fig. 9(d), while holes at the 100 surface react with water to generate oxygen. Hence, the hexahedron with a medium denser arm generated the most CH<sub>4</sub> by the reduction of CO<sub>2</sub> at the rate of 0.86  $\mu\text{mol h}^{-1} \text{g}^{-1}$  while in presence of MnO<sub>x</sub> co-catalyst the production rate was further increased to 1.12  $\mu\text{mol h}^{-1} \text{g}^{-1}$  as depicted in Fig. 9(e).<sup>84</sup>

Recently Hezam *et al.* reported a novel preparation method, *i.e.* solar light assisted combustion synthesis, for the production of 12–18 nm diameter CeO<sub>2</sub> particles containing a high amount of surface defects. Under simulated solar light, the as-prepared O<sub>v</sub> CeO<sub>2</sub> exhibited the highest photocatalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH at the rate of 0.702 μmol h<sup>-1</sup> g<sup>-1</sup> with a quantum efficiency of 0.23% at 350 nm, while the conventional solution combustion assisted CeO<sub>2</sub> displayed only a rate of 0.397 μmol h<sup>-1</sup> g<sup>-1</sup>. From DFT simulation it was found that the generated oxygen vacancy increases its light absorption by narrowing the band gap of CeO<sub>2</sub>, and enhances its CO<sub>2</sub> capture ability. Moreover, the mean crystallite size, low crystallinity and mesoporous structure played a crucial role in the selectivity of CO<sub>2</sub> reduction to methanol.<sup>106</sup> Further, Ullah *et al.* carried out photothermal CO<sub>2</sub> reduction over transition metal (Cu, Co) loaded CeO<sub>2</sub> and found that transition metal loaded CeO<sub>2</sub> exhibits the highest activity as well as selectivity towards methane production compared to pristine CeO<sub>2</sub>. The improved photoactivity was attributed to the generation of hot electrons from transition metals which directly activate the CO<sub>2</sub> molecule to undergo smooth degradation and further create *in situ* vacancies in the CeO<sub>2</sub> support which act as localized charge density sites.<sup>206</sup>

In addition to these, a number of articles have recently been reported for various heterostructures/composites of CeO<sub>2</sub> with different metal oxides,<sup>207,211</sup> metal sulphides<sup>212,213</sup> carbonaceous materials,<sup>214–218</sup> *etc.* For example, Wang *et al.* prepared an ordered mesoporous (OM) CeO<sub>2</sub>-TiO<sub>2</sub> composite of 2D hexagonal structure with a high specific surface area and hierarchical porosity by using SBA-15 as the template. The introduction of CeO<sub>2</sub> species increased the surface chemisorbed oxygen of the ordered mesoporous TiO<sub>2</sub> and effectively extended the spectral response of the nanohybrid from UV to visible. The composite was effectively utilized for CO<sub>2</sub> photoreduction under simulated solar light with excellent selectivity and catalytic efficiency. The work demonstrated that the 3DOM CeO<sub>2</sub>/TiO<sub>2</sub> catalyst showed the highest CO production, *i.e.* nearly 70 mmol g<sub>cat</sub><sup>-1</sup>, and nearly 11.5 mmol g<sub>cat</sub><sup>-1</sup> CH<sub>4</sub> during 325 min light irradiation. The higher activity was attributed to the 2D-open pore structure, which allows fast interparticle reactant diffusion, and the presence of CeO<sub>2</sub> which helped in the effective electric field formation through which photogenerated electrons effectively drifted from the TiO<sub>2</sub> surface to CeO<sub>2</sub> where they took part in the photoreduction reaction.<sup>207</sup> In another work, Dai *et al.* synthesized a series of CeO<sub>2</sub>/Bi<sub>2</sub>MoO<sub>6</sub> microsphere nanocomposites (0D–2D) towards CO<sub>2</sub> photoreduction and studied the inside mechanism. They found that the CeO<sub>2</sub> surface strengthens the bonding of CO<sub>2</sub> and enhances the formation of intermediates like CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. Moreover, the heterojunction accelerates electron-hole transfer and separation which ultimately uplifts the reduction activity. For this system, the total yield of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH was 58.4 μmol g<sub>cat</sub><sup>-1</sup> over 5C-BM, which was about 4.1 and 1.9 times higher than that of the neat CeO<sub>2</sub> (14.1 μmol g<sub>cat</sub><sup>-1</sup>) and Bi<sub>2</sub>MoO<sub>6</sub> (30.9 μmol g<sub>cat</sub><sup>-1</sup>), respectively.<sup>211</sup> Again, Dong and co-workers developed a very interesting p–n heterojunction composite of Cu<sub>2</sub>O/CeO<sub>2</sub> for photon driven CO<sub>2</sub> reduction. They found that the deposition of Cu<sub>2</sub>O over the CeO<sub>2</sub> surface created more surface defects and also accelerated the charge transfer

process at the Cu<sub>2</sub>O and CeO<sub>2</sub> interface. Furthermore, Cu<sub>2</sub>O plays an important role by creating Lewis acid–base sites, while the oxygen vacancy over CeO<sub>2</sub> increases the pace of CO<sub>2</sub> reduction to CO. In brief they systematically studied the reaction pathway and the mechanism as presented in Fig. 9(f), and concluded that first Cu atoms of Cu<sub>2</sub>O perfectly bound the carbon atoms of CO<sub>2</sub> molecules *via* d-orbital electrons leading to the formation of the carboxylate ion. Further, under light irradiation photo-generated electrons transferred from Cu to the C–O bond of carboxylate, and the O atom of carboxylate interacted with the oxygen vacancy (O<sub>v</sub>) on the CeO<sub>2</sub> surface, and then the O atom transferred to O<sub>v</sub>. Finally, the above interaction promoted the breaking of the C–O bond of the adsorbed carboxylate species, and thus the CO molecule was generated.<sup>210</sup>

In addition to oxide heterostructures, metal sulphides have also been used as a component for CeO<sub>2</sub> in the CO<sub>2</sub> reduction reaction. For example, a core–shell structure of CdS@CeO<sub>2</sub> towards visible light assisted CO<sub>2</sub> reduction was reported by Ijaz *et al.* In the experiment performed, two types of reduction products are observed, *i.e.* methanol as the major product because of the thermodynamic and kinetic concern and methane as the minor product. The type II heterojunction at the core/shell interface enhances the photogenerated charge pair separation and hence improves the stability of the CdS core as the CeO<sub>2</sub> outer layer inhibits the photocorrosion of CdS. In brief, under the visible light irradiation condition photogenerated electrons and holes were produced on the surface of CdS, and then the electrons transferred from CdS to the conduction band of CeO<sub>2</sub>. Further, on the surface of CeO<sub>2</sub> these electrons reduced the adsorbed CO<sub>2</sub> into the negative and metastable superoxide (•CO<sub>2</sub><sup>-</sup>) radicals, which then eventually led to the formation of CH<sub>4</sub> at the rate of 1100 μmol g<sup>-1</sup> for 8 h.<sup>212</sup>

Liang's group demonstrated an interesting synthetic strategy for the formation of a hollow heterostructure of g-C<sub>3</sub>N<sub>4</sub>@CeO<sub>2</sub> with enough oxygen vacancies by using SiO<sub>2</sub> as a template. The catalytic ability of the vacancy enriched heterostructure was tested towards CO<sub>2</sub> photoreduction and the obtained products were CO (16.8 μmol g<sup>-1</sup>), CH<sub>3</sub>OH (5.2 μmol g<sup>-1</sup>) and CH<sub>4</sub> (3.5 μmol g<sup>-1</sup>), demonstrating the higher ability of this heterostructure compared to most of the other reported g-C<sub>3</sub>N<sub>4</sub> based photocatalysts. Further, the apparent quantum efficiency for CO<sub>2</sub> reduction to methane was found to be 17.1% at 525 nm. They concluded that the reason behind the increment in the performance is mainly due to its unique structure and a delayed charge pair recombination rate as confirmed from SPS analysis (shown in Fig. 9(g)). Although both g-C<sub>3</sub>N<sub>4</sub> and CeO<sub>2</sub> showed SPS response the 3D heterostructure exhibited the most intensive response under visible light which confirmed the effective charge carrier separation.<sup>214</sup> As shown in Fig. 9(h), the separation of excitons occurs at the g-C<sub>3</sub>N<sub>4</sub> and CeO<sub>2</sub> interface, while the photogenerated electrons accumulate over the CeO<sub>2</sub> surface where the electrons combine with Ce<sup>4+</sup> to generate Ce<sup>3+</sup>. Further, Ce<sup>3+</sup> reacts with the gas phase CO<sub>2</sub> to form •CO<sub>2</sub><sup>-</sup> which is further reduced to yield CO, and hence the yield of CO is very high in this case. Further in the presence of adsorbed H and •CO<sub>2</sub><sup>-</sup> hydrogenation occurs resulting in other products like methanol and methane.



## 6. Nitrogen reduction reaction (NRR)

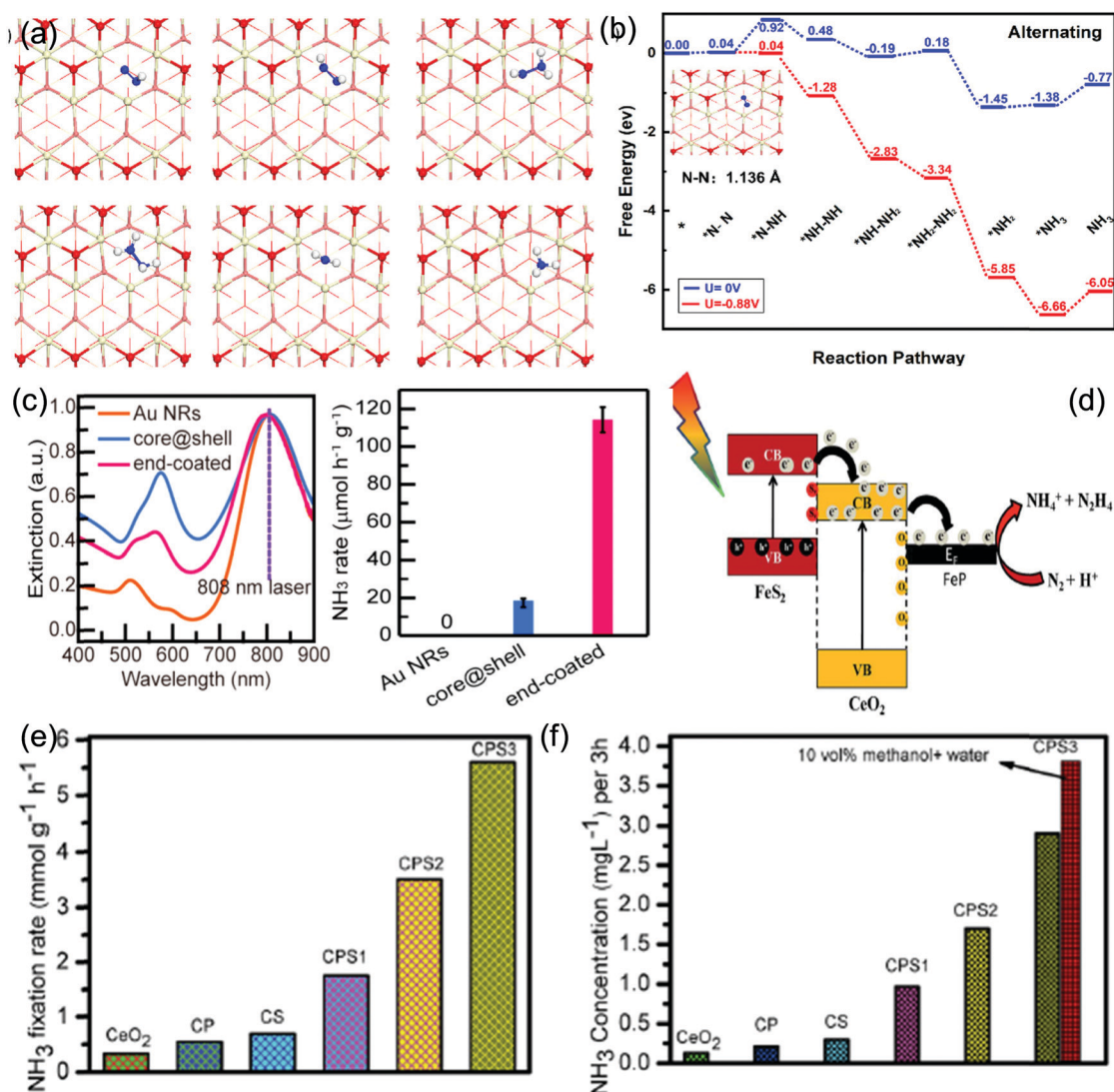
NH<sub>3</sub> is considered as an important chemical for both industries (explosive, resin, plastics and fibres) and agriculture (fertilizer). Recently, the global need for ammonia has seen a sharp increment due to its additional application, *i.e.* as a carbon-neutral fuel and specifically as a potential energy carrier due to its high hydrogen density (17.6 wt%), easy handling/storage and low liquefiable condition (8 bar). Currently, about 150 million tonnes of ammonia is produced per year *via* the traditional energy-intensive Haber-Bosch process (HB) to satisfy the population's food requirement and various other applications. This HB process generally operates under extremely harsh conditions, *i.e.* 400–450 °C and 100–200 atm, and also utilizes 1–3% of global electrical energy (*i.e.*  $3.5 \times 10^4$  to  $5 \times 10^4$  J g<sub>NH<sub>3</sub></sub><sup>−1</sup>). Moreover, the supplied H<sub>2</sub> comes from natural gas (3–5%), and unfortunately releases a substantial amount of CO<sub>2</sub> (1.87 tons per ton of NH<sub>3</sub>) which creates an environmental catastrophe.<sup>219–225</sup> To replace the HB process, a renewable, scalable, and eco-friendly strategy towards ammonia production is highly essential. Among different ongoing strategies, photocatalytic reduction of N<sub>2</sub> to NH<sub>3</sub> is a very hot topic of research towards the development of renewable technologies. Photocatalytic nitrogen reduction generally operates under mild reaction conditions and utilizes renewable feedstock, *i.e.* solar light and water. So far many photocatalytic systems have been developed and tested for effective nitrogen fixation. It is found that the materials with intrinsic surface defects are the most suitable candidates for this process.<sup>220</sup> In this perspective, CeO<sub>2</sub> with surface oxygen defects and Ce<sup>3+</sup> has emerged as one of the active catalytic systems for the NRR.<sup>226–232</sup>

In this context, Qi *et al.* using first principles calculations investigated the NRR process over CeO<sub>2</sub> and found that defective CeO<sub>2</sub> with Ce<sup>3+</sup> sites (Lewis acid) facilitates N<sub>2</sub> adsorption (Lewis base) *via* an acid–base adduct mechanism as shown in Fig. 10(a). The exposed CeO<sub>2</sub> sites on CeO<sub>2</sub>((111), (110), (100)) can cause N<sub>2</sub> to get adsorbed in a lying down manner, which encourages N<sub>2</sub> activation and thus leads to an efficient reduction. The surface oxygen vacancy weakens the adsorbed N≡N bond strength and lowers the adsorption energy of the N<sub>2</sub>H\* intermediate as shown in Fig. 10(b) and thereby facilitates further reduction. In brief, in the pristine CeO<sub>2</sub> with (111), (110) and (100) exposed facets, N<sub>2</sub> adsorbs on the surface of Ce sites in a standing up manner indicating weak physical adsorption. Hence the N<sub>2</sub> molecule can't be activated on the surface of perfect/pristine CeO<sub>2</sub> and further, the energy barrier for the first protonation of N<sub>2</sub>\* seems to be very high leading to inefficiency of the NRR. However, defective CeO<sub>2</sub>(111), (110) and (100) facets containing multiple oxygen vacancies and unsaturated Ce<sup>3+</sup> Lewis acid cluster sites (tri/bi and tetra-Ce sites) could cause N<sub>2</sub> to be adsorbed in a lying down manner, which further promotes N<sub>2</sub> activation. Moreover, the unsaturated tri and bi-Ce sites could stabilize the intermediate N<sub>2</sub>H\*, while lowering ΔG for the first protonation, and then the alternate mechanistic pathway of ammonia formation proceeds. Further, it was found that the NRR activity over the different planes of CeO<sub>2</sub> is determined by their unsaturated Ce sites which are in the following order: (100) > (110) > (111), as the (100) plane contains tetra and tri-Ce sites.<sup>226</sup>

Different CeO<sub>2</sub> based electrocatalysts for NRR activity have also been reported so far<sup>227–229</sup> with a high production rate and selectivity. For example, Xu *et al.* prepared oxygen vacancy enriched CeO<sub>2</sub> nanorods and achieved a great enhancement for the electrocatalytic NRR. However, no significant works regarding CeO<sub>2</sub> and CeO<sub>2</sub> based materials have been explored in the field of photo-fixation of N<sub>2</sub> (PNRR). Among the countable research works, Feng *et al.* prepared a series of ternary photocatalysts CeCO<sub>3</sub>OH/g-C<sub>3</sub>N<sub>4</sub>/CeO<sub>2</sub> by using CeCl<sub>3</sub> and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) as reaction precursors *via facile in situ* self-sacrificing hydrothermal methods. Without using any sacrificial agent, the photocatalyst prepared at 180 °C exhibited the highest nitrogen photoreduction activity, *i.e.* 1.16 mM g<sup>−1</sup> h<sup>−1</sup>, which was four times that of pristine g-C<sub>3</sub>N<sub>4</sub>. The enhanced nitrogen photofixation performance was attributed to the surface defects in CeO<sub>2</sub> where Ce<sup>3+</sup> acts as a chemisorption site for N<sub>2</sub> molecule adsorption and subsequent activation and the heterostructure interface provides a higher charge transfer and separation efficiency.<sup>230</sup> In another case, Jia *et al.* proposed an innovative synthesis idea of the Au–CeO<sub>2</sub> nanostructure, unlike the reported core–shell structure, *via* a facile wet-chemistry route, where crystalline CeO<sub>2</sub> was selectively grown over the ends of gold nanorods (Au NRs) in the presence of a small amount of bi-functional K<sub>2</sub>PtCl<sub>4</sub>. A large number of oxygen vacancies were generated in the surface grown ceria which further enhanced the adsorption and the subsequent reduction of di-nitrogen molecules. They tuned their longitudinal plasmon wavelengths finely so that the materials can be adjusted as closely as possible to the laser wavelength as shown in Fig. 10(c). Further, the generation of plasmon-induced hot electrons and the presence of oxygen vacancies enabled the unique structural Au/end-CeO<sub>2</sub> to function as a photocatalyst for nitrogen photo-fixation. The obtained nanostructured catalyst under 808 nm laser illumination led to a high rate of production of NH<sub>3</sub>, *i.e.* 114.3 μmol h<sup>−1</sup> g<sup>−1</sup>, which was 6.2-fold more in comparison to the other synthesized core@shell (Au@CeO<sub>2</sub>) nanostructure (Fig. 10(c)). As a proof-of-concept, the photocatalytic N<sub>2</sub> fixation ability of the Au/end-CeO<sub>2</sub> nanostructures was also evaluated under 1 sun illumination and the NH<sub>3</sub> generation rate was found to be 25.6 μmol h<sup>−1</sup> g<sup>−1</sup>.<sup>113</sup> The author's group have also studied different CeO<sub>2</sub> based materials for photocatalytic nitrogen fixation.<sup>231,232</sup> For example, 3D/2D-FeS<sub>2</sub>–FeP–CeO<sub>2</sub> nanohybrids with high surface defects were successfully synthesized through an *in situ* hydrothermal technique followed by a combined sulphidation and phosphidation technique. The as-prepared samples were tested towards PNRR under UV-vis light without the use of any organic scavenger or noble metal co-catalyst. CeO<sub>2</sub> acts as a building block photocatalyst and supports the FeP/FeS<sub>2</sub> particles, and under light irradiation FeS<sub>2</sub> acts as an electron donor and injects photoelectrons on to the CeO<sub>2</sub>. Further the presence of oxygen vacancies along with FeP encouraged the productive N<sub>2</sub> activation and photoreduction to ammonia. The key to the remarkable photocatalytic performance was the presence of Fe based materials where FeP serves as the catalytic site for N<sub>2</sub> adsorption and facilitates the photo-generated charge transfer mechanism from CeO<sub>2</sub> to nitrogen as







**Fig. 10** (a) Optimized geometries of the NRR pathway on defective CeO<sub>2</sub>(111). (b) Corresponding Gibbs free energy profiles. Reprinted from ref. 226 with permission from Elsevier. (c) Extinction spectra of three photocatalyst nanostructures and N<sub>2</sub> photofixation rates of Au nanorods, Au@CeO<sub>2</sub> and Au-end coated CeO<sub>2</sub> photocatalysts under NIR light illumination. Reprinted with permission from ref. 113, copyright 2019 American Chemical Society. (d) Proposed mechanism of nitrogen reduction over FeS<sub>2</sub>/P-CeO<sub>2</sub> based defective materials. (e) and (f) NH<sub>3</sub> concentration from PNRR over a CeO<sub>2</sub> based catalyst in acidic medium and distilled water.<sup>231</sup> Reproduced by permission of The Royal Society of Chemistry.

shown in Fig. 10(d). The optimized FeP-FeS<sub>2</sub>-CeO<sub>2</sub> displayed a very high ammonia production, *i.e.* 2.91 mg L<sup>-1</sup>, without a sacrificial agent whereas in the presence of aqueous methanol solution, the ammonia production rate was increased significantly. This suggests that methanol both acts as a sacrificial electron donor and produces CO<sub>2</sub>\*<sup>-</sup> which facilitates the N<sub>2</sub> fixation ability. Further, the nitrogen fixation rate was 5.66 mmol h<sup>-1</sup> g<sup>-1</sup> with selectivity in acidic distilled water under mild reaction conditions (Fig. 10(e and f)).<sup>231</sup>

## 7. Photocatalytic pollution abatement

The 21st century is the era of rapid development covering all sectors of the world but the serious side effect of this progress

may result in an environmental catastrophe. The continuous rise of industrial activities and different technological advancements have damaged the growth of society by releasing their additional waste to water bodies, soil and air without proper treatment causing a serious threat to biodiversity. Mainly the wastewater effluents contain maximum contaminants in the form of various organic pollutants such as dyes, phenolic compounds, antibiotics, halogenated hydrocarbons and inorganic toxic pollutants such as highly dangerous heavy metals and radioactive nuclides.<sup>233–239</sup> These pollutants are highly toxic and take a very long time to degrade naturally. So the effective removal and degradation of these pollutants have taken many years of research. A variety of technologies such as chemical oxidation, adsorption, electrochemical conversion, and biodegradation have been used so far but most of them are highly energy demanding and cannot

be used on a regular basis.<sup>240–245</sup> However, the photocatalytic detoxification process has emerged as a more efficient, cost-effective and green strategy which has the ability to clean up all the detrimental pollutants from wastewater as well as air bodies. In this technique, highly energetic radicals such as hydroxyl, superoxide, and hydrogen peroxide along with photogenerated electrons and holes are produced which effectively convert the organic/inorganic pollutant to a non-toxic form very quickly.<sup>246–248</sup> With regard to this, many researchers have developed different photocatalytic materials for their effective utilization towards pollutant removal from different sources.

In the context of the environment cleanup process, various nanostructured CeO<sub>2</sub> and CeO<sub>2</sub> based materials have been reported for air purification and wastewater treatment by efficient photocatalytic degradation/mineralization of different dyes (RhB, MB, acid orange, eosin yellow, *etc.*),<sup>249–274</sup> antibiotics<sup>275–284</sup> and organic pollutants (phenol-based materials),<sup>285–289</sup> as summarized in Table 3. Morphology alteration enhances the surface defects such as Ce<sup>3+</sup> state and oxygen vacancies, which increases the light absorption parameter with a red-shifted absorption edge and also retards the photogenerated electron-hole recombination rate. Further, these sites act as strong binding and dissociation sites for adsorbate molecules, and hence act as good sites for the photocatalytic degradation process. And it was also found that these CeO<sub>2</sub> materials generate more radical species (hydroxyl and superoxide) because of the prolonged lifetime of excitons and the presence of surface defects. Recently, Amoresi *et al.* studied the photocatalytic decolourization efficiency of RhB over different morphology oriented CeO<sub>2</sub>. According to theoretical models and experimental studies, it was found that the photodegradation rate varies with the morphology and exposed planes. Since the electron density is different for different planes and is of the order (110) > (100) > (111) > (311), different morphologies showed different photocatalytic activity. For the bean (100) shaped morphology, h<sup>+</sup> are the dominant species and for rods (110) it is e<sup>-</sup>, while e<sup>-</sup>/h<sup>+</sup> are equally responsible for the photocatalytic activity of hexagon (311). For the (111) dominant morphology, OH\* act as the major species for degradation purposes, since they have strong e<sup>-</sup>/h<sup>+</sup> interaction. Hence different morphologies exhibited different photoactivity for a selected pollutant molecule.<sup>62</sup>

### Dye degradation

Zhang *et al.* reported CeO<sub>2</sub> hierarchical nanowires (Fig. 11(a)) and nanorods (Fig. 11(b)) grown on Cu substrates for the photocatalytic degradation of methyl orange (MO) and found that as compared to CeO<sub>2</sub> NPs, the 1-D nanostructure exhibited higher degradation efficiency. Both CeO<sub>2</sub> HNRs and HNWs removed 98.2% and 99.3% of MO under light irradiation for 180 min, revealing a performance which is substantially higher than that of the commercial CeO<sub>2</sub> NPs (68.8%) and P25 (89.5%) as shown in Fig. 11(c) respectively. The high performance in comparison to CeO<sub>2</sub> NPs was achieved only due to their hierarchical 1D nanostructure derived active sites, resulting in a shorter diffusion length of photogenerated holes and increased surface areas. Further, of the two 1-D structures,

although both the materials possessed a 3.2 eV band gap, the nanowires exhibited higher absorption in the wavelength range between 400 and 750 nm (Fig. 11(d)), suggesting higher photonic energy absorption.<sup>77</sup> Further, Yu *et al.* reported uniform single crystalline hexagonal CeO<sub>2</sub> nanosheets for RhB degradation and found that the degradation efficiency of the above nanosheets was more than that of the conventional CeO<sub>2</sub> nanoparticles. The activity improvement was attributed to their 2D nanosheet structure which suppressed the charge pair recombination and their intrinsic single-crystal structure which decreased the charge transfer resistance, thereby yielding much stronger reducible electrons.<sup>79</sup> Further, Arul *et al.* synthesized 3D hierarchical rose-flower-like CeO<sub>2</sub> where CeO<sub>2</sub> nanosheets are stalked to form a flower. Under UV light irradiation, the flower like catalyst showed a degradation rate of 65% for the AO7 dye. The 2D NSs provided better diffusion of generated holes and reduced the agglomeration of the 2D NSs which was responsible for the enhanced activity.<sup>249</sup> In another experiment, Yuan *et al.* reported hierarchical CeO<sub>2</sub> sheets for the photocatalytic decomposition of toxic acetaldehyde. They found that CeO<sub>2</sub> HSs decomposed acetaldehyde more efficiently than CeO<sub>2</sub> NPs and as well as the well known P25. This superior degradation activity is mainly attributed to the high surface to volume ratio of the catalyst and the presence of surface defects.<sup>250</sup> Though nanostructured CeO<sub>2</sub> possesses an impressive degradation property it is active only under UV-light illumination. Hence, the fabrication of a CeO<sub>2</sub> based heterostructure is investigated, which visibly improves the interfacial charge transfer, light absorption and the charge separation and lowers the recombination resulting in enhanced photocatalytic degradation. So far, nanostructured CeO<sub>2</sub> has been combined with different metal oxides,<sup>251–257</sup> sulphides,<sup>258–262</sup> carbonaceous materials,<sup>263–267</sup> *etc.* for efficient dye degradation. For example, Arul *et al.* reported CeO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> spindles as recyclable photocatalysts for the degradation of Eosin Yellow (EY) under visible light irradiation. The degradation was achieved in a very short duration of time (98% in 25 min) in comparison to neat CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> NRs, because of the excellent charge separation and transfer property derived from the heterostructure (Fig. 11(e)). Fig. 11(f) shows the recycling study of the CeO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> heterostructure, where the photocatalyst was found to be very stable and the photocatalytic efficiency was reduced by less than 10% even after 4 cyclic runs. Further they calculated the electrical energy per order of the photocatalyst, a term used to calculate the electrical energy required to remove unit mass of the pollutant. From the calculations, they found that the photocatalyst required much less energy to degrade the EY dye by one order of magnitude. Hence they deduced that the heterostructure possesses greater potential for use as a visible light driven catalyst. They deduced the photodegradation mechanism as shown in Fig. 11(g): upon light irradiation photogenerated electrons migrate from Fe<sub>2</sub>O<sub>3</sub> to the Ce 4f band where they react with oxygen to generate superoxide radicals, while holes migrate from the VB of CeO<sub>2</sub> towards the VB of Fe<sub>2</sub>O<sub>3</sub> yielding hydroxyl radicals. Both the superoxide and hydroxyl radicals were found to be essential for the photodegradation process.<sup>252</sup> Another low cost recyclable CeO<sub>2</sub>-metal oxide heterostructure was reported by Tian *et al.*, where CeO<sub>2</sub> nanoparticles assembled on the rough surface of TiO<sub>2</sub>



Table 3 Complete results of the pollutant degradation performance of CeO<sub>2</sub> and CeO<sub>2</sub> based heterostructures

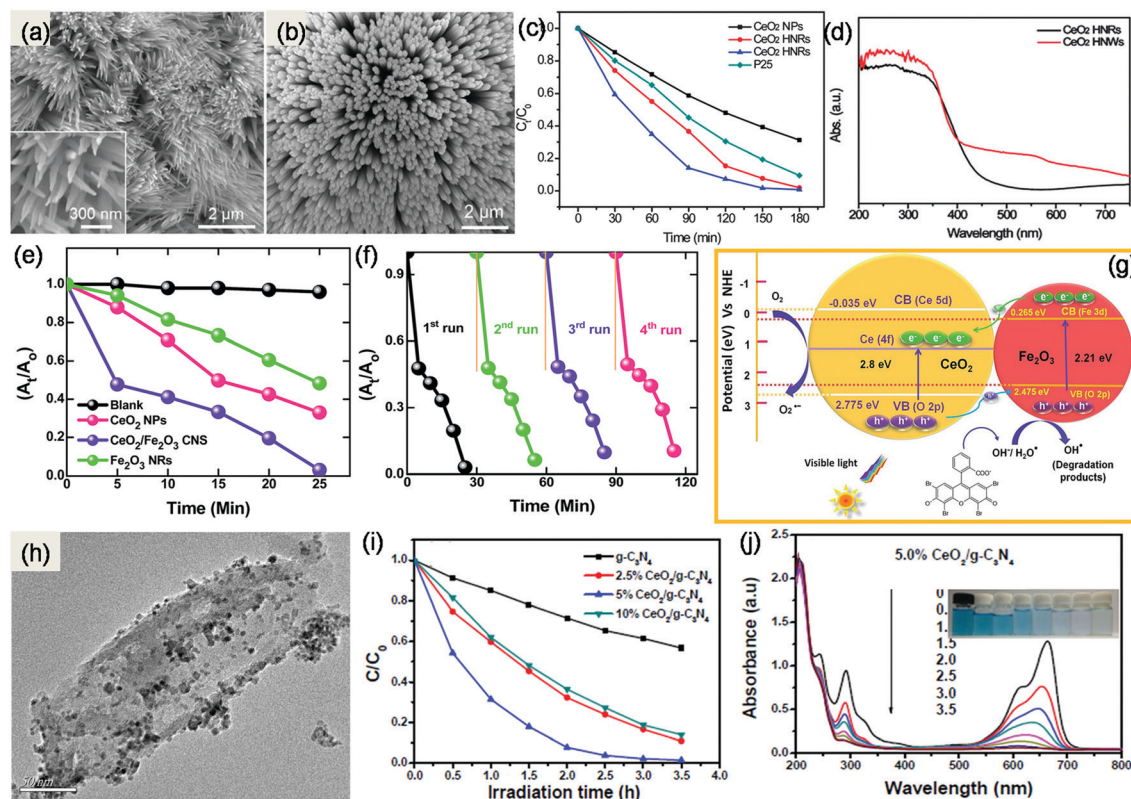
Catalyst	Light source	Reaction conditions	Activity	Ref.
CeO <sub>2</sub> hierarchical NRs	White light, 500 W Xe lamp	20 mg L <sup>-1</sup> MO, 20 mg	98.2% in 180 min	77
CeO <sub>2</sub> hierarchical NWs			99.3% in 180 min	
Single crystalline mesoporous CeO <sub>2</sub> nanosheet	250 W high pressure mercury lamp	1.0 × 10 <sup>-5</sup> mol L <sup>-1</sup> RhB, 20 mg	Nearly 80% in 120 min	79
Ordered meso-CeO <sub>2</sub>	1000 W Xe lamp ( $\lambda > 420$ nm)	70 mg L <sup>-1</sup> AO 7, 50 mg	95% in 7 h	89
Flower-like CeO <sub>2</sub>	UV light ( $\lambda = 365$ nm)	0.3 mM AO 7, 1 cm <sup>2</sup>	~ 65% in 10 h	249
CeO <sub>2</sub> microspheres	1000 W Xe lamp ( $\lambda > 420$ nm)	50 mg L <sup>-1</sup> AO 7, 50 mg	69.7% in 180 min	268
CeO <sub>2</sub> NSs	450 W Xe lamp ( $\lambda > 420$ nm)	26.7 $\mu$ M MB, 30 mg	90% in 6 h	269
CeO <sub>2</sub> NCs	310 nm < $\lambda$ < 400 nm	RhB, 50 mg	30% in 2 h	270
CeO <sub>2</sub> lamellar	UV light, 120 W uviol lamp	5 mg L <sup>-1</sup> MB, 50 mg	96.5% in 60 min	271
Octahedral CeO <sub>2</sub>	UV	5, 20 mg L <sup>-1</sup> MO, 20 mg	98.1% in 5 h	272
CeO <sub>2</sub> NTs			92.8% in 5 h	
Au/CeO <sub>2</sub>	400 W Xe lamp ( $\lambda > 400$ nm)	10 mg L <sup>-1</sup> MO, MB, 2 mg	80% in 6 h, 95% in 5 h	273
BiVO <sub>4</sub> /CeO <sub>2</sub>	Halogen lamp, visible ( $\lambda > 400$ nm)	2 × 10 <sup>-5</sup> M MB, 50 mg	~ 80% in 30 min	251
CeO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub> nanospindles	White, 150 W Xe lamp	0.1 mM EY, 1 mg	98% in 25 min	252
CuO/CeO <sub>2</sub>	15 W UV tube	0.15 mM MB, 100 mg	91.3% in 2 h	253
CeO <sub>2</sub> /TiO <sub>2</sub> nanobelt	350 W mercury lamp (max. emission 356 nm)	20 mg L <sup>-1</sup> MO, 20 mg	100% in 25 min	254
	300 W Xe arc lamp ( $\lambda > 410$ nm)		87% in 25 min	
CeO <sub>2</sub> -TiO <sub>2</sub>	300 W Xe arc lamp ( $\lambda > 400$ nm)	Bph-dye	~ 72% in 3 h	255
CeO <sub>2</sub> /ZnO nanodisks	Natural solar light	50 mg L <sup>-1</sup> direct blue 15, 50 mg	93% in 5 h	256
Hierarchical CeO <sub>2</sub> /ZnO	300 W Xe lamp	10 mg L <sup>-1</sup> RhB, 50 mg	96% in 80 min	257
CdS/CeO <sub>2</sub>	154 W halogen lamps	3 mg L <sup>-1</sup> MB, 20 mg	70% in 120 min	258
CdS NRs-CeO <sub>2</sub> NPs	300 W Xe lamp	40 mg L <sup>-1</sup> dye, 40 mg	96.68% in 48 min	259
CdS NWs/CeO <sub>2</sub> nanoparticles	300 W Xe arc lamp ( $\lambda > 400$ nm)	10 mg L <sup>-1</sup> nitroaromatics, 6 mg	4-nitrophenol ~90% in 3 min	260
Flower like CeO <sub>2</sub> /MoS <sub>2</sub>	150 W Xe lamp-visible light	25 mg L <sup>-1</sup> MO, 25 mg	96.1% in 90 min	261
CeO <sub>2</sub> /CuS composite nanofibers	Strip blue LED lamp	3 mg L <sup>-1</sup> MB	96.38% in 40 min	262
CeO <sub>2</sub> /C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp ( $\lambda > 400$ nm)	10 mg L <sup>-1</sup> MB, 100 mg	95% in 2 h	274
CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp ( $\lambda > 400$ nm)	10 mg L <sup>-1</sup> MB, 25 mg	~ 98.59% in 3.5 h	263
CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	36 W UV lamp (OS72) with a wavelength of 254 nm	10 mg L <sup>-1</sup> MB, 50 mg	90.1% in 180 min	264
CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	8 W Xe lamp	10 <sup>-5</sup> M concentration, 10 mg	97% (MB dye) and 96% (Rh-B dye) in 60 min	265
rGO/CeO <sub>2</sub> NCs	Hg lamp UV	1 × 10 <sup>-5</sup> M MB, 30 mg	~ 87% in 90 min	266
rGO/CeO <sub>2</sub>	Visible light source with intensity 14.5 W m <sup>-2</sup>	1 mM MO	88.3% in 60 min	267
CeO <sub>2</sub>	300 W Xe lamp	10 mg L <sup>-1</sup> CIP, 50 mg	More than 90% in 15 min	275
Hollow BiOCl@CeO <sub>2</sub>	300 W Xe lamp ( $\lambda > 400$ nm)	10 mg L <sup>-1</sup> TC, 50 mg	92% for TC in 120 min	276
CeO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> -MXene	350 W Xe lamp	10 mg L <sup>-1</sup> TC, 30 mg	80.2% of TC in 60 min	277
Nebula-like ZnO/CeO <sub>2</sub> @HNTs	300 W Xe lamp (780–1100 nm)	20 mg L <sup>-1</sup> TC, 30 mg	87% in 60 min	278
Ag <sub>2</sub> O/CeO <sub>2</sub>	300 W Xe lamp ( $\lambda > 420$ nm)	10 mg L <sup>-1</sup> enrofloxacin, 50 mg	87.1% in 120 min	279
CeO <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub> porous nanosheet	Xe lamp (350 nm < $\lambda$ < 780 nm)	10 mg L <sup>-1</sup> MB	96.42% in 70 min	280
		5 mg	85.35% in 30 min	
		20 mg L <sup>-1</sup> TC		
Bi <sub>2</sub> O <sub>3</sub> @CeO <sub>2</sub>	500 W Xe lamp ( $\lambda > 420$ nm)	10 mg L <sup>-1</sup> TC, 20 mg	100% in 180 min	281
Shuttle-like CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	150 W high pressure Xe lamp ( $\lambda > 420$ nm)	10 mg L <sup>-1</sup> NOR, 50 mg	88.6% in 60 min	282
CeO <sub>2</sub> /nitrogen-doped carbon quantum dot/g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp ( $\lambda > 420$ nm)	20 mg L <sup>-1</sup> TC, 100 mg	100% in 60 min	283
2D-CeO <sub>2</sub> on 2D-MoS <sub>2</sub>	250 W Xe lamp ( $\lambda > 420$ nm)	10 mg L <sup>-1</sup> CIP, 50 mg	88.5% in 120 min	284
Defective CeO <sub>2</sub>	Direct sunlight visible region (420–800 nm)	50 ppm phenol 200 mg	35% in 180 min	105
		50 ppm chlorophenol	98% in 180 min	
		50 ppm bromophenol	96% in 180 min	
		50 ppm nitrophenol	99% in 180 min	
CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> nanosheet	300 W Xe lamp ( $\lambda > 420$ nm)	Phenol, bisphenol-A	93.7% in 80 min (BPA)	285
			97.5% (phenol)	
CeO <sub>2</sub> /ZnCo-layered double hydroxide	—	20 mg L <sup>-1</sup> phenol	99.8% in 30 min	286
CoS/CeO <sub>2</sub>	300 W Xe lamp ( $\lambda > 420$ nm)	25 mg L <sup>-1</sup> phenol, 50 mg	85.5% in 60 min	287
		20 mg L <sup>-1</sup> TC	96.5% in 60 min	
CeO <sub>2</sub> -rod/g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp ( $\lambda > 300$ nm)	0.10 g benzylamine, 50 mg	81.2% in 5 h	288

nanobelts producing the CeO<sub>2</sub>-TiO<sub>2</sub> heterostructure. The heterostructure was tested for MO degradation under both UV and visible light, and they found that MO molecules were preferentially captured by CeO<sub>2</sub> nanoparticles and were degraded by the free radicals and further released to the solution, and hence a capture,

photodegradation and release process was followed. The heterostructure possessed enhanced photoactivity due to the efficient charge separation and transfer due to the well matching energy band between CeO<sub>2</sub> and TiO<sub>2</sub> and the large active surface area.<sup>254</sup> Further Parida and co-workers prepared a series of 2D/2D-BiOI/CeO<sub>2</sub>







**Fig. 11** (a and b) SEM micrographs of  $\text{CeO}_2$  nanowires and nanorods respectively. (c) Photocatalytic degradation of MO over  $\text{CeO}_2$  HNRS and  $\text{CeO}_2$  HNWS in addition to that over  $\text{CeO}_2$  NPs and P25 with respect to light irradiation time. (d) UV-DRS spectra of  $\text{CeO}_2$  nanowires and nanorods.<sup>77</sup> Reproduced by permission of The Royal Society of Chemistry. (e) Degradation efficiency of the blank EY with  $\text{CeO}_2$  nanoparticles,  $\text{CeO}_2/\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  nanorod catalysts versus irradiation time. (f) Reusability test of the  $\text{CeO}_2\text{-Fe}_2\text{O}_3$  photocatalyst in degrading EY under visible light irradiation. (g) Proposed photodegradation mechanism of  $\text{CeO}_2/\text{Fe}_2\text{O}_3$  CNSs in degrading the EY dye under visible light irradiation.<sup>252</sup> Reproduced by permission of The Royal Society of Chemistry. (h) TEM micrographs of  $\text{CeO}_2\text{-g-C}_3\text{N}_4$ . (i) Photodegradation efficiency of the MB dye by  $\text{g-C}_3\text{N}_4$  and  $\text{CeO}_2/\text{g-C}_3\text{N}_4$  catalysts versus light irradiation. (j) Changes in the ultraviolet-visible absorbance spectra of MB dye solutions with optimized  $\text{CeO}_2\text{-g-C}_3\text{N}_4$ .<sup>263</sup> Reproduced by permission of The Royal Society of Chemistry.

nanocomposites and tested their effectivity towards RhB decolourization efficiency. Among the very best catalysts, 40%BiOI- $\text{CeO}_2$  was proven to be the best and within a very short time 89% decolourization efficiency was achieved for 100 ppm RhB under sunlight. The major cause behind the enhanced photoactivity was found to be the presence of excess surface oxygen vacancies and better charge separation efficiency through the Z-scheme at the interface.<sup>117</sup> Further, Gu *et al.* reported a heterostructure photocatalyst consisting of one-dimensional (1D) CdS nanorods (NRs) and  $\text{CeO}_2$  nanoparticles (NPs). They found that the photocatalytic degradation of RhB was around 97% for the CdS/ $\text{CeO}_2$  heterostructure, which was much higher than that of its neat counterparts. The rate constant of CdS/ $\text{CeO}_2$  was nearly 28 times and 3.4 times higher than that of neat  $\text{CeO}_2$  and CdS respectively, due to the inhibition of electron-hole pair recombination benefiting from efficient electron transfer from CdS NRs to  $\text{CeO}_2$  NPs producing effective superoxide radicals. They studied the degradation pathway of RhB and found that after 16 min *N*-de-ethylated intermediates were formed but further with time, these products' intensity decreased down. Further, a high mineralization rate (86% TOC removal) was observed, which confirmed the complete mineralization of RhB.<sup>259</sup> Additionally, She *et al.* reported an important synthetic strategy to design a beautiful heterostructure

between the  $\text{CeO}_2(111)$  cube and the  $\text{g-C}_3\text{N}_4$  nanosheet as shown in Fig. 11(h and i). The heterostructure exhibited 98.59% degradation efficiency of MB within 3.5 h under visible light which was much higher than that of the neat materials. The variation in the optical absorption spectra of MB degradation over 5% $\text{CeO}_2\text{-g-C}_3\text{N}_4$  is shown in Fig. 11(j). With light irradiation, as the time passed the colour of MB gradually disappeared which confirmed the photodegradation process.<sup>263</sup> Verma *et al.* reported an *in situ*  $\text{CeO}_2/\text{rGO}$  nanocomposite prepared through the one step ammonia assisted hydrothermal method for the elimination of MO under visible light. The heterostructure between  $\text{CeO}_2$  (0D) and graphene (2D) increased charge separation and transportation ability simultaneously and extended the range of the solar absorption spectrum as well as increased the dye molecule absorptivity over its surface. In brief, under light irradiation photogenerated electrons and holes are produced over the  $\text{CeO}_2$  surface; since rGO acts as a sink, electrons drift to the rGO surface and produce superoxide radicals, while the holes at the  $\text{CeO}_2$  surface react with water to generate hydroxyl radicals. Through the  $\pi\text{-}\pi$  interaction between rGO and the MO dye molecule, the dyes are efficiently adsorbed over the surface of rGO where they react with both superoxide and hydroxyl radicals to yield the degraded product.<sup>267</sup>

## Antibiotics removal

Nowadays, the excessive use of antibiotics like tetracycline, norfloxacin, enrofloxacin, ciprofloxacin (CIP), *etc.* is a major headache for society, as these are non-biodegradable and cause adverse effects on the ecosystem. Amoresi *et al.* verified the morphological effect of different exposed plane  $\text{CeO}_2$  on CIP drug molecule photodegradation. They found that nanostructured  $\text{CeO}_2$  with different exposed planes has a site selective tendency for CIP molecule cleavage and yields different degraded products. In brief, the CIP molecule contains multiple functional groups; hence electrostatic potential maps show negative sites corresponding to nitrogen atoms and oxygen atoms of COOH termination and positive sites corresponding to low electron density aromatic rings and cyclopropyl groups as shown in Fig. 12(a). As we have already discussed in the above section, rod and bean morphologies with the (110) and (100) predominant surfaces have a more negative surface layer, hence show higher affinity towards the positive site of the CIP drug during the photodegradation process. On the other hand, the hexagon with the (311) exposed plane and the rod/cube morphology with the (111) exposed plane show good affinity for the negative site of the CIP molecule, as these morphologies contain a more positive surface layer.<sup>62</sup> Further, a number of bismuth based materials along with other low-dimensional materials have been studied with  $\text{CeO}_2$  towards the elimination of different antibiotics.<sup>127,276–284</sup> Recently an efficient hollow  $\text{BiOCl}@ \text{CeO}_2$  heterostructured microsphere with type-II staggered-arrangement was reported for the photodegradation of an antibiotic, *i.e.* tetracycline (TC). The authors observed that the above heterostructure degraded 92% TC within 120 min owing to the distinctive hollow

structures and better charge carrier transportation and separation. Due to the matched band energy between n- $\text{CeO}_2$  and p- $\text{BiOCl}$  an effective p-n junction was formed *via* Fermi level equilibration, which enhanced the interfacial charge transfer, because of which energetic electrons are now available at the  $\text{CeO}_2$  surface while holes are present at  $\text{BiOCl}$ . From the ESR trapping experiment, the authors concluded that both superoxide and hydroxyls were found to be active species, while the higher peak strength of  $\text{DMPO-O}_2^-$  confirmed the greater participation of superoxide radicals in TC degradation.<sup>276</sup> Liu *et al.* presented a method of preparation of a 1D–2D heterostructure composite between shuttle like  $\text{CeO}_2$  and g- $\text{C}_3\text{N}_4$  nanosheets and tested its photocatalytic activity towards norfloxacin degradation. The group found that the composite exhibited higher mineralization efficiency, *i.e.* 63.8%, than that of neat 1D- $\text{CeO}_2$  (31.8%) and g- $\text{C}_3\text{N}_4$  (39.4%) in a duration of 60 min. They found that gradual shedding of functional groups in norfloxacin molecules occurred during the course of reaction and ultimately the molecules decomposed into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .<sup>282</sup> A series of 2D/2D  $\text{MoS}_2/\text{CeO}_2$  heterojunctions were successfully prepared by Ji *et al.* following a facile hydrothermal method. In comparison to neat  $\text{MoS}_2$  and  $\text{CeO}_2$ , the optimized  $\text{MoS}_2/\text{CeO}_2$  heterojunction (88.5%) exhibited higher photocatalytic performance for ciprofloxacin (CIP) degradation as shown in Fig. 12(b). The enhanced degradation efficiency of the  $\text{MoS}_2/\text{CeO}_2$  heterojunction was attributed to its 2D/2D structure. Due to the presence of an effective 2D–2D interface, the photogenerated charge carriers were effectively separated and transferred, and meanwhile, the generated oxygen vacancies broadened the light absorption range of the heterojunction and overall both the factors helped to generate reactive oxidizing

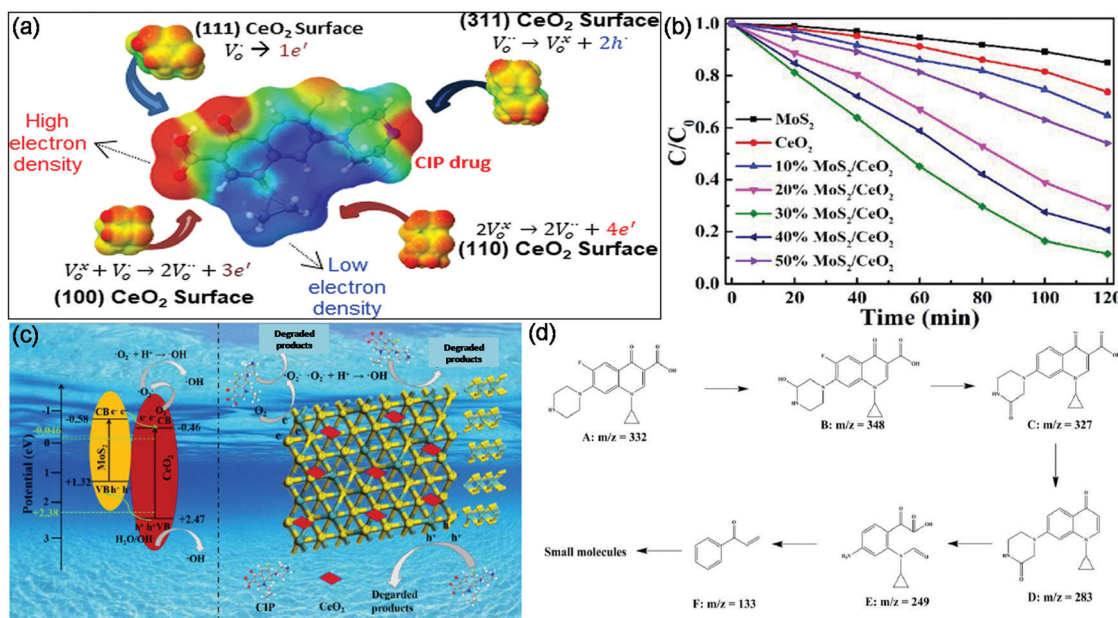


Fig. 12 (a) Electrostatic potential maps showing different positive and negative sites for the ciprofloxacin molecule and the attacking affinity of (111), (311), (110), and (100) surfaces of  $\text{CeO}_2$  towards CIP. Reprinted with permission from ref. 62, copyright 2019 American Chemical Society. (b) Degradation efficiency of the CIP drug in the presence of different  $\text{MoS}_2/\text{CeO}_2$  samples under visible light irradiation. (c) Schematic illustration of charge transfer and generation of active species for photodegradation by optimized  $\text{MoS}_2/\text{CeO}_2$ . (d) Proposed degradation pathway of the CIP drug. Reprinted from ref. 284 with permission from Elsevier.



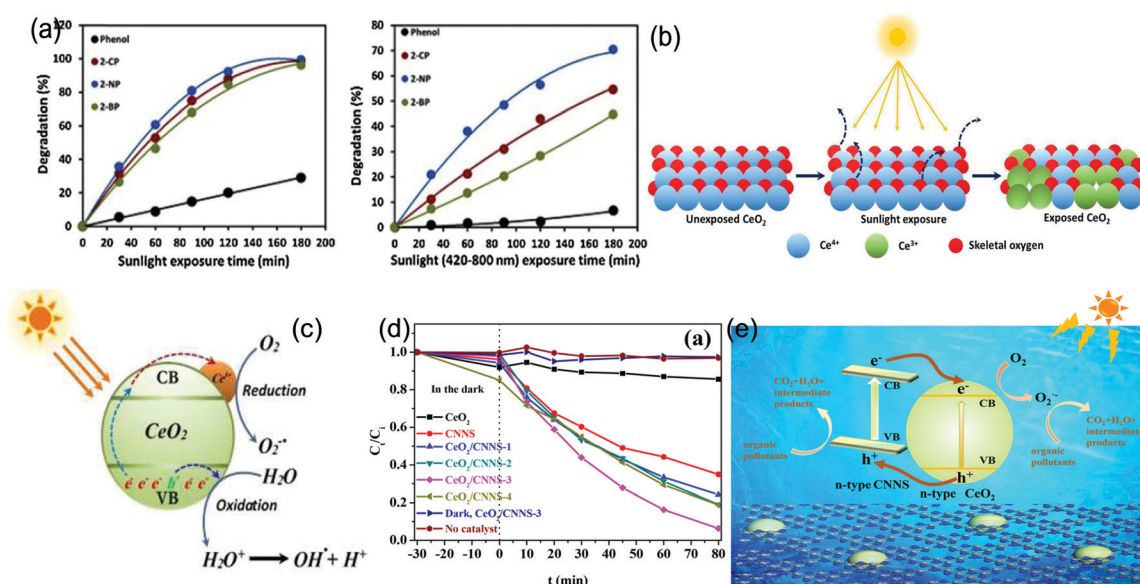


species for the degradation purpose (Fig. 12(c)). Further, they analyzed the CIP degradation pathway which can be described as follows: as CIP contains a piperazine ring, the generated hydroxyl radicals at first cleaved the piperazine ring to yield B ( $m/z = 348$ ). Then the degradation reaction continued, where by losing the F and OH groups, C ( $m/z = 327$ ) was formed. Further, the product D ( $m/z = 283$ ) was formed from the subsequent cleavage of the carboxyl group. Meanwhile, E ( $m/z = 249$ ) was formed by the cleavage of the carbon-carbon double bond adjacent to the carboxylic acid group. Finally, F ( $m/z = 133$ ) was further degraded into smaller molecules, *i.e.*  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The complete degradation pathway is given in Fig. 12(d).<sup>284</sup>

### Phenolic compound degradation to non-toxic products

Phenolic group organic materials are now the major threat to air, water and soil. In light of this, different  $\text{CeO}_2$  based materials were synthesized and tested for the effective removal of these pollutants. For example, Aslam *et al.* studied the photocatalytic degradation of phenolic compounds such as phenol, 2-bromophenol (bp), 2-chlorophenol (cp) and 2-nitrophenol (np) over a uniform particle sized (11 nm)  $\text{CeO}_2$  nanostructure upon exposure to the visible region (420–800 nm) and the complete spectrum of sunlight (Fig. 13(a)) and found an enhanced degradation rate in the full spectrum of sunlight. The exposure to direct sunlight enhanced the defect formation as the irradiated photons help the surface oxygen to escape from the  $\text{CeO}_2$  surface as shown in Fig. 13(b). The induction of defects composed of  $\text{CeO}_{2-x}$  states which act as trap and transfer centers for the effective separation of electrons resulted in the formation of reactive oxidative species. Further, they found that  $\text{Ce}^{3+}$  played a key role in the generation of superoxide anion radicals (Fig. 13(c)) which were held responsible

for complete mineralization of 2-NP and 2-CP, while less toxic aromatic intermediates were formed from phenol and 2-BP.<sup>105</sup> Further, Ma *et al.* reported a type-II n-n heterostructure containing  $\text{CeO}_2$  over  $\text{g-C}_3\text{N}_4$  nanosheets and tested its efficiency towards bisphenol-A degradation. Under visible light irradiation, only 65% removal efficiency was obtained for the  $\text{g-C}_3\text{N}_4$  nanosheet and 14.4% for  $\text{CeO}_2$ . However, the removal efficiency was found to be 93.7% at a time span of 80 min as shown in Fig. 13(d) with an apparent rate constant of  $0.0199 \text{ min}^{-1}$  for the type-II heterostructure. The higher efficiency of the heterostructure is mainly due to the efficient photogenerated charge transfer and separation process across the interface of the n-n junction. As the VB potential of n-type CNNS is unable to produce hydroxyl radicals, only the photogenerated superoxide combined with holes actively takes part in the degradation process as shown in Fig. 13(e).<sup>285</sup> Recently, Gao *et al.* prepared a  $\text{CeO}_2$  incorporated ZnCo layered double hydroxide and employed it for phenol degradation in the presence of peroxydisulfate. The generated oxidising species such as sulphate, hydroxyl, superoxide and holes were held responsible for the 99.8% degradation of phenol.<sup>286</sup> Moreover, Chai *et al.* reported another 1D/2D heterostructure containing  $\text{CeO}_2$  NRs and  $\text{g-C}_3\text{N}_4$  NSs and tested its efficiency towards oxidative coupling of benzylamine. Under UV-visible light irradiation, the 1D/2D heterostructure exhibited a 3 times higher oxidation rate constant compared to neat  $\text{g-C}_3\text{N}_4$  and  $\text{CeO}_2$ . They found that the presence of surface defects on  $\text{CeO}_2$  was the major reason behind the higher oxidation activity. In brief, the oxygen vacancy traps the oxygen and generates superoxide radicals which break to form hydroxyl species; along with the hydroxyl species, holes also take part in the oxidative coupling process.<sup>288</sup>



**Fig. 13** (a) Degradation curve of 50 ppm phenol, 2-CP, 2-BP, and 2-NP over  $\text{CeO}_2$  under direct sunlight and in the visible region (420–800 nm). (b) Schematic illustration of defect formation in  $\text{CeO}_2$  under sunlight exposure. (c) Schematic illustration of the generation of active species over defective  $\text{CeO}_2$ . Reprinted from ref. 105 with permission from Elsevier. (d) Photocatalytic degradation of phenol in the presence of different  $\text{CeO}_2$ -CNNS heterojunctions. (e) Plausible mechanism of charge transfer and photodegradation of phenol in  $\text{CeO}_2$  and CNNS n-n junction. Reprinted with permission from ref. 285, copyright 2019 American Chemical Society.

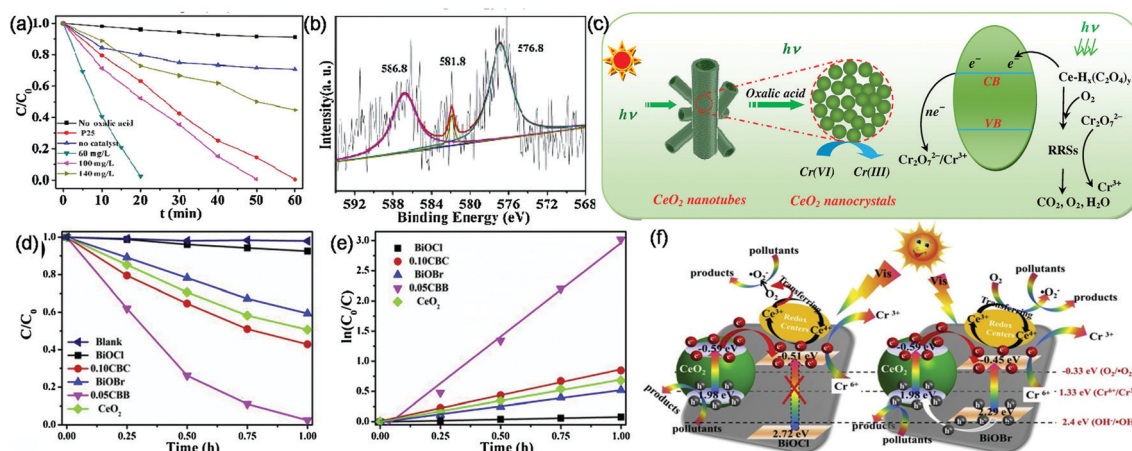


## Heavy metal removal

Worldwide industrialization and technological advancement have brought a lot of troubles to the environment by releasing large quantities of heavy metals to the wastewater which represents a serious threat to global health. Now the heavy metal contaminants are beyond the recommended limit (Cr ( $0.1 \text{ mg L}^{-1}$ ), Pb ( $0.015 \text{ mg L}^{-1}$ ), As ( $0.010 \text{ mg L}^{-1}$ ), Cd ( $0.005 \text{ mg L}^{-1}$ ) and Hg ( $0.00003 \text{ mg L}^{-1}$ )) and are non-biodegradable which has attracted wide public concern. Unlike organic pollutants or dyes, heavy metals can't be easily broken down biologically or chemically; however they can be reduced/transformed to a less toxic form.<sup>289–294</sup> Hence, a variety of nanostructured  $\text{CeO}_2$  and  $\text{CeO}_2$  based heterostructures have been designed in this respect.<sup>295–304</sup>

To start with, Wu *et al.* synthesized  $\text{CeO}_2$  nanotubes (NTs) *via* the template-assisted method and tested their photocatalytic activity for  $\text{Cr(VI)}$  reduction in the presence of oxalic acid. Under UV light irradiation, the photocatalytic reduction efficiency of 100 ppm  $\text{Cr(VI)}$  reached up to 99.6% within 50 min (Fig. 14(a)) with an apparent rate constant of  $0.10294 \text{ min}^{-1}$ . The effective reduction of  $\text{Cr(VI)}$  to  $\text{Cr(III)}$  was confirmed by the XPS spectra shown in Fig. 14(b) where a prominent Cr 2p peak corresponding to  $\text{Cr(III)}$  is visualised. The template directed  $\text{CeO}_2$  nanotube showed good potential towards chromium reduction because of the high photonic energy capture ability arising from its one dimensional characteristic and more importantly the oxalic acid– $\text{CeO}_2$  surface complex formation. In brief, the small molecular weight oxalic acid formed a metal complex with the Ce of  $\text{CeO}_2$ , and enabled intramolecular electron transfer from the oxalic acid ligand to the Ce metal leading to the formation of organic radicals promoting  $\text{Cr(VI)}$  reduction under light irradiation as shown in Fig. 14(c).<sup>75</sup> Further, a lot of work has been reported on the photoreduction of  $\text{Cr(VI)}$  by using different  $\text{CeO}_2$  based materials. For example, Yang and co-workers reported 0D/2D  $\text{CeO}_2$  QDs/ $\text{BiOX}$  (X = Cl, Br)

nanoplate heterojunctions. Under 5 W white LED light irradiation, the as-prepared 0D/2D heterojunction exhibited high photocatalytic performance not only for the reduction of  $\text{Cr(VI)}$  but also for the degradation of tetracycline (TC). After 1 h irradiation, the photoreduction rates of  $\text{Cr(VI)}$  over  $\text{CeO}_2$  QDs/ $\text{BiOBr}$  (CBB) and CBC were found to be 97% and 57% respectively with a pseudo first order kinetics as shown in Fig. 14(d and e). As compared to  $\text{CeO}_2$  QD decorated  $\text{BiOBr}$ , the  $\text{BiOCl}$  based composite possessed lower photoactivity due to its higher band gap and incapability of visible light absorption. However, the superior photocatalytic activity of the composite compared to pristine materials was attributed to mutual interaction of carriers leading to the efficient transfer and separation of photoexcited carriers and increment in the light absorption ability. Further, the formation of a strongly coupled interface between  $\text{BiOX}$  nanoplates and  $\text{CeO}_2$  QDs and inner  $\text{Ce}^{4+}/\text{Ce}^{3+}$  redox centres enhances the activity further (Fig. 14(f)).<sup>297</sup> Later by the same group, another heterojunction between  $\text{CeO}_2$  QDs and  $\text{Bi}_2\text{MoO}_6$  (BMO) was reported which exhibited more efficient charge carrier transfer and separation capacity. Under light irradiation, the optimized  $\text{CeO}_2$ –BMO heterojunction showed maximum  $\text{Cr(VI)}$  reduction (97%) within 90 min, which was higher than that of  $\text{CeO}_2$  (30%) and  $\text{Bi}_2\text{MoO}_6$  (19%) respectively.<sup>298</sup> Parida and his team recently reported a 1D–2D heterostructure between  $\text{CeO}_2$  nanorods and  $\text{BiFeO}_3$  nanosheets and *in situ* decorated nitrogen doped carbon over it. Interestingly,  $\text{MgCeO}_2$ –BFO was found to be the best photocatalyst (98.2%) for  $\text{Cr(VI)}$  reduction compared to the neat counterparts  $\text{CeO}_2$  (35%),  $\text{MgCeO}_2$  (56%) and BFO (75%), which was attributed to the effective charge separation and transfer at the heterojunction.<sup>232</sup> Li *et al.* fabricated sandwiched  $\text{TiO}_2@\text{Pt}@\text{CeO}_2$  double shell hollow spheres and tested their photocatalytic performance towards hexavalent chromium reduction. Under solar light irradiation, they found the highest reduction rate for  $\text{TiO}_2@\text{Pt}@\text{CeO}_2$  (1.901) as compared to neat  $\text{TiO}_2$  (1.040) and



**Fig. 14** (a) Photoreduction activity of  $\text{Cr(VI)}$  solutions of different ppm over  $\text{CeO}_2$  nanotubes in the presence of oxalic acid. (b) High-resolution Cr 2p XPS spectra of the  $\text{CeO}_2$  catalyst after photoreduction. (c) Proposed scheme of the underlying mechanism of  $\text{Cr(VI)}$  photoreduction assisted by oxalic acid over  $\text{CeO}_2$  nanotubes under UV light irradiation.<sup>75</sup> (d) and (e) The hexavalent chromium photoreduction curves and (e) the pseudo-first-order kinetics curves of  $\text{BiOX}$ ,  $\text{CeO}_2$  and  $\text{BiOX}$  modified  $\text{CeO}_2$ . (f) Schematic illustration of the photogenerated charge transfer and separation mechanism across  $\text{CeO}_2/\text{BiOCl}$  and  $\text{CeO}_2/\text{BiOBr}$  heterojunction photocatalysts.<sup>297</sup> Reprinted with permission from Elsevier.



CeO<sub>2</sub> (0.992). The enhanced photoreduction activity was mainly due to the unique sandwiched double shell structure and the presence of two oxides (TiO<sub>2</sub> and CeO<sub>2</sub>). Further, the addition of the Pt co-catalyst (electron trap site) stores and shuttles the photogenerated excitons, and increases the formation of active radicals responsible for photoreduction reaction.<sup>300</sup> Additionally, Kashinath and his unit reported a facile *in situ* fabrication method for the development of cerium oxide decorated graphene oxide (CeO<sub>2</sub>-GO) binary nanocomposites. The hexagonal nano CeO<sub>2</sub> were embedded on the layered graphene oxide sheets *via* a simple microwave irradiation technique and the binary hybrid was tested for the removal of hexavalent chromium ions, dye degradation and antibacterial activities. Under UV (ultraviolet) light irradiation, the binary hybrid showed a rapid hexavalent chromium removal efficiency compared to neat GO and CeO<sub>2</sub>.<sup>301</sup>

## 8. Conclusion and further prospective

Nanostructured CeO<sub>2</sub> and CeO<sub>2</sub> based heterostructure materials with distinct morphology, exposed planes/facets and interfaces have aroused extensive research interest across the globe due to their extraordinary properties and widespread application in the field of photocatalysis. In this review, we have systematically summarized various synthetic routes towards the fabrication of several morphology oriented CeO<sub>2</sub> and its heterostructures as well as their application towards different solar energy conversion-based reactions (hydrogen production, O<sub>2</sub> production, CO<sub>2</sub> reduction and nitrogen reduction) and environmental pollutant (organic/inorganic) remediation. Additionally, theoretical aspects and experimental evidence behind the enhancement in the activity have been well explained. Although a large number of experimental and theoretical studies relating to nanostructured CeO<sub>2</sub> and CeO<sub>2</sub> based materials have been published in recent years, some fundamental aspects still need more attention. However, research in this area still faces a lot of challenges and encouragingly is filled with a lot of opportunities to explore new science. CeO<sub>2</sub> has two key features, *i.e.* abundant oxygen defects and flexible oxidation state ( $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$ ) shuttling ability, which make it a promising candidate for various photocatalytic applications. This rare earth oxide and its composites are also extensively studied for different electrocatalytic reactions because upon forming a hybrid, the number of active site increases which strongly influences the electronic structure of the other combining unit (novel metals, metal nitrides, phosphides, *etc.*) which ultimately improves the performance and durability of the system.

But in this review, we mainly focused on the photocatalytic aspect. However, the major shortcoming of CeO<sub>2</sub> as a semiconductor photocatalyst is its low solar light absorption efficiency, fast carrier recombination and higher bandgap. Yet, intrinsic O<sub>v</sub> have the ability to alter the band gap of CeO<sub>2</sub> without causing serious damage to the crystal lattice. Hence, a low band gap CeO<sub>2</sub> (3 to 2.6 eV) with a stable surface structure can bring about a revolution in the field of visible light driven photocatalysis. We have also discussed different modification techniques adopted

for enhancing the catalytic efficiency of CeO<sub>2</sub> and its composites by taking examples from reported literature.

Adding more to it, the oxygen vacancy is largely responsible for the higher photoactivity; however its controlled generation is very challenging and needs more experimental exploration. Further, the surface oxygen vacancy is very crucial for determining the tensile or compressive strain, which is also an issue for vacancy stabilization. For example, Wu *et al.* stated that tensile strain stabilizes the reduced states of ceria such as oxygen vacancies and surface hydroxyls, while compressive strain destabilizes the reduced states. In addition to these, there are many theoretical and experimental studies which have stated the qualitative influence of the oxygen vacancy and Ce<sup>3+</sup>, but have not stated how to control the amount of defects to achieve an optimum result. So the controlled generation of surface defects and inhibition of the bulk vacancy still suffer from the lack of a viable facile synthetic route. In order to know more about the electronic and geometric structure of surface vacancies over CeO<sub>2</sub> based materials, more advanced techniques such as scanning tunnelling microscopy, HDAAF, XAFS, XANES, *etc.* should be used in more detail and in a regular manner. Further, the effect of O<sub>v</sub> and the Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio on photocatalytic reactions needs more *in situ* characterization and computation studies. Additionally, current articles mainly give qualitative ideas on the effect of O<sub>v</sub> and Ce<sup>3+</sup> on catalytic efficiency but it needs direct confirmation which can be achieved by advanced *in situ* characterization and theoretical optimization that can develop a strong understanding of structure–activity inter-linkage and hence guide researchers to design extraordinary photocatalytic systems. In brief, the precise synthesis of CeO<sub>2</sub> based systems with a required amount of O<sub>v</sub> and Ce<sup>3+</sup>/Ce<sup>4+</sup> is very essential as it helps in providing useful information on the catalytic mechanism.

Considerable work has been done with regard to the preparation of morphology oriented CeO<sub>2</sub> based materials and their catalytic as well as photocatalytic application. However, exposure of one facet or controlled growth of one or two facets changes the photoactivity drastically in comparison to the bulk nanostructure. For example, the exposed (100) plane is more suitable for dye degradation, while the (311) plane is more efficient for organic pollutant removal. Hence, this field needs more scientific attention. In this aspect, theoretical studies can show the path of designing desired exposed facet CeO<sub>2</sub> based materials towards a particular type of photocatalytic reaction. In addition to the above stated modification, it is also quite effective to prepare specific nanostructured oriented CeO<sub>2</sub> based systems such as core-shell, porous, hollow structures, hydrophilic/hydrophobic surfaces, *etc.* to achieve benchmark conversion efficiency.

Moreover, a viable, soft and precise synthetic route for designing nanostructured CeO<sub>2</sub> and CeO<sub>2</sub> based materials with higher yield also needs more attention. Different green, environmentally friendly approaches should be followed for the preparation of morphology oriented CeO<sub>2</sub>. In addition to using organic solvents and a lot of structure directing agents, common solvents like water, alcohol and biosurfactants should be used for the preparation of the above.



Further, in the preparation of CeO<sub>2</sub> based heterostructures selection of a compatible lower dimensional other half photocatalyst with a distinctly shaped facet is also crucial for constructing an efficient photocatalytic system. So the design of a CeO<sub>2</sub> based photocatalytic system with appropriate interfacial contact between CeO<sub>2</sub> and the other photocatalyst still needs more study. This interface generally inhibits the photogenerated charge pair recombination, and hence the atomic level interaction of different nanostructures also needs more scientific research. In addition to this, the interfacial charge separation and transfer across the interface of two materials and the mechanism behind it are still in ambiguity. The charge transfer may be junctional type (p–n, n–n) or may be Z-scheme type or heterostructure type; hence more thorough theoretical as well as experimental evidence is required in this field. Moreover, coupling of CeO<sub>2</sub> with other materials apart from conventional metal oxides, CdS, g-C<sub>3</sub>N<sub>4</sub>, and materials like metal phosphides, selenides, and borides can provide a better compatible partner for CeO<sub>2</sub>, and hence this field needs more experimental verification. Furthermore, the charge conducting ability of CeO<sub>2</sub> framed systems can be increased by either integrating CeO<sub>2</sub> with highly conductive substances or nucleating CeO<sub>2</sub> on conductive materials like carbon cloth, metal foam, etc.

Theoretical analysis of different photocatalytic reactions especially water oxidation, CO<sub>2</sub> reduction and active radical generation over normal and defective CeO<sub>2</sub> with different exposed planes needs more systematic study. Further, there are a handful of attractive reports citing the photocatalytic dye degradation and organic pollutant oxidation, but very few studies have been carried out on photocatalytic water splitting and the NRR. However the oxygen vacancy enriched CeO<sub>2</sub> has shown some outstanding results in photocatalytic water splitting. So, efficient O<sub>v</sub> enriched CeO<sub>2</sub> based catalysts with appropriate exposed facets, higher light absorption capacity and lower photogenerated charge recombination still need continuous research. Further, with the increasing efforts of the research community, we strongly believe that future CeO<sub>2</sub> based photocatalytic systems will act as promising materials towards sustainable energy generation and environmental pollution abatement on an industrial scale.

## Conflicts of interest

There are no conflicts to declare.

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