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# Defective TiO<sub>2</sub> for photocatalytic CO<sub>2</sub> conversion to fuels and chemicals

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Photocatalytic conversion of CO<sub>2</sub> into fuels and valuable chemicals using solar energy is a promising technology to combat climate change and meet the growing energy demand. Extensive effort is going on for the development of a photocatalyst with desirable optical, surface and electronic properties. This review article discusses recent development in the field of photocatalytic CO<sub>2</sub> conversion using defective TiO<sub>2</sub>. It specifically focuses on the different synthesis methodologies adapted to generate the defects and their impact on the chemical, optical and surface properties of TiO<sub>2</sub> and, thus, photocatalytic CO<sub>2</sub> conversion. It also encompasses theoretical investigations performed to understand the role of defects in adsorption and activation of CO<sub>2</sub> and identify the mechanistic pathway which governs the formation and selectivity of different products. It is divided into three parts: (i) general mechanism and thermodynamic criteria for defective TiO<sub>2</sub> catalyzed CO<sub>2</sub> conversion, (ii) theoretical investigation on the role of defects in the CO<sub>2</sub> adsorption–activation and mechanism responsible for the formation and selectivity of different products, and (iii) the effect of variation of physicochemical properties of defective TiO<sub>2</sub> synthesized using different methods on the photocatalytic conversion of CO<sub>2</sub>. The review also discusses the limitations and the challenges of defective TiO<sub>2</sub> photocatalysts that need to be overcome for the production of sustainable fuel utilizing solar energy.

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## 1. Introduction

Extensive use of fossil fuels leads to the depletion of natural resources and is a major source of anthropogenic CO<sub>2</sub>. Hence, there is an active search going on for the replacement of fossil fuels with renewable energy sources.<sup>1,2</sup> According to the

International Panel on Climate Change (IPCC) prediction, by 2100, the global temperature may rise by 1.9 °C, due to continuous increase in anthropogenic CO<sub>2</sub>.<sup>3</sup> Thus, CO<sub>2</sub> capture, utilization, and storage are key in reducing its increased concentration in the earth's atmosphere. The use of solar energy, an abundant and renewable source of energy available on the earth, is one of the best solutions to tackle energy challenges. The total solar energy falling on the earth is  $1.3 \times 10^5$  TW, which is four orders of magnitude higher than the current

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interests focus on the design and synthesis of nanomaterials for their application in photocatalytic H<sub>2</sub> generation and CO<sub>2</sub> conversion.



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overall human energy consumption ( $1.85 \times 10$  TW in 2017). Conversion of inexhaustible solar energy into renewable energy carriers such as electricity using solar cells or hydrogen generated by photocatalytic water splitting is a promising approach. However, the storage of the renewable electricity generated from solar cells, as well as hydrogen gas, is challenging, preventing the development of these technologies.

The catalytic conversion of CO<sub>2</sub> to fuels and chemicals using solar energy can provide a solution to excessive anthropogenic CO<sub>2</sub> in the atmosphere as well as an alternative to the storage of electricity or hydrogen gas. Photocatalytic CO<sub>2</sub> conversion offers a viable solution for the abatement of climate change by converting CO<sub>2</sub> into valuable fuels using solar energy.<sup>4–8</sup> The use of CO<sub>2</sub> from the atmosphere as a carbon source and its conversion into the hydrocarbons (fuel) which can be further utilized as an energy source in a closed-loop is often termed as ‘artificial photosynthesis’.<sup>9</sup>

The first report on photocatalytic CO<sub>2</sub> reduction came in 1978 by Halmann *et al.*<sup>10</sup> They studied the photoelectrochemical conversion of CO<sub>2</sub> to formic acid, formaldehyde, and methane under UV-visible light illumination using single crystal gallium phosphide. In 1979, Inoue *et al.*<sup>11</sup> reported the generation of organic compounds like formic acid, formaldehyde, methanol and methane by photocatalytic CO<sub>2</sub> conversion using an aqueous suspension of different semiconductors such as WO<sub>3</sub>, TiO<sub>2</sub>, CdS, GaP, SiC, and ZnO under UV-visible light

illumination.<sup>11</sup> After these initial discoveries, although a large number of photocatalysts have been explored, the desired productivity, selectivity, and catalyst stability have not yet been achieved.

The efficiency of the photocatalytic processes lies in the development of a suitable semiconductor as a photocatalyst having extensive absorption in the visible region of solar light, low rate of recombination of charge carriers and stability. Among various semiconductors, TiO<sub>2</sub> is widely studied as a photocatalyst because of its properties such as inexpensiveness, chemical and thermal stability, low toxicity and desired conduction and valence band edge for CO<sub>2</sub> reduction.<sup>12–15</sup> However, the photocatalytic activity of TiO<sub>2</sub> is low in solar light, due to poor absorption in the visible region, which constitutes 43% of the solar spectrum, and a high rate of recombination of photogenerated charge carriers.<sup>16–20</sup> To address these issues, different strategies were adopted, such as heteroatom doping, heterojunction formation, dye sensitization, defect engineering *etc.*<sup>21–30</sup>

Among these, defect engineering holds promise as the presence, concentration and distribution of defects play a key role in tuning the electronic, chemical and surface properties of TiO<sub>2</sub>. It was reported that the light absorption property of TiO<sub>2</sub> can be extended up to the IR region and also, the defect sites assist in adsorption and activation of the CO<sub>2</sub> molecule.<sup>4</sup> Not only the oxygen vacant site but also the uncoordinated bonds near the oxygen vacant sites help in the activation of the CO<sub>2</sub> molecule.<sup>4</sup>

There are few review articles published on the application of defective TiO<sub>2</sub> for CO<sub>2</sub> conversion.<sup>31–34</sup> However, they have not discussed the impact brought about by introducing defects using different synthesis methodologies on the electronic, surface and chemical properties of TiO<sub>2</sub> and its correlation with the photocatalytic CO<sub>2</sub> conversion, which is the main focus of this review article. Moreover, this article also encompasses both theoretical and experimental studies carried out on defective TiO<sub>2</sub> to understand the adsorption and activation of CO<sub>2</sub> molecules and the mechanistic insights. This review article discusses the recent development in photocatalytic CO<sub>2</sub> conversion using defective TiO<sub>2</sub>. It includes the general mechanism and thermodynamic criteria for defective TiO<sub>2</sub> catalyzed CO<sub>2</sub> conversion, the theoretical investigation on the role of defects in CO<sub>2</sub> adsorption and activation, and the mechanism responsible for the formation and selectivity of different products. It also summarizes the effect of variation of structural and electronic properties of defective TiO<sub>2</sub> synthesized using various protocols on the photocatalytic conversion of CO<sub>2</sub> into value-added products.

## 2. General mechanism and thermodynamic criteria for photocatalytic CO<sub>2</sub> conversion

The photocatalytic CO<sub>2</sub> conversion process using semiconductor-based catalysts involves the following steps: (1) CO<sub>2</sub> adsorption on the surface of the catalyst, (2) generation of

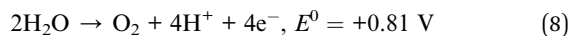
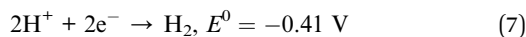
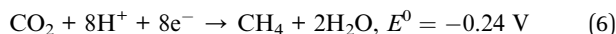
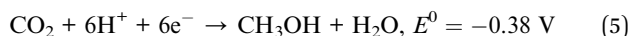
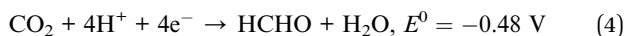
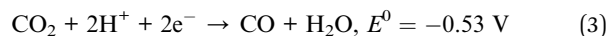
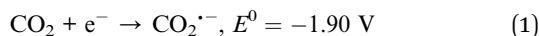


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electron and hole pairs after the absorption of light, (3) separation and transfer of charges to the surface active sites, and the generated charges may recombine back in the (4) bulk or (5) on the surface, (6) reduction of the adsorbed CO<sub>2</sub> by accepting an electron, and (7) oxidation of water to give oxygen. The processes occurring on the semiconductor surface are given in Fig. 1. Photocatalytic CO<sub>2</sub> conversion is a complex process and different pathways result in different products.<sup>4</sup> The potential energy ( $E^0$  V vs. NHE at pH 7) required to form different products such as carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCOH), methanol (CH<sub>3</sub>OH), methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) is given as follows:



The water reduction process involves two electrons, whereas the reduction of CO<sub>2</sub> to organic products is a multielectron process. The water reduction process can compete with the CO<sub>2</sub> reduction reaction, and therefore, it is essential to tailor the surface of the photocatalyst in such a way that it will preferentially reduce CO<sub>2</sub> rather than water. Also, the single-electron transfer to the CO<sub>2</sub> molecule has the highest reduction potential *i.e.*  $-1.9 \text{ V}$  vs. NHE (at pH = 7); hence it is the rate-limiting step in most of the photocatalytic CO<sub>2</sub> conversion reactions.<sup>35</sup>

### 3. Defective TiO<sub>2</sub> as a photocatalyst

#### 3.1 Background

In 2011, Chen *et al.*<sup>36</sup> reported “black TiO<sub>2</sub>” where the light absorption of anatase TiO<sub>2</sub> could be enhanced until 1200 nm by introducing a shell of a disordered surface layer over the core crystalline TiO<sub>2</sub> nanocrystal *via* a hydrogenation process. HR-TEM images after hydrogenation showed the presence of a disordered layer and a crystalline core. The hydrogenation process was carried out at 200 °C under 20 bar pressure of H<sub>2</sub> gas for five days. TiO<sub>2</sub> synthesized by this method is referred to as black TiO<sub>2</sub>. The black TiO<sub>2</sub> showed enhanced photocatalytic H<sub>2</sub> generation in visible light with a yield of 10 000 μmol g<sup>-1</sup> h<sup>-1</sup>. They attributed the enhanced photocatalytic activity to the improved light absorption of black TiO<sub>2</sub> until 1200 nm, having an optical bandgap of 1.54 eV. The introduction of mid-gap electronic states within the bandgap of TiO<sub>2</sub> was due to the presence of lattice disorder with H atom doping, which improved light absorption.

After this discovery, a range of methodologies for defect creation was adopted to improve the light absorption of TiO<sub>2</sub> in the visible region. Defects were generated in TiO<sub>2</sub> using different synthesis methodologies such as hydrogen gas treatment, inert gas treatment, plasma treatment, metallothermic reduction, using a reducing agent, bombardment with high energy particles, hydrolysis of Ti<sup>4+</sup> salt in the presence of a reductant, doping with a heteroatom, *etc.*<sup>31–34</sup>

#### 3.2 Role of defects in CO<sub>2</sub> adsorption-activation and light harvesting

The electronic, optical, surface and chemical properties of TiO<sub>2</sub> are dependent on the type and concentration of the defects present in it. These properties play a crucial role in determining the photocatalytic activity of the material. Defects in crystals are classified depending on the dimensionality as 0D point defects, 1D line defects, 2D planar defects and 3D bulk defects.<sup>37</sup> Point defects in TiO<sub>2</sub> include Ti vacancies, oxygen vacancies, and Ti

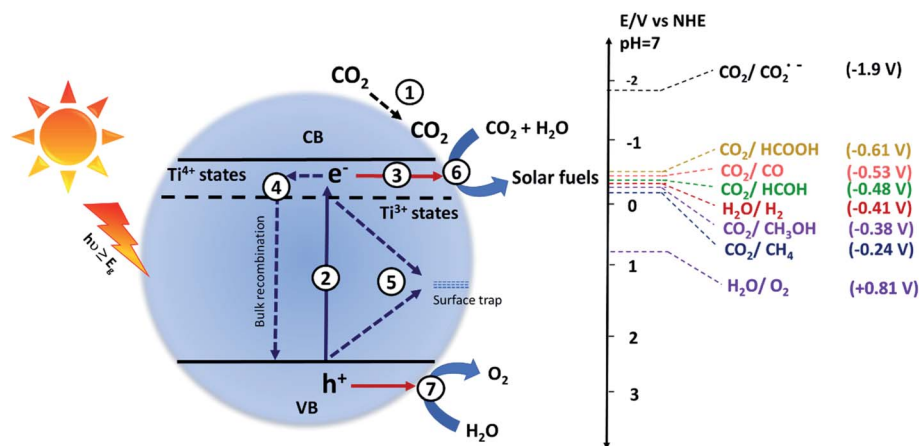


Fig. 1 Schematic illustration of different processes occurring during the photocatalytic conversion of CO<sub>2</sub> into useful products. The absorption of light energy equal to or greater than the bandgap ( $E_g$ ) resulting in excitation of the electrons from the valence band (VB) to the conduction band (CB), leaving behind holes in the VB. The electrons and holes promote the reduction and oxidation of the reactant molecules, respectively.





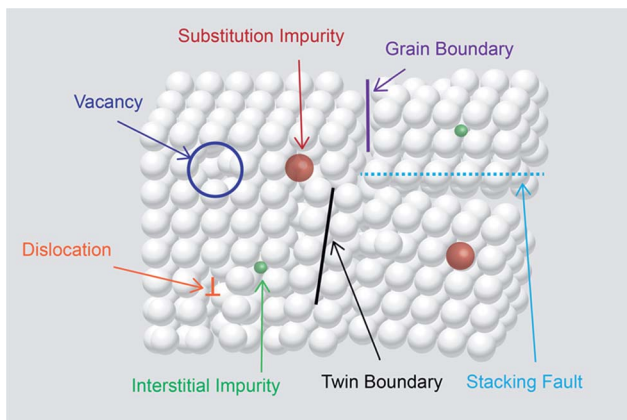


Fig. 2 Schematic of the different types of defects present in the TiO<sub>2</sub> crystal.

interstitial and substitutional or interstitial impurity.<sup>37,38</sup> Line defects are described as extended dislocations.<sup>39</sup> 2D defects (planar defects) contain grain boundaries, twin boundaries and stacking faults. Bulk defects (volume defects) include inclusions, cracks, voids and pores.<sup>37</sup> Fig. 2 shows the types of defects present in the crystal.

The generation of oxygen vacancies is the easiest as compared to the generation of interstitial vacancies.<sup>40</sup> Oxygen removal leaves behind two electrons at the vacant oxygen site. These electrons were accepted by the adjacent Ti<sup>4+</sup> present near the oxygen vacant site to generate Ti<sup>3+</sup> sites.<sup>41</sup> The preliminary step in CO<sub>2</sub> conversion is the adsorption of CO<sub>2</sub> molecules on the catalyst surface. The presence of oxygen defects not only facilitates the reduction of the bandgap of pristine TiO<sub>2</sub> but also generates active sites for CO<sub>2</sub> adsorption and activation, thus making it a suitable candidate for photocatalytic CO<sub>2</sub> conversion using solar energy. Several theoretical studies have been performed to understand the role of defects in CO<sub>2</sub> activation and conversion into different products.

Oxygen vacant sites offer a stronger binding site for CO<sub>2</sub> adsorption. Thompson *et al.*<sup>42</sup> studied the adsorption and desorption of CO<sub>2</sub> on the oxidized and defective TiO<sub>2</sub> (110) surfaces by temperature-programmed desorption. In the case of a fully oxidized surface, CO<sub>2</sub> binds to the fivefold coordinated

Ti<sup>4+</sup> atoms, whereas in the case of the defective TiO<sub>2</sub> surface, CO<sub>2</sub> binds to both the regular sites and to the oxygen vacant sites. They also found that the CO<sub>2</sub> binds to the oxygen vacant sites with a higher binding energy of 54 kJ mol<sup>-1</sup> than the regular sites (48.5 kJ mol<sup>-1</sup>).

Huygh *et al.*<sup>43</sup> studied the adsorption, dissociation and diffusion of CO<sub>2</sub> on the oxidized and reduced (001) surfaces of anatase TiO<sub>2</sub> using density functional theory (DFT) calculations with long-range dispersion energy corrections. Fig. 3a shows the different vacancy sites present on the (001) anatase surface, namely V<sub>O1</sub>, V<sub>O2</sub>, V<sub>O3</sub> and V<sub>O4</sub>. They identified the monodentate carbonate structure as the stable adsorption configuration after the interaction of CO<sub>2</sub> with the oxidized surface. A small energy barrier exists for the conversion of physisorbed CO<sub>2</sub> to a chemisorbed one. CO<sub>2</sub> dissociation is not possible on an oxidized surface because of having a barrier of 113.6 kcal mol<sup>-1</sup>. However, the presence of an oxygen vacancy provides a new, highly stable adsorption configuration of CO<sub>2</sub> with the elongation of the C–O bond (Fig. 3b). The activation of the C–O bond results in exothermic dissociation of CO<sub>2</sub> with a barrier of 22.2 kcal mol<sup>-1</sup>. The CO<sub>2</sub> dissociation on the vacant oxygen site has a lower barrier than on the oxidized surface as the former provides a way to stabilize the end product by taking up the oxygen from CO<sub>2</sub> to fill the vacant oxygen site. This results in the formation of a CO molecule, which is desorbed by filling the vacant site.

Lee *et al.*<sup>44</sup> studied the electron-induced dissociation of CO<sub>2</sub> adsorbed at the oxygen vacant site on the TiO<sub>2</sub> (110) surface by scanning transmission microscopy (STM). Fig. 4a shows the schematic of the TiO<sub>2</sub> (110) surface having the oxygen vacancy (V<sub>O</sub>), bridged hydroxyl group (OH<sub>b</sub>) and CO<sub>2</sub> adsorbed at the vacant site. The inset shows the tilted configuration of CO<sub>2</sub> adsorbed at the vacant oxygen site. They found that the most stable adsorption of CO<sub>2</sub> at the vacant site was a nearly linear configuration with an adsorption energy of 0.44 eV. Fig. 4b shows the STM images recorded after exposure to CO<sub>2</sub> at 55 K. The inset shows the STM images of the same area before and after CO<sub>2</sub> thermal diffusion. They observed that the two CO<sub>2</sub> molecules shown in the dotted ellipse in the upper inset diffused away from their V<sub>O</sub> site, leaving behind two intact V<sub>O</sub> sites as seen in the dotted ellipse of the lower inset. This revealed that the CO<sub>2</sub> was adsorbed at the V<sub>O</sub> site. Fig. 4c shows

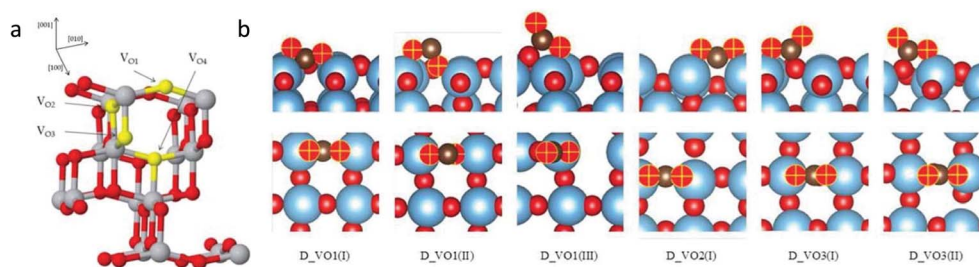


Fig. 3 (a) Type of oxygen vacancies on the (001) surface of anatase TiO<sub>2</sub> (Ti = gray, O = red, oxygen vacancy = yellow) and (b) adsorption configurations of CO<sub>2</sub> on the reduced TiO<sub>2</sub> anatase surface with different vacancies in side view (upper panel) and top view (lower panel) (Ti = blue, O<sub>TiO<sub>2</sub></sub> = red, O<sub>CO<sub>2</sub></sub> = red and yellow plus sign and C = brown) (reproduced from ref. 43 with permission from the American Chemical Society, copyright 2016).



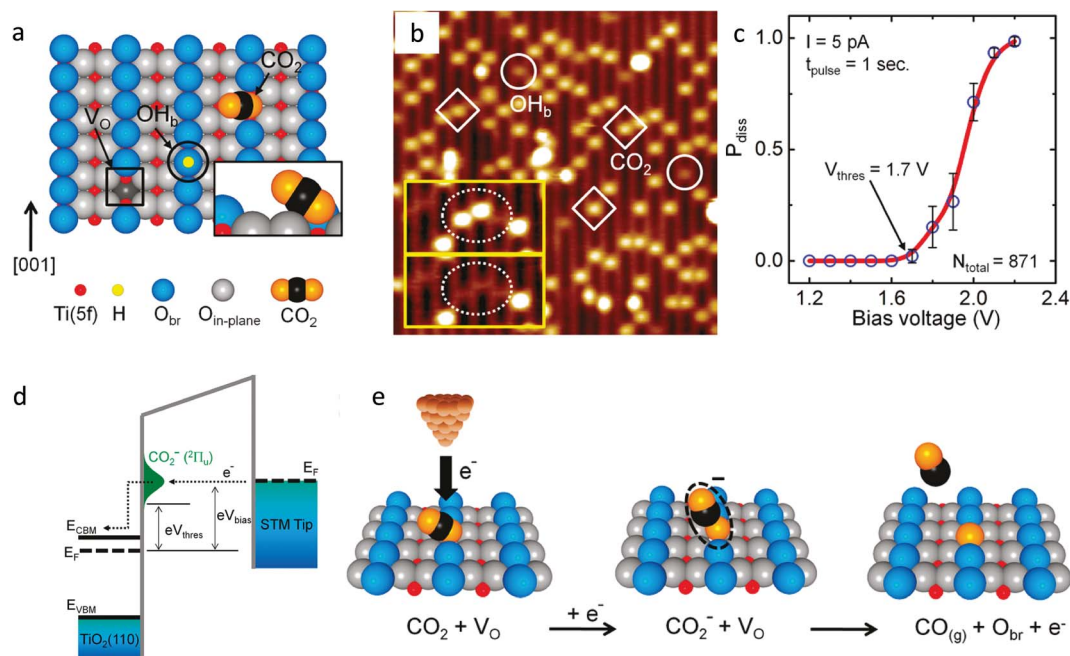


Fig. 4 (a) Schematic showing the oxygen vacancy ( $V_O$ , in a black color square), bridged hydroxyl group ( $OH_b$ , black color circle) and  $CO_2$  molecule adsorbed at the  $V_O$  site on the reduced  $TiO_2(1) (1 \times 1)$  surface. The fivefold-coordinated  $Ti(5f)$  atoms and bridged oxygen ( $O_{br}$ ) are indicated in red and blue, respectively. The inset shows that the molecular axis of  $CO_2$  is perpendicular to the direction of the bridging-oxygen row ( $[001]$  azimuth) and is tilted away from the surface normal by  $57^\circ$ ; (b) STM image ( $1.5$  V,  $5$  pA,  $15$  nm  $\times$   $15$  nm) of the  $TiO_2(110)$  surface after adsorption of  $CO_2$  at  $55$  K. Three  $CO_2$  and two  $OH_b$  features are shown as diamonds and circles, respectively. The inset shows two STM images ( $5.1$  nm  $\times$   $2.6$  nm) of the same area on the surface. The upper inset shows two  $CO_2$  molecules (in the dotted ellipse) that diffused away from their  $V_O$  sites, leaving two intact  $V_O$  sites visible, as shown in the lower inset image; (c) dissociation probability ( $P_{diss}$ ) plotted as a function of bias voltage. The threshold voltage was  $V_{thres} = +1.7$  V, and  $P_{diss}$  approached 1 at  $+2.2$  V. (d) The electron-transfer process at the STM tip/ $CO_2$ / $TiO_2$  interface. Above  $eV_{thres} = 1.7$  eV, the electrons start to tunnel into the negative-ion state of the adsorbed  $CO_2$  and (e) schematics of an electron-induced  $CO_2$  dissociation process (reproduced from ref. 44 with permission from the American Chemical Society, copyright 2011).

that  $1.7$  V is the threshold energy required for the dissociation of  $CO_2$  and the probability of dissociation depends on the energy of the injected electron from STM tip.

The electron from the Fermi level of STM tip can tunnel into  $CO_2$  to form  $CO_2^-$  in the  ${}^2\Pi_u$  state if the energy of the electron is greater than  $1.7$  eV (Fig. 4d). As the Fermi level lies  $0.3$  eV below the CB, the threshold energy is located  $1.4$  eV above the CB. They demonstrated that the dissociation of  $CO_2$  is a one-electron process with a threshold energy of  $1.4$  eV above the conduction band minimum of  $TiO_2$ . The  $CO_2$  adsorbed at the oxygen vacant sites dissociates by accepting an electron and heals the vacancy by the oxygen released during dissociation reaction (Fig. 4e). The CO molecule formed could be desorbed from the surface by the excess energy gained during the dissociation process. The formation of  $CO_2^-$  species is the key intermediate in  $CO_2$  dissociation. Similar results were also reported by Tan *et al.*<sup>45</sup> where they studied the activation of  $CO_2$  on the rutile  $TiO_2(110) (1 \times 1)$  surface by injecting an electron to  $CO_2$  by *in situ* STM at  $80$  K.

The presence of point defects creates energy levels within the bandgap and hence light absorption by  $TiO_2$  can extend up to the near IR region. Hossain *et al.*<sup>46</sup> used *Ab initio* density functional theory to calculate the formation energy of intrinsic point defects and position of the defect-induced energy levels within the bandgap of reduced rutile  $TiO_{2-x}$ . They reported the energy

levels for the oxygen vacancy ( $V_O$ ), titanium vacancy ( $V_{Ti}$ ) and titanium interstitial ( $Ti_{int}$ ) as  $1.17$ ,  $1.15$  and  $1.23$  eV, respectively (Fig. 5). The presence of these defects can be thoroughly analyzed by the scanning transmission microscopy (STM) in combination with density functional theory (DFT), high-resolution transmission electron microscopy (HR-TEM), positron annihilation spectroscopy (PAS), electron paramagnetic resonance (EPR), magnetism testing, temperature-programmed desorption (TPD), Fourier transform infrared spectroscopy (FTIR), optical absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy.<sup>31–34</sup>

### 3.2 Mechanistic pathways for photocatalytic $CO_2$ conversion using defective $TiO_2$

Two pathways were proposed based on the adsorption and the binding of  $CO_2$  to the catalyst surface. One is the carbene pathway and the other is the formaldehyde pathway.<sup>47</sup> In the carbene pathway, the  $CO_2^{\cdot-}$  radical is formed by accepting an electron from the  $TiO_2$  catalyst.  $CO_2^{\cdot-}$  binds in a bidentate mode to the two Ti atoms on the surface *via* a carbon atom. These radicals undergo reduction by accepting hydrogen radicals and electrons to form CO. The adsorbed CO on further reduction in multiple steps gives a  $\cdot CH$  radical, carbene, and a methyl radical as intermediates to finally give methanol or methane as the final product.



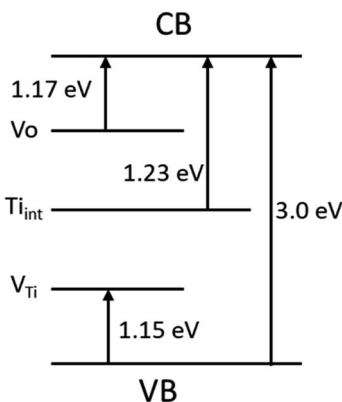


Fig. 5 Energy levels formed due to the presence of defects such as oxygen vacancy, titanium vacancy and titanium interstitial within the bandgap of reduced rutile  $\text{TiO}_{2-x}$ . Energy levels were taken from ref. 46.

In the formaldehyde pathway, the carboxy radical ( $\cdot\text{COOH}$ ) is primarily formed as a result of binding of the  $\text{CO}_2$  molecule in a monodentate mode either through binding of the oxygen atom of  $\text{CO}_2$  to Ti or binding of the oxygen atom of the surface to the carbon atom of the  $\text{CO}_2$ . The  $\cdot\text{COOH}$  forms formic acid by accepting hydrogen radicals. On further reduction of formic acid, formaldehyde, methanol and methane is produced through a series of electron transfer and dehydrating steps.

To understand the mechanism of  $\text{CO}_2$  reduction on the perfect and defective (101) surfaces of anatase  $\text{TiO}_2$ , Ji *et al.*<sup>48</sup> carried out first principles calculation. They concluded that in the case of both defective and non-defective  $\text{TiO}_2$ , the fast hydrogenation (FH) pathway, generally known as the formaldehyde pathway, is most preferred over the fast deoxygenation (FDO) pathway (known as the carbene pathway). FDO is not possible due to the formation of the energetically unfavorable  $\cdot\text{C}$  intermediate. They also found that the surface oxygen vacancies are more active than Ti atoms on the surface. A new mechanism was proposed to explain the selectivity of the reaction in which fast hydrogenation occurs at both Ti as well as oxygen vacancies and is shown in Fig. 6. On the  $\text{V}_\text{O}$  site, the deoxygenation of  $\text{CO}_2$  is easier and the two electrons provided by the defect sites could prevent the photooxidation of the intermediate species and promote their further reduction.

To further understand the mechanism proposed by Ji *et al.*,<sup>48</sup> Liu *et al.*<sup>49</sup> performed a DFT calculation to study the pathway for methane and methanol formation from  $\text{CO}_2$  reduction over the defective anatase phase of  $\text{TiO}_2$  with the (101) surface. They

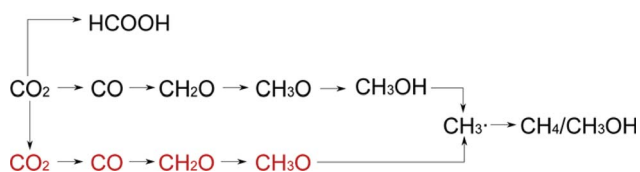


Fig. 6 Reaction pathway for the photocatalytic  $\text{CO}_2$  conversion (red and black color font indicate the species adsorbed at the oxygen vacancy and on surface Ti, respectively) (reproduced from ref. 48 with permission from the American Chemical Society, copyright 2016).

found that the reaction proceeds through the two plausible pathways (Fig. 7) as follows  $\text{CO}_2 \rightarrow \text{CO}(\text{A})/\text{CO}(\text{B}) \rightarrow \text{CHO}(\text{CHO}) \rightarrow \text{CHOH}(\text{CH}_2\text{O}) \rightarrow \text{CH}_2\text{OH}(\text{CH}_3\text{O}) \rightarrow \text{CH}_3\text{OH}^*$  or  $\text{CH}_4$ .  $\text{CO}(\text{A})$  and  $\text{CO}(\text{B})$  stand for a more stable monodentate configuration with C binding to  $\text{Ti}^{3+}$  and a less stable bidentate configuration of CO on the  $\text{V}_\text{O}$  site of the surface, respectively. The desorption energy of methanol is high as 1.66 eV, indicating that it will be difficult to desorb from the  $\text{V}_\text{O}$  site of the surface and thus stable on the surface at room temperature. The barrier for the conversion of adsorbed methanol to  $\text{CH}_3$  is very low *i.e.*, 0.18 eV, and thus, the formation of  $\text{CH}_3$  is more favorable than the desorption of the adsorbed methanol. Methane is expected as the reaction product as the desorption energy of methane is only 0.20 eV. The predicted mechanism matches with the experimental findings as CO and  $\text{CH}_4$  were the experimentally observed products.

Furthermore, they also considered a carbene-like deoxygenation pathway to form the CH species on the vacant site, which could generate methane by successive hydrogenation steps.<sup>49</sup> The proposed direct deoxygenation and hydrogenation pathway is  $\text{CO}_2 \rightarrow \text{CO}(\text{A}) \rightarrow \text{CHO} \rightarrow \text{CHOH} \rightarrow \text{CH} \rightarrow \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \text{CH}_4$ . The rate-limiting step in this pathway is  $\text{CHOH} \rightarrow \text{CH}$  with a barrier of 1.96 eV, which is much lower than that reported by Ji *et al.*<sup>48</sup> All the pathways from  $\text{CO}_2$  are thermodynamically feasible but the barriers between the steps are high mainly in the carbene pathway. The energy *via* electric field or electrochemical potential could be used to increase the rate of the reaction and, thus, product yield. From the theoretical study, it was concluded that the formaldehyde pathway is more preferred over the carbene pathway for  $\text{CO}_2$  conversion in defective  $\text{TiO}_2$ . Methane formation is preferred over methanol due to its high desorption energy.

## 4. Defect generation in $\text{TiO}_2$ and its impact on photocatalytic $\text{CO}_2$ conversion

The various synthesis procedures, the physicochemical changes in  $\text{TiO}_2$  due to the presence of defects and applications of defective  $\text{TiO}_2$  for photocatalytic  $\text{CO}_2$  conversion are summarized in this section. Point defects in  $\text{TiO}_2$  can be introduced by different ways, such as reduction using hydrogen gas, inert gas treatment, a reducing agent like  $\text{NaBH}_4$ , metallothermic reduction by using metals like Al, Mg, Li, Zn, *etc.*, bombardment with high energy particle such as electron beam, proton beam, hydrogen plasma, electrochemical reduction method, doping with a heteroatom, *etc.* The details of the synthesis methodologies have been given in more detail in several other articles.<sup>31–34,37</sup> This review primarily focuses on the defects generated using different synthesis methodologies and their impact on the physicochemical and photocatalytic properties of  $\text{TiO}_2$ .

### 4.1 Defect generation under a reducing atmosphere

**4.1.1 Hydrogen atmosphere.** In this method, defects were generated under a hydrogen atmosphere. Pure  $\text{H}_2$  gas or a mixture of  $\text{H}_2/\text{Ar}$  or  $\text{H}_2/\text{N}_2$  gases and also the hydrides (such as  $\text{NaBH}_4$  and  $\text{CaH}_2$ ), which releases active hydrogen species, were





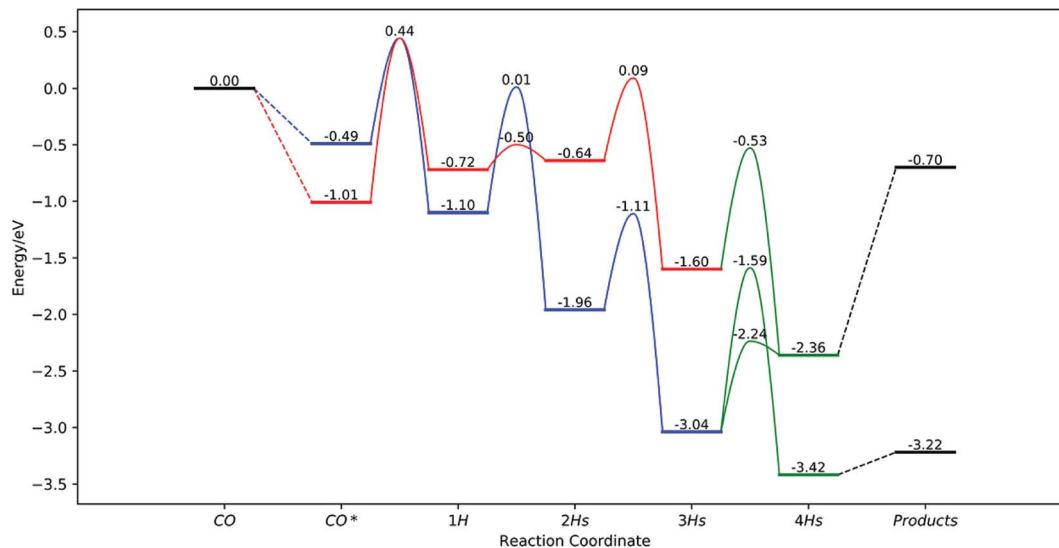


Fig. 7 Overall potential energy surface from CO to CH<sub>4</sub>. Black, red, blue, and green bars and curves represent a desorption state, the most favorable pathway for CO(A), the most favorable pathway for CO(B) and pathways after merged, respectively (reproduced from ref. 49 with permission from the American Chemical Society, copyright 2019).

used as the hydrogen source.<sup>50</sup> The application of hydrogen treated defective TiO<sub>2</sub> was reported for CO<sub>2</sub> conversion by different research groups.

The general representation of the TiO<sub>2</sub> reduction reaction in the presence of hydrogen gas can be given by the below equation. The hydrogen reacts with the lattice oxygen of TiO<sub>2</sub> to form oxygen vacancies and Ti<sup>3+</sup> in TiO<sub>2</sub>.

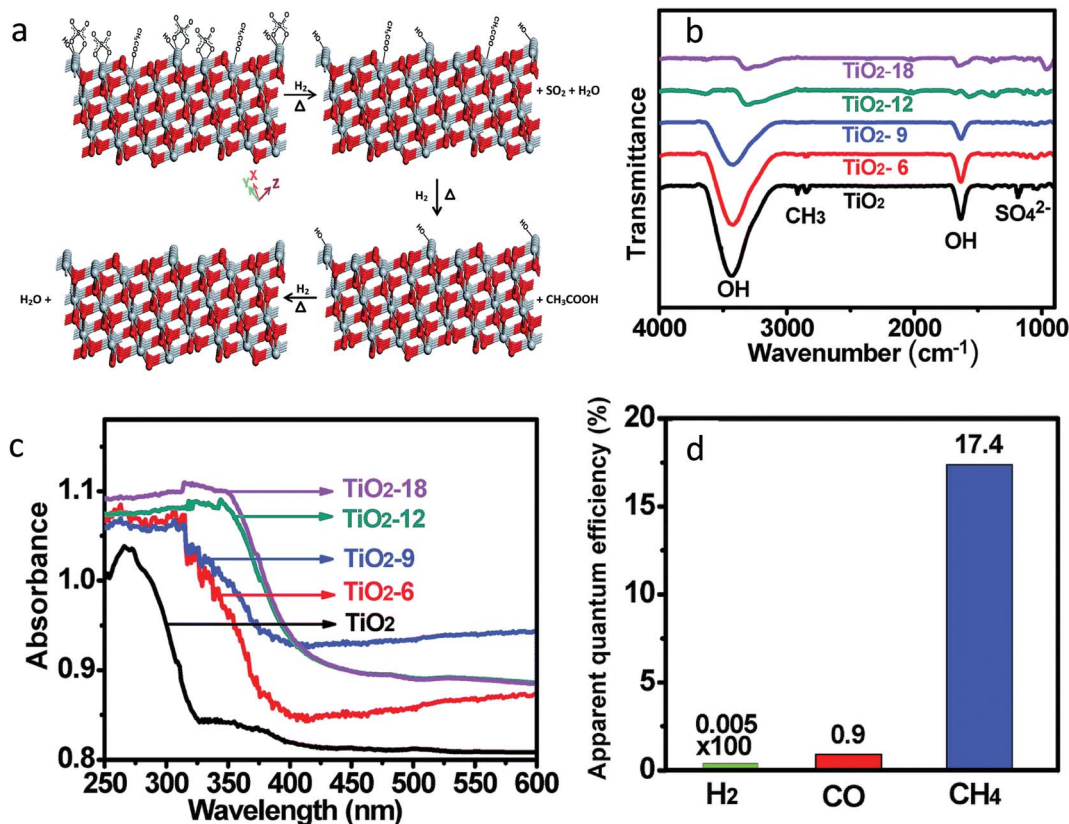
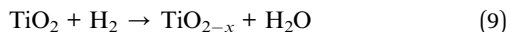


Fig. 8 (a) Schematic of the chemical reaction that occurred on the surface of the TiO<sub>2</sub> during hydrogenation (gray color: Ti and red color: O), (b) FTIR spectra of non-hydrogenated and hydrogenated TiO<sub>2</sub> samples, (c) diffuse reflectance spectra of TiO<sub>2</sub> and hydrogenated samples and (d) apparent quantum efficiency (AQE) for H<sub>2</sub>, CO and CH<sub>4</sub> using the TiO<sub>2</sub>-12 sample (reproduced from ref. 51 with permission from the Royal Society of Chemistry, copyright 2019).





The chemical properties of  $\text{TiO}_2$  nanomaterials are greatly affected by their size, morphology, shape, exposed facets on the surface and the concentration of defects.<sup>31</sup> These factors make hydrogen thermal treatment more complicated. The experimental parameters such as the amount of  $\text{TiO}_2$ , pressure and concentration of the hydrogen and reaction temperature and time affect the chemical, optical and electronic properties as well as the concentration of defects in the hydrogenated  $\text{TiO}_2$ . Hydrogenation helps in the generation of the  $\text{Ti}^{3+}$  sites as well as cleaning the surface of the photocatalyst. Recently, Liu *et al.*<sup>51</sup> synthesized  $\text{TiO}_2$  nanotubes/nanowires with exposed {111} facets by heating a mixture of titanium(IV) oxysulfate–sulfuric acid hydrate, glacial acetic acid and water. These as-synthesized  $\text{TiO}_2$  nanotubes/nanowires were hydrogenated at 650 °C under  $\text{H}_2$  gas flow of 2.0 L  $\text{h}^{-1}$  for 6, 9, 12 and 18 h and referred to as  $\text{TiO}_2$ -6,  $\text{TiO}_2$ -9,  $\text{TiO}_2$ -12 and  $\text{TiO}_2$ -18, respectively. No change in morphology after hydrogenation was observed. The hydrogenation process causes the expansion and distortion of the  $\text{TiO}_2$  crystal lattice as revealed from the XRD pattern. The chemical reactions that occurred on the surface during hydrogenation are shown in the schematic in Fig. 8a. The absorption band corresponds to  $\text{SO}_4^{2-}$  and  $\text{CH}_3\text{COO}^-$  species which accumulated in the course of synthesis and disappeared completely after 6 h of hydrogenation (Fig. 8b). During the hydrogenation process, these species get removed and the surface becomes clean. The amount of  $\text{Ti}^{3+}$  increases with an increase in the hydrogenation time, as revealed from the XPS spectra. Fig. 8c shows that the light absorption enhanced in the visible region with the increase in the duration of hydrogenation. The bandgap value varies from 3.40 eV for  $\text{TiO}_2$  to 2.64 eV for  $\text{TiO}_2$ -18.

Photocatalytic  $\text{CO}_2$  conversion was carried out in the presence of isopropanol as a sacrificial reagent at 0.2 MPa of  $\text{CO}_2$  and 373 K temperature. The photocatalytic  $\text{CO}_2$  reduction activity increases in the order  $\text{P25} < \text{TiO}_2 < \text{TiO}_2$ -6 <  $\text{TiO}_2$ -9 <  $\text{TiO}_2$ -12 <  $\text{TiO}_2$ -18, indicating that the activity of  $\text{TiO}_2$  nanostructures could be increased by hydrogenation.  $\text{H}_2$ , CO and  $\text{CH}_4$  were generated at a rate of 2.11, 463.2 and 1708.08  $\mu\text{mol g}^{-1} \text{h}^{-1}$  using  $\text{TiO}_2$ -12, respectively. 17.4% apparent quantum efficiency (AQE) for methane generation was observed using a hydrogenated  $\text{TiO}_2$ -12 sample (Table 1, Fig. 8d). The improved activity was attributed to the exposed clean {111} facets and enhanced light absorption. The author proposed a mechanism where photogenerated electrons and holes transferred to  $\text{TiO}_2$  (111) and ( $\bar{1}\bar{1}\bar{1}$ ) surfaces due to the generated spontaneous electric field between the two polar planes, respectively. Thus, the redox reaction takes place at two different Ti– $\text{TiO}_2$  (111) and O– $\text{TiO}_2$  ( $\bar{1}\bar{1}\bar{1}$ ) polar planes. This resulted in a better separation of charge carriers and improved photocatalytic activity.

Furthermore, the effect of particle size on the degree of hydrogenation and its impact on photocatalytic  $\text{CO}_2$  conversion was studied by Xuan *et al.*<sup>52</sup> In this work, the  $\text{TiO}_2$  nanoparticles were loaded over dendritic porous silica nanospheres (DPSNs), also known as dendritic fibrous nanosilica (DFNS). The particle size of  $\text{TiO}_2$  was tuned from 1–2 to 9–12 nm by varying the amount of titanium isopropoxide precursor. To create oxygen

vacancies, hydrogen thermal reduction treatment at ambient pressure was carried out by flowing a mixture of gas containing 5 vol%  $\text{H}_2$  and 95 vol% argon at 600 °C for 3 h. The synthesis methodology is given in Fig. 9a. Samples were referred to as DPSNs@X%  $\text{TiO}_2$ -x where x is the weight ratio of  $\text{TiO}_2$ /DPSNs. The only signal that corresponded to the oxygen vacancy was observed in the EPR spectrum. The sample DPSNs@X%  $\text{TiO}_2$ -x (X%  $\leq$  20%) having a particle size of 1–3 nm of  $\text{TiO}_2$ -x nanoparticles (NPs) showed CO as the only product of  $\text{CO}_2$  conversion, whereas 3–12 nm  $\text{TiO}_2$ -x NPs on DPSNs@X%  $\text{TiO}_2$ -x (X%  $\geq$  40%) showed the generation of both the CO and  $\text{CH}_4$  (Fig. 9b). The maximum  $\text{CH}_4$  and CO generation at a rate of 124.3 and 14.7  $\mu\text{mol g}^{-1}$  of  $\text{TiO}_2$ -x  $\text{h}^{-1}$  was observed using DPSNs@80%  $\text{TiO}_2$ -x having a particle size of 8–12 nm of  $\text{TiO}_2$ -x, respectively. They found that 1–3 nm  $\text{TiO}_2$ -x nanoparticles showed a higher reduction degree during hydrogen thermal treatment leading to a higher decrease in the bandgap. This could have resulted in the lowering of the reduction power of the electrons, which inhibited the kinetics of the reduction reaction of  $\text{CO}_2$  to methane involving eight electrons (Fig. 9c and d). The exact reason for the improved selectivity of 89.4% for methane production in DPSNs@80%  $\text{TiO}_2$ -x was unclear and they attributed it to the improved light absorption efficiency and suitable CB edge, which help maintain the reduction ability of photogenerated electrons. The other factors such as the better dispersion of particles, appropriate particle size, highly accessible specific surface area, the lower recombination rate of photogenerated charge carriers, and enhanced carrier transfer and separation also contributed to the improvement of the photocatalytic  $\text{CO}_2$  conversion yield in DPSNs@80%  $\text{TiO}_2$ -x.

Hydrogenation using  $\text{H}_2$  atmosphere was also beneficial to reduce metal ions into metals along with the generation of oxygen vacancies and  $\text{Ti}^{3+}$  in  $\text{TiO}_2$ . Billo *et al.*<sup>53</sup> introduced dual active sites, Ni nanocluster and the oxygen vacancies for the enhanced  $\text{CO}_2$  conversion. For this, Ni nanocluster supported oxygen-deficient black  $\text{TiO}_2$  was synthesized *via* the one-pot hydrothermal process, followed by hydrogenation under pure  $\text{H}_2$  gas flow at 300 °C for 3 h. The sample before and after hydrogenation was referred to as Ni/ $\text{TiO}_2$  and Ni/ $\text{TiO}_2$ [V<sub>O</sub>], respectively. The hydrogenation treatment brings about the instantaneous reduction of NiO to Ni nanoclusters on black  $\text{TiO}_2$ . The lattice disorder and Ni nanoclusters on the hydrogenated  $\text{TiO}_2$  surface resulted in the formation of mid-gap states and enhanced light-harvesting capability in Ni/ $\text{TiO}_2$ [V<sub>O</sub>], as shown in Fig. 10a. The Ni/ $\text{TiO}_2$ [V<sub>O</sub>] catalyst showed an acetaldehyde yield of 10  $\mu\text{mol g}_{\text{cat}}^{-1}$  in 6 h with 100% selectivity, which was 2 and 18 times higher than that of Ni/ $\text{TiO}_2$  and commercial  $\text{TiO}_2$  (P25) under (300 W) halogen lamp illumination, respectively (Fig. 10b). The reaction mechanism for improved selectivity was not clear. The band edge position was derived from ultraviolet photoelectron spectroscopy (UPS) and DRS absorption data. From this data, they concluded that the improved selectivity for acetaldehyde in Ni/ $\text{TiO}_2$ [V<sub>O</sub>] could be because of the higher CB position at  $-1.3$  V vs. NHE than the Ni/ $\text{TiO}_2$  ( $-1.16$  V vs. NHE) (Fig. 10c). The proposed mechanism for  $\text{CO}_2$  conversion is shown in Fig. 10d. The work function of Ni metal (5 eV) was higher than that of the Ni/ $\text{TiO}_2$ [V<sub>O</sub>] (3.75 eV),





Table 1 Photocatalytic CO<sub>2</sub> conversion using defective TiO<sub>2</sub>

Sr no.	Reference	Chemicals used to create defects	Photocatalytic experimental conditions	Light source used	Products	Yield	AQE/SFE
1	Liu <i>et al.</i> <sup>51</sup>	H <sub>2</sub> gas	10 mg catalyst dispersed in 1.0 mL (CH <sub>3</sub> ) <sub>2</sub> CHOH and 4.0 mL H <sub>2</sub> O, (0.2 MPa) CO <sub>2</sub>	300 W Xe lamp	CH <sub>4</sub> CO	1708.1 μmol g <sup>-1</sup> h <sup>-1</sup> 463.2 μmol g <sup>-1</sup> h <sup>-1</sup>	AQE: 17.40% —
2	Xuan <i>et al.</i> <sup>52</sup>	H <sub>2</sub> gas	25 mg of catalyst, CO <sub>2</sub> was generated inside the reactor	300 W Xe lamp, intensity on the sample was 0.5W cm <sup>-2</sup>	CH <sub>4</sub> CO	124.3 μmol g <sup>-1</sup> h <sup>-1</sup> 14.7 μmol g <sup>-1</sup> h <sup>-1</sup>	— —
3	Billo <i>et al.</i> <sup>53</sup>	H <sub>2</sub> gas	CO <sub>2</sub> bubbled through water, co-catalyst: Ni	300 W Xe lamp	CH <sub>3</sub> CHO	10 μmol g <sup>-1</sup> in 6 h	—
4	Fu <i>et al.</i> <sup>54</sup>	H <sub>2</sub> gas	100 mg of catalyst, CO <sub>2</sub> bubbled through water	Solar simulator AM 1.5	CH <sub>3</sub> CHO CH <sub>3</sub> OH	11.3 μmol g <sup>-1</sup> in 6 h 1.2 μmol g <sup>-1</sup> in 6 h	— —
5	Ye <i>et al.</i> <sup>55</sup>	H <sub>2</sub> gas	Sample concentration 1 g L <sup>-1</sup> , CO <sub>2</sub> flow rate 100 mL min <sup>-1</sup> , NaOH = 0.20 mol L <sup>-1</sup> , Na <sub>2</sub> SO <sub>3</sub> = 0.20 mol L <sup>-1</sup> , reaction temperature 5 °C	300 W Xe lamp	CO	12.1 μmol g <sup>-1</sup> h <sup>-1</sup>	—
6	Liu <i>et al.</i> <sup>56</sup>	H <sub>2</sub> gas	50 mg catalyst, CO <sub>2</sub> passed through water	150 W solar simulator (90 mW cm <sup>-2</sup> )	CH <sub>4</sub> CO	4.4 μmol g <sup>-1</sup> in 6.5 h 25 μmol g <sup>-1</sup> in 6.5 h	— —
7	Li <i>et al.</i> <sup>57</sup>	N <sub>2</sub> : H <sub>2</sub> (9 : 1)	50 mg catalyst dispersed in 2 mL of water, CO <sub>2</sub> gas passed through it temperature: 393 K, co-catalyst: CoO <sub>x</sub>	150 W UV lamp (20 mW cm <sup>-2</sup> at 365 nm)	CH <sub>4</sub> (selectivity: 71.02%) CO (selectivity: 28.98%)	10.1 μmol g <sup>-1</sup> h <sup>-1</sup> 16.4 μmol g <sup>-1</sup> h <sup>-1</sup>	0.0126 —
8	Sorcar <i>et al.</i> <sup>59</sup>	NaBH <sub>4</sub>	40 mg of catalyst, moist CO <sub>2</sub> (40 mL min <sup>-1</sup> ), co-catalyst: Pt (0.33 wt%)	100 W Xe solar simulator (AM1.5 filter)	CH <sub>4</sub>	80.3 μmol g <sup>-1</sup> h <sup>-1</sup>	12.4
9	Sorcar <i>et al.</i> <sup>60</sup>	NaBH <sub>4</sub>	40 mg of catalyst, moist CO <sub>2</sub> (40 mL min <sup>-1</sup> ), co-catalyst: Pt 1 wt%	100 W Xe solar simulator (AM1.5 filter)	C <sub>2</sub> H <sub>6</sub> CH <sub>4</sub>	77 μmol g <sup>-1</sup> in 7 h 259 μmol g <sup>-1</sup> in 7 h	2.7 5.2
10	Sorcar <i>et al.</i> <sup>61</sup>	NaBH <sub>4</sub>	40 mg of catalyst, moist CO <sub>2</sub> (40 mL min <sup>-1</sup> ), co-catalyst: Cu-Pt	100 W Xe solar simulator AM1.5 filter	C <sub>2</sub> H <sub>6</sub> CH <sub>4</sub>	150 μmol g <sup>-1</sup> in 6 h 3000 μmol g <sup>-1</sup> in 6 h	Total AQE: 86%, SFE: 1% —
11	Yan <i>et al.</i> <sup>62</sup>	H <sub>2</sub> plasma	90 mg photocatalyst, CO <sub>2</sub> bubbled through water	550 W Xe-lamp with an AM 1.5 G filter, 100 mW cm <sup>-2</sup>	CH <sub>4</sub> CO	14.03 nmol h <sup>-1</sup> in 90 mg 21.67 nmol h <sup>-1</sup> in 90 mg	— —
12	Liu <i>et al.</i> <sup>63</sup>	He gas	100 mg catalyst, CO <sub>2</sub> and H <sub>2</sub> O vapor (H <sub>2</sub> O ≈ 2.3 v/v%),	150 W solar simulator, AM1.5 filter; 90 mW cm <sup>-2</sup>	CH <sub>4</sub> + CO	18.9 μmol g <sup>-1</sup> in 6 h	—
13	Xin <i>et al.</i> <sup>64</sup>	Oxidation-based hydrothermal method	Flow reactor (2 mL min <sup>-1</sup> ) CO <sub>2</sub> bubbled through water	300 W Xe lamp, visible light, 0.216W cm <sup>-2</sup> (≥420 nm)	CH <sub>4</sub> CO	11.9 μmol g <sup>-1</sup> h <sup>-1</sup> 23.5 μmol g <sup>-1</sup> h <sup>-1</sup>	— —
14	Zhao <i>et al.</i> <sup>65</sup>	Vacuum annealing	20 mg catalyst dispersed over a quartz disc with a diameter of 50 cm <sup>2</sup> , CO <sub>2</sub> from NaHCO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub>	500 W Xe lamp, 0.220 W cm <sup>-2</sup> , (400–800 nm)	CO CH <sub>4</sub>	48.5 μmol g <sup>-1</sup> in 6 h 8 μmol g <sup>-1</sup> in 6 h	— —
15	Kar <i>et al.</i> <sup>66</sup>	Flame reduction method	TiO <sub>2</sub> nanotube array with an area of 1 cm × 2 cm, 50 psi CO <sub>2</sub> pressure and 80 °C to vaporize the water, a few droplets of water were placed in the reactor beside the catalyst without direct contact with the catalyst	300 W Xe lamp AM1.5 filter	CH <sub>4</sub>	156.5 μmol g <sup>-1</sup> h <sup>-1</sup>	—



Table 1 (Contd.)

Sr no.	Reference	Chemicals used to create defects	Photocatalytic experimental conditions	Light source used	Products	Yield	AQE/SFE
16	Tu <i>et al.</i> <sup>67</sup>	<i>In situ</i> simultaneous reduction-hydrolysis technique	100 mg photocatalyst, CO <sub>2</sub> at ambient pressure, 0.4 mL H <sub>2</sub> O	300 W Xe lamp	CH <sub>4</sub> C <sub>2</sub> H <sub>6</sub>	8 μmol g <sup>-1</sup> h <sup>-1</sup> 16.8 μmol g <sup>-1</sup> h <sup>-1</sup>	— —
17	Yin <i>et al.</i> <sup>69</sup>	Aluminothermic reduction	50 mg catalyst, 2 bar CO <sub>2</sub> , 6 mL H <sub>2</sub> O	300 W Xe lamp	CH <sub>4</sub> (selectivity: 74%)	14.3 μmol g <sup>-1</sup> h <sup>-1</sup>	—
18	Gao <i>et al.</i> <sup>70</sup>	Aluminothermic reduction	Two pieces of the black TiO <sub>2</sub> NTAs catalyst – equivalent to 0.01 g TiO <sub>2</sub> , CO <sub>2</sub> is introduced in solution	300 W Xe lamp with a 420 nm cut-off filter	CO	185.39 μmol g <sup>-1</sup> h <sup>-1</sup>	—
19	Wang <i>et al.</i> <sup>72</sup>	Lithiothermic reduction	100 mg photocatalyst, 0.4 mL water, CO <sub>2</sub> , co-catalyst: 1 wt% Pt	300 W xenon arc lamp equipped with a UV light filter (~100 mW cm <sup>-2</sup> )	CH <sub>4</sub> (visible light) CH <sub>4</sub> (UV-visible light)	3.37 μmol g <sup>-1</sup> in 8 h 8.85 μmol g <sup>-1</sup> in 8 h	— —
20	Sasan <i>et al.</i> <sup>73</sup>	One-step combustion and hydrothermal methods	100 mg catalyst held on a Teflon holder, 4 mL liquid water at the bottom of reactor, CO <sub>2</sub> , co-catalyst: Cu(I)-Pd (1 wt%)	Xe lamp (300 W) with 400 nm cut-on filter	CH <sub>4</sub>	~6 μmol g <sup>-1</sup> in 6 h	—
21	Fang <i>et al.</i> <sup>74</sup>	Hydrothermal method using HCl and a small amount of HF	0.03 g of catalyst amount, 1 mL pure water, batch reactor, no co-catalyst	300 W Xe lamp AM1.5 filter	CH <sub>4</sub> CO	~0.9 μmol g <sup>-1</sup> in 4 h ~0.8 μmol g <sup>-1</sup> in 4 h	— —
22	Liu <i>et al.</i> <sup>75</sup>	NaBH <sub>4</sub> reduction	40 mg catalyst spread over a glass fiber filter, CO <sub>2</sub> bubbled through water, temperature: 150 °C, no cocatalyst	100 W Hg vapor lamp with 10 mW cm <sup>-2</sup> at λ < 390 nm 300 W Xe lamp with UV filter 28 mW cm <sup>-2</sup> in visible range	CO (UV-visible) (Visible)	54.5 μmol g <sup>-1</sup> in 5 h 26.5 μmol g <sup>-1</sup> in 5 h	0.31 0.134
23	Liu <i>et al.</i> <sup>76</sup>	Ultrathin nanosheets of TiO <sub>2</sub> by hydrothermal synthesis	10 mg of sample spread in a chamber, CO <sub>2</sub> passed through water (0.08 MPa), co-catalyst: Pt	300 W xenon lamp	CH <sub>4</sub> CO	66.4 μmol g <sup>-1</sup> h <sup>-1</sup> 54.2 μmol g <sup>-1</sup> h <sup>-1</sup>	— —
24	Shi <i>et al.</i> <sup>77</sup>	Solvothermal method using HF	50 mg sample, CO <sub>2</sub> bubbled through water, H <sub>2</sub> O/CO <sub>2</sub> = 2.3v/v%	100 W mercury lamp (λ = 365 ± 10 nm)	CH <sub>4</sub>	2.49 μmol g <sup>-1</sup> h <sup>-1</sup>	—
25	Qingli <i>et al.</i> <sup>78</sup>	Treatment of the Ti plate in H <sub>2</sub> O <sub>2</sub> solution at 110 and 130 °C (hydrothermal treatment)	TiO <sub>2</sub> film, CO <sub>2</sub> bubbled through water	Two 300 W Xe lamps	CH <sub>4</sub> CO	12 μmol g <sup>-1</sup> h <sup>-1</sup> 115 μmol g <sup>-1</sup> h <sup>-1</sup>	— —
26	Liu <i>et al.</i> <sup>79</sup>	Fluoride mediated self-transformation pathway	30 mg of photocatalyst, Na <sub>2</sub> CO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> , batch reactor, cocatalyst: Au	300 W Xe lamp	CO CH <sub>4</sub>	~2.1 μmol g <sup>-1</sup> h <sup>-1</sup> ~1.2 μmol g <sup>-1</sup> h <sup>-1</sup>	— —
27	Yin <i>et al.</i> <sup>80</sup>	Solvothermal method with Li-dissolved EDA as solution. (Considerable number of defects (V <sub>O</sub> or Ti <sup>3+</sup> ) existed in H-TiO <sub>2-x</sub> )	50 mg catalyst, 2 bar CO <sub>2</sub> , 6 mL H <sub>2</sub> O	300 W Xe lamp, simulated solar AM1.5 filter	CH <sub>4</sub> CO H <sub>2</sub>	16.2 μmol g <sup>-1</sup> h <sup>-1</sup> 4.2 μmol g <sup>-1</sup> h <sup>-1</sup> 13 μmol g <sup>-1</sup> h <sup>-1</sup>	— — —



Table 1 (Contd.)

Sr no.	Reference	Chemicals used to create defects	Photocatalytic experimental conditions	Light source used	Products	Yield	AQE/SFE
28	Zhu <i>et al.</i> <sup>81</sup>	<i>In situ</i> photodeposition of Cu generates <i>in situ</i> oxygen vacancies	30 mg catalyst, 6 $\mu$ L of water	300 W commercial Xe lamp	CH <sub>4</sub>	8.68 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	—
29	Lan <i>et al.</i> <sup>82</sup>	No such defect is created. Doping of Cu metal by the solvothermal method induced oxygen vacancies	30 mg of catalyst, CO <sub>2</sub> bubbled through solution	300 W Xe lamp	CO	32.5 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	—
30	Pham <i>et al.</i> <sup>83</sup>	Codoping of Ag and Cu into the TiO <sub>2</sub> lattice	2 g of catalyst CO <sub>2</sub> passed through water was injected inside the reactor	Visible light. (Two 20 W bulbs of 0.05 W cm <sup>-2</sup> )	CO CH <sub>4</sub>	550 $\mu$ mol g <sup>-1</sup> in 6 h 880 $\mu$ mol g <sup>-1</sup> in 6 h	— —
31	Pham <i>et al.</i> <sup>84</sup>	Co-doping of V and Cu into TiO <sub>2</sub> lattice	2 g of catalyst CO <sub>2</sub> was injected inside the reactor	Visible light. (Two 20 W bulbs of 0.05 W cm <sup>-2</sup> )	CH <sub>4</sub> CO	933 $\mu$ mol g <sup>-1</sup> in 6 h 588 $\mu$ mol g <sup>-1</sup> in 6 h	— —
32	Wang <i>et al.</i> <sup>85</sup>	Cobalt-doped titanium dioxide	100 mg of photocatalyst dispersed on a porous quartzose film in the reaction cell, and 3 mL of deionized H <sub>2</sub> O and 80 kPa pure CO <sub>2</sub> gas	A 300 W xenon arc lamp with an L-42 glass filter was used as the light source lamp with a cut-off filter ( $\lambda > 420$ nm)	CH <sub>4</sub> CO H <sub>2</sub> O <sub>2</sub>	0.09 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> 1.94 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> 0.74 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> 0.133 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	— — — —
33	Yaghoubi <i>et al.</i> <sup>86</sup>	Oxygen vacancy and Ti <sup>3+</sup> originated during synthesis (synthesis form peroxy-titanium complex)	100 mg of photocatalyst + CO <sub>2</sub> bubbled through water, (20 psi pressure), 40 °C	Both solar and visible light 300 W Xe lamp  Solar light 80 mW cm <sup>-2</sup> Visible light 408 to 1650 nm	CH <sub>4</sub> (solar light) CO (solar light) CH <sub>4</sub> (visible light) CO (visible light)	79.5 ppm g <sup>-1</sup> h <sup>-1</sup> 303 ppm g <sup>-1</sup> h <sup>-1</sup> 60 ppm g <sup>-1</sup> h <sup>-1</sup> 226 ppm g <sup>-1</sup> h <sup>-1</sup>	0.0289 (250–564 nm) — — —
34	Han <i>et al.</i> <sup>87</sup>	TiB <sub>2</sub> is used to prepare (self doped) Ti <sup>3+</sup> in TiO <sub>2</sub>	30 mg catalyst was dispersed into 20 mL of <i>N,N</i> -dimethylformamide and 10 mL ultrapure water	300 W Xe lamp	CO (simulated solar light) H <sub>2</sub> (simulated solar light) CO (visible light)	724 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> 5.5 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> 58 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	— — —
35	Shi <i>et al.</i> <sup>88</sup>	<i>In situ</i> pyrolysis of MIL-125-NH <sub>2</sub> (Ti) with melamine	5 mg photocatalyst dispersed in 5 mL of solution of 4 mL of methyl cyanide (MeCN) solvent, 1 mL of (TEOA), bipyridine (bpy) (10 mmol L <sup>-1</sup> ) and 25 $\mu$ L of 20 mmol L <sup>-1</sup> CoCl <sub>2</sub> purged with CO <sub>2</sub> , co-catalyst: Co(bpy) <sub>3</sub> <sup>2+</sup>	300 W xenon lamp  UV cut-off filter ( $\lambda > 400$ nm)	CO H <sub>2</sub>	388.9 $\mu$ mol g <sup>-1</sup> in 5 h 75 $\mu$ mol g <sup>-1</sup> in 5 h	— —
36	Feng <i>et al.</i> <sup>89</sup>	During MgO deposition by ALD	10 mg photocatalyst loaded over glass fiber paper, CO <sub>2</sub> passed through water, no co-catalyst	450 W Xe lamp	CO	54 $\mu$ mol g <sup>-1</sup> in 4 h	—

which could have resulted in the transfer of an electron from the CB of TiO<sub>2</sub> to the Ni nanocluster and further to the adsorbed CO<sub>2</sub> molecule. The hole remaining on TiO<sub>2</sub> transferred to the water to generate H<sup>+</sup>. The enhanced photocatalytic activity and selectivity were attributed to the synergistic effect of Ni nanoclusters and oxygen vacancies on black TiO<sub>2</sub>.

To further improve the photocatalytic activity, Fu *et al.*<sup>54</sup> loaded KSCN along with Ni over oxygen vacant TiO<sub>2</sub>. The H–Ni–TiO<sub>2</sub> photocatalyst was synthesized by a hydrothermal process,

followed by hydrogenation in the presence of pure H<sub>2</sub> gas. At the same time, SCN–H–Ni–TiO<sub>2</sub> was synthesized by modifying H–Ni–TiO<sub>2</sub> with potassium thiocyanate passivation. No structural and morphological changes were observed after modification with KSCN. DRS absorption spectra showed that the absorption in the region of 400–1600 nm decreased after modification with thiocyanate and this could be due to the passivation of surface defects (Fig. 11a). Similar results were observed in the XPS data as no peak corresponding to Ti<sup>3+</sup> was found after passivation.





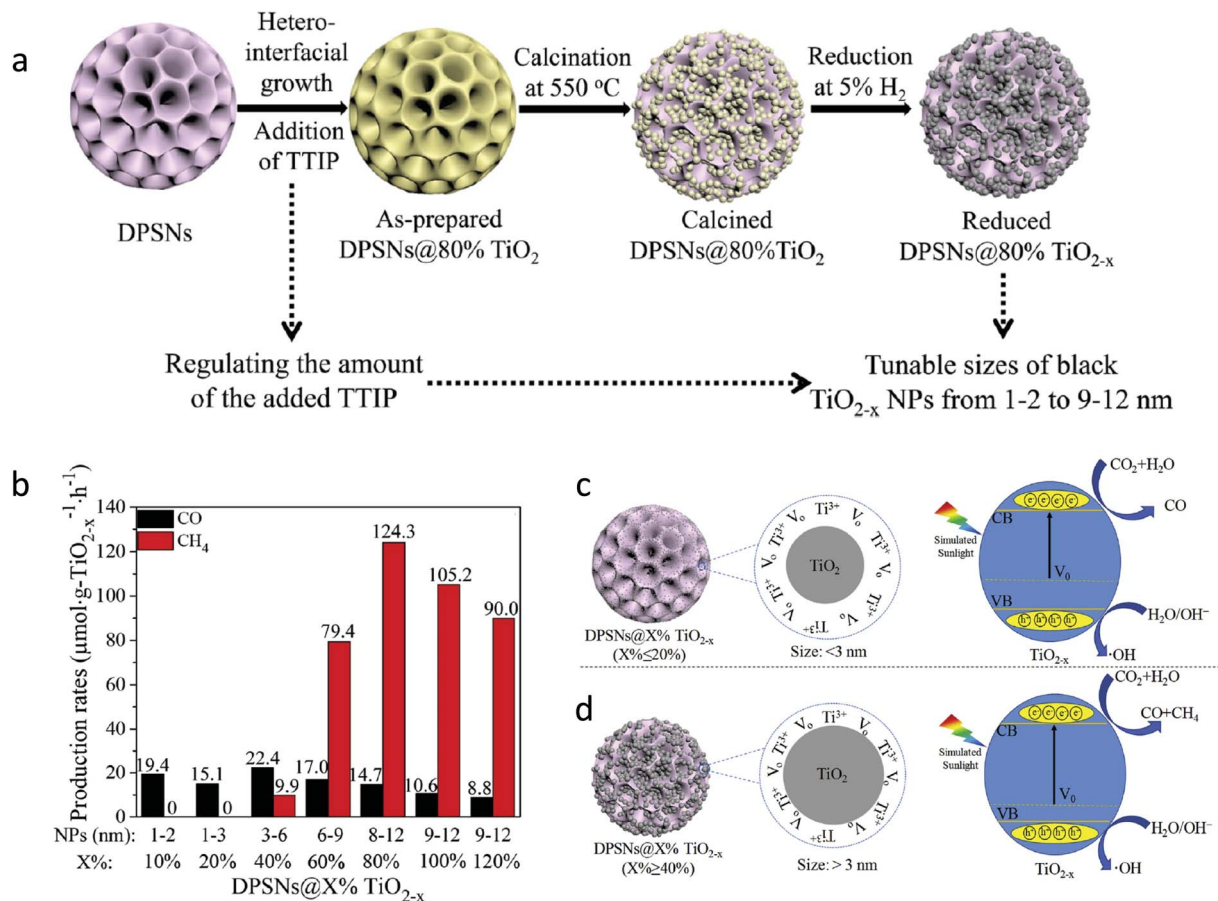


Fig. 9 (a) Synthesis protocol for reduced DPSNs@X% TiO<sub>2-x</sub> NPs, (b) photocatalytic CO<sub>2</sub> conversion using different samples, (c and d) a probable mechanism for the different activity and selectivity of DPSNs@X% TiO<sub>2-x</sub> NPs with the varied particle size of black TiO<sub>2-x</sub> NPs for CO<sub>2</sub> conversion (reproduced from ref. 52 with permission from Elsevier, copyright 2019).

The SCN-H-Ni-TiO<sub>2</sub> photocatalyst showed the maximum yield of 11.30 and 1.20 μmol g<sup>-1</sup> in 6 h for acetaldehyde and methanol, respectively (Fig. 11b). Acetaldehyde production was 2.80 times higher than that observed using H-Ni-TiO<sub>2</sub> under solar light illumination. Also, it retained the catalytic activity up to 88% after 40 h of reaction, whereas the H-Ni-TiO<sub>2</sub> sample retained only 40% of the catalytic activity after 10 h of reaction. Thus, modification of KSCN further helped improve the catalytic activity as well as stability. Fig. 11c shows the band alignment derived from UPS and DRS absorption data. The induced interfacial dipole in SCN-H-Ni-TiO<sub>2</sub> shifted the Fermi level as well as the CB and VB edge and also induced an electric field at the interface, which assisted in the separation of charges by driving away hole over the surface. The improvement in activity and stability in the case of SCN-H-Ni-TiO<sub>2</sub> was attributed to the surface passivation and improved charge separation due to the formation of the interfacial dipole.

Similarly, Ye *et al.*<sup>55</sup> synthesized inverse opal (IO) structured three-dimensional nickel loaded black TiO<sub>2</sub> (referred to as IO-B-TiO<sub>2</sub>/Ni) from IO-W-TiO<sub>2</sub>/NiO *via* the hydrogenation process at 550 °C for 3 h under H<sub>2</sub> atmosphere. The hydrogenation treatment reduced NiO to Ni nanoparticles and Ti<sup>4+</sup> to Ti<sup>3+</sup> in TiO<sub>2</sub>. EPR and XPS analysis confirmed the presence of Ti<sup>3+</sup> centres.

The IO-B-TiO<sub>2</sub> showed narrow bandgap width and the highest light absorption as compared to P25 because of the slow photon effect of IO structured material and the existence of Ti<sup>3+</sup> centres (Fig. 12A). They found that the CO production rate of 12.13 μmol g<sup>-1</sup> h<sup>-1</sup> using IO-B-TiO<sub>2</sub>/Ni under a 300 W Xe lamp was 10.1, 5.1, and 2.0 times higher than that using P25, IO-W-TiO<sub>2</sub> and IO-B-TiO<sub>2</sub>, respectively (Fig. 12B). The photocatalyst IO-B-TiO<sub>2</sub>/Ni was stable over five cycles. The introduction of Ni and the presence of Ti<sup>3+</sup> on the outer layer of black TiO<sub>2</sub> both improved the rate of separation of photogenerated e<sup>-</sup>-h<sup>+</sup> by trapping of photogenerated electrons *via* a synergistic effect, thus enhancing photocatalytic activity. PL spectra, photocurrent transient response and electrochemical impedance spectroscopy proved that the recombination rate of photogenerated e<sup>-</sup>-h<sup>+</sup> was the slowest in the case of IO-B-TiO<sub>2</sub>/Ni as compared to P25, IO-W-TiO<sub>2</sub>, and IO-B-TiO<sub>2</sub>. Under light irradiation, an electron could transfer from the CB of TiO<sub>2</sub> to Ni where adsorbed CO<sub>2</sub> was reduced to CO by accepting photogenerated electrons concentrated on the surface of Ni (Fig. 12C). The improved photocatalytic activity was ascribed to the enhanced light absorption due to the slow photon effect of the IO structure, the formation of a disorder layer and better charge separation efficiency.



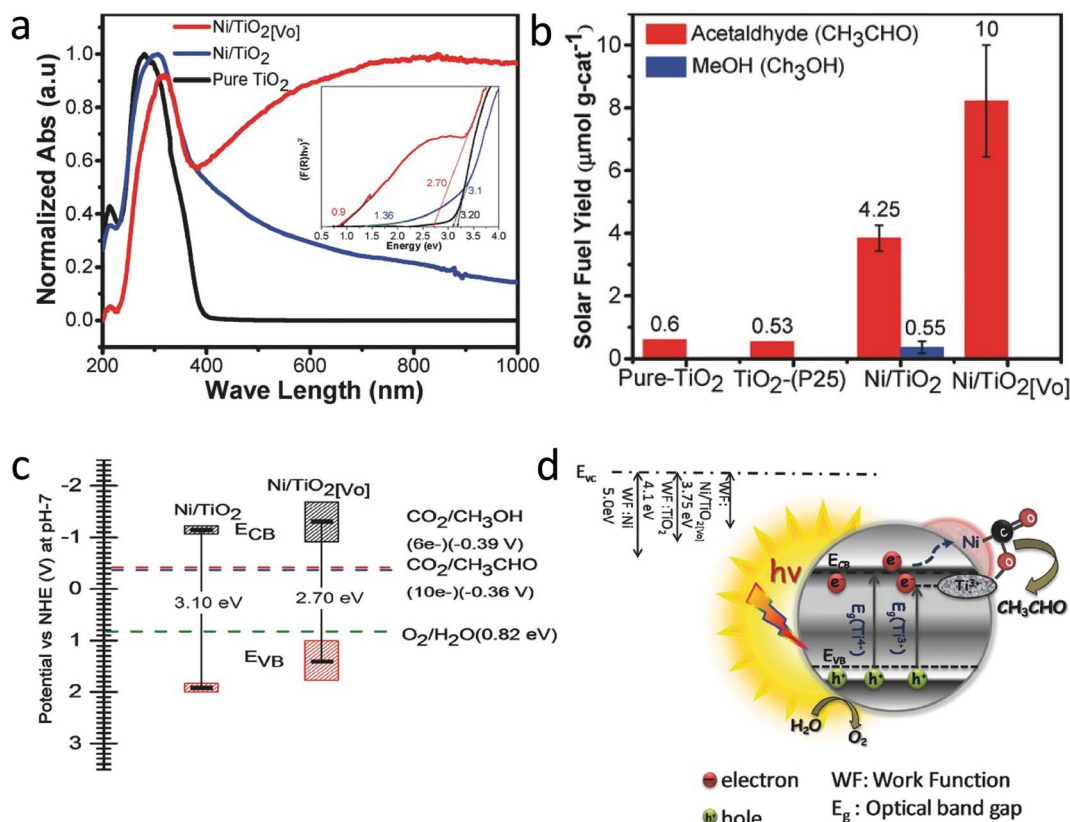


Fig. 10 (a) DRS absorption spectra (inset shows Tauc plots with fitting), (b) the cumulative yield of acetaldehyde for 6 h on pure TiO<sub>2</sub>, TiO<sub>2</sub>-P25, Ni/TiO<sub>2</sub>, and Ni/TiO<sub>2</sub>[Vo] using a halogen lamp as a light source, (c) band-edge positions of Ni/TiO<sub>2</sub>, and Ni/TiO<sub>2</sub>[Vo] estimated using UPS and DRS bandgap and (d) schematic illustration of a mechanism for photocatalytic CO<sub>2</sub> reduction of Ni/TiO<sub>2</sub>[Vo]. (reproduced from ref. 53 with permission from Wiley, copyright 2018).

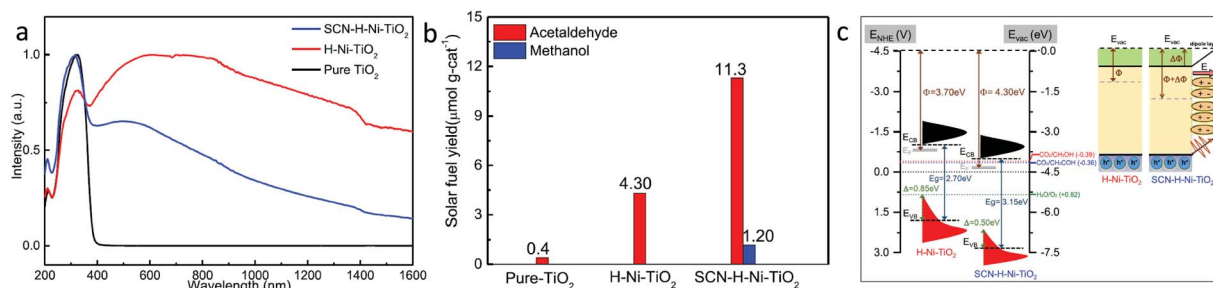


Fig. 11 (a) DRS absorption spectra of the samples, (b) photocatalytic CO<sub>2</sub> conversion yield under light illumination, (c) comparative band diagram and interfacial dipole effect of H-Ni-TiO<sub>2</sub> and SCN-Ni-TiO<sub>2</sub> (reproduced from ref. 54 with permission from the American Chemical Society, copyright 2019 American Chemical Society).

Liu *et al.*<sup>56</sup> compared the photocatalytic properties of the Cu doped TiO<sub>2</sub> sample by calcining it in He and H<sub>2</sub> atmosphere. They synthesized Cu doped TiO<sub>2</sub> by the precipitation method followed by the calcination of the as-synthesized sample in the air at 400 °C. Furthermore, the sample was calcined in He and H<sub>2</sub> atmosphere at 220 °C for 1.5 h. During heat treatment in He and H<sub>2</sub>, the formation of defects, namely oxygen vacancies and Ti<sup>3+</sup>, were found. He and H<sub>2</sub> treated samples formed predominantly Cu<sup>1+</sup> and mixed Cu<sup>1+</sup>/Cu<sup>0</sup>, respectively. The color of the H<sub>2</sub> treated sample was found to be darker and it also showed enhanced absorption in the visible region compared to the He

treated sample. This enhancement in the light absorption in the case of the H<sub>2</sub> treated sample was due to the high concentration of oxygen vacancies and the presence of interstitial H. The sample treated in the H<sub>2</sub> atmosphere showed the highest activity for CH<sub>4</sub> and CO generation compared to the He treated samples. The improvement in activity was attributed to the presence of oxygen vacancies and Ti<sup>3+</sup>, which provided a site for CO<sub>2</sub> adsorption and subsequent transfer of an electron to the adsorbed CO<sub>2</sub>. Also, the presence of the Cu<sup>1+</sup>/Cu<sup>0</sup> redox couple generated by H<sub>2</sub> reduction resulted in higher activity for the trapping of photogenerated electrons and holes than the



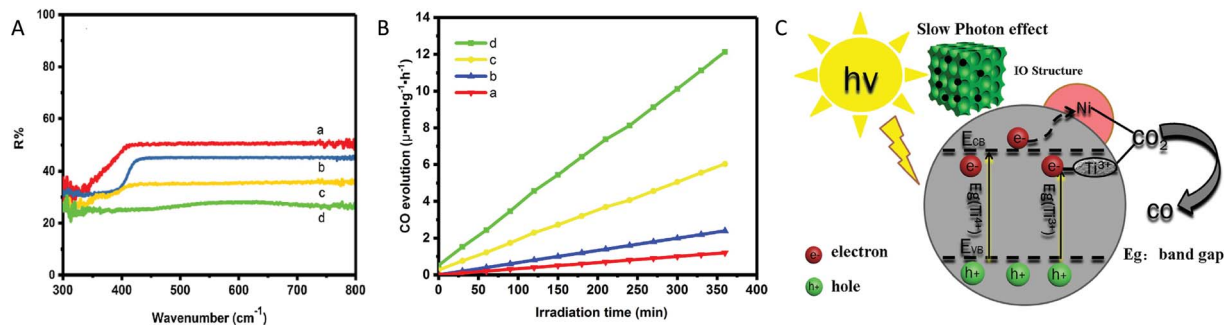


Fig. 12 (A) UV-vis DRS and (B) rate of CO generation during the photocatalytic reduction of CO<sub>2</sub> using (a) P25, (b) IO-W-TiO<sub>2</sub>, (c) IO-B-TiO<sub>2</sub> and (d) IO-B-TiO<sub>2</sub>/Ni. (C) Schematic representation of the mechanism for photocatalytic CO<sub>2</sub> conversion (reproduced from ref. 55 with permission from Elsevier, copyright 2019).

presence of only Cu<sup>1+</sup> species induced by He treatment. 1 atom% Cu doped TiO<sub>2</sub> after hydrogen treatment showed the highest activity of 25 and 4.4 μmol g<sup>-1</sup> in 6.5 h for CO and CH<sub>4</sub> production, respectively.

The impact of hydrogenation before and after metal oxide loading was studied by Li *et al.*<sup>57</sup> They observed that the dispersion of CoO<sub>x</sub> over TiO<sub>2</sub> nanotubes varies on changing the sequence of hydrogenation treatment. In this work, nanotubes of TiO<sub>2</sub> with the mixture of anatase and TiO<sub>2</sub>(B) phase (referred to as AB) were synthesized. The impregnation method was used to load CoO<sub>x</sub> over AB (referred to as (AB-Co)) and then the sample was calcined in the air (referred to as AB-A). The AB-Co sample was calcined in the presence of N<sub>2</sub>/H<sub>2</sub> (1 : 9) and referred to as AB-Co-H. In another approach, AB was first calcined in N<sub>2</sub>/H<sub>2</sub> and then Co ions were loaded over it by the impregnation method and referred to as AB-H-Co. TEM shows the well-dispersed CoO<sub>x</sub> over the TiO<sub>2</sub> nanotubes. It was found that the CoO<sub>x</sub> nanoparticles on AB-Co and AB-H-Co were amorphous, while AB-Co-H showed the crystalline CoO nanoparticles. The size of the CoO<sub>x</sub> nanoparticles was found to be in the order AB-Co-H > AB-Co > AB-H-Co. The stronger interaction between the oxygen vacancy of TiO<sub>2</sub> and the CoO<sub>x</sub> nanoparticles resulted in the high dispersion and smaller size of CoO<sub>x</sub> in AB-H-Co as compared to other samples. DRS absorption spectra did not show much change in the absorption edge, indicating the introduction of a smaller number of oxygen defects. d-d transition of Co<sup>2+</sup> species was observed in the range of 550–670 nm. They compared the CO<sub>2</sub> conversion yield obtained *via* photocatalysis (PT) and photo-thermo-catalysis (PTC). A significant increase in the yield of CO and CH<sub>4</sub> was observed for the reaction carried out photo-thermo-catalytically at 120 °C. The calcined sample of AB-Co showed a lower yield for CH<sub>4</sub>. This could be due to the aggregation of the CoO<sub>x</sub> after calcination. The highest yield of 16.4 and 10.05 μmol g<sup>-1</sup> h<sup>-1</sup> of CO and CH<sub>4</sub> generation was observed in the case of the AB-H-Co sample, respectively. The improved activity was attributed to two factors: the first is the presence of oxygen vacancies, which helped in better charge separation, dispersion of CoO<sub>x</sub> and adsorption of CO<sub>2</sub> and the second is the role of CoO<sub>x</sub> as the co-catalyst, which acted as a hole trap and enhanced the proton generation from water oxidation.

**4.1.2 Using hydrides.** The use of hydrides for the generation of defects is an easy and safe method. NaBH<sub>4</sub> is used as a source of hydrogen as it has a hydrogen content of 10.66 wt% and decomposes in a single step to give hydrogen.<sup>58</sup> One of the methods to produce defects is heating a mixture of TiO<sub>2</sub> and NaBH<sub>4</sub> in an Ar atmosphere. The *in situ* generation of the active hydrogen species creates oxygen vacancies on the surface of TiO<sub>2</sub>.

Sorcar *et al.*<sup>59</sup> reported reduced blue titania (referred to as BT) synthesis by mixing P25 TiO<sub>2</sub> with NaBH<sub>4</sub> followed by heating at 350 °C for 30 min under an Ar atmosphere. Samples were referred to as BT-x where x is the amount of NaBH<sub>4</sub> in mg used during synthesis for 200 mg of P25 TiO<sub>2</sub>. Pt was photo-deposited over the BT-30 sample and the amount of Pt was varied from 0.25–0.5 wt%, and the sample was named y-BT-30 where y is the amount of Pt. The color of the sample becomes darker, with an increase in NaBH<sub>4</sub> content. They found that the treatment of TiO<sub>2</sub> with NaBH<sub>4</sub> introduced a shell of a disorder layer over the crystalline core. The enhancement of light absorption in the visible region was attributed to the formation of the disorder surface layer and the existence of Ti<sup>3+</sup>. The particle size of the Pt was varied from 1.82 nm for 0.25 wt% to 3.5 nm for 0.5 wt%. The highest methane generation at the rate of 80.35 μmol g<sup>-1</sup> h<sup>-1</sup> with AQE of 12.4% was observed using 0.35-BT-30 having a Pt content of 0.35 wt% under solar light irradiation with 100% selectivity. The catalytic activity was stable for five cycles. The decrease in activity in the second cycle was due to the saturation of active sites by the adsorption of the intermediate products. Therefore, after the 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> cycle, the catalyst was subjected to the vacuum treatment to desorb the products from the catalyst surface. The improved yield of 0.35-BT-30 was attributed to the presence of defects, optimum amount and size of Pt nanoparticles, and appropriate band alignment.

To further modify the performance of the catalyst, Sorcar *et al.* decorated the blue titania (referred to as RBT) with graphene.<sup>60</sup> Graphene wrapped RBT samples (G/RBT) were prepared by annealing the graphene oxide-RBT composite (GO/RBT) samples in a vacuum oven at 230 °C for 90 minutes. On this composite, the generation of 77 μmol g<sup>-1</sup> of ethane (C<sub>2</sub>H<sub>6</sub>) and 259 μmol g<sup>-1</sup> of CH<sub>4</sub> in 7 h under solar light illumination





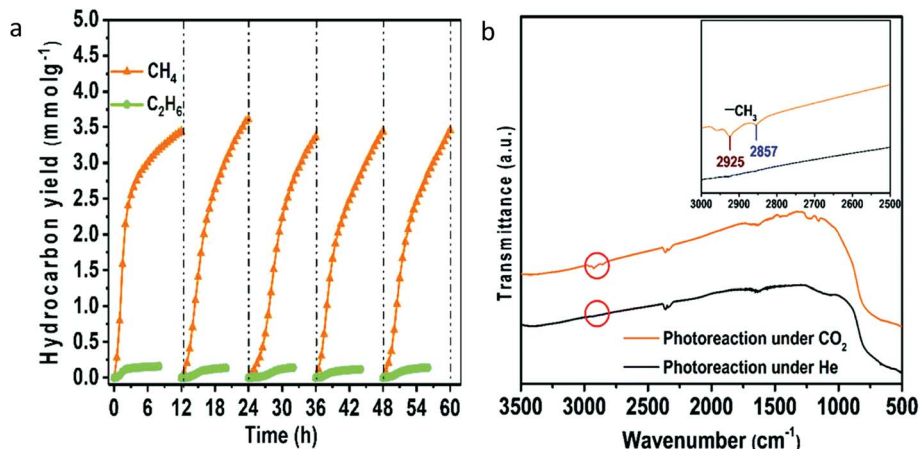


Fig. 13 (a) Stability evaluation of Cu–Pt modified blue titania for photocatalytic CO<sub>2</sub> conversion, (b) FTIR analysis of the sample after photocatalytic reaction carried out in the presence of CO<sub>2</sub> and He gas (reproduced from ref. 61 with permission from the Royal Society of Chemistry, copyright 2019).

with an AQE of 7.9% was observed. The stability of the photocatalyst was evaluated for 42 h. UPS studies revealed the formation of Ti–O–C bonds at the interface, resulting in upward band bending, which was responsible for the hole transfer from RBT to the graphene. The transient absorption spectroscopy studies revealed the accumulation of photogenerated holes and electrons on the graphene and Ti<sup>3+</sup> sites, respectively. The generation of C1 and C2 products was attributed to the efficient charge separation and accumulation of photogenerated electrons and holes is attributed to the RBT and graphene surface, respectively.

To further improve the performance of blue titania, Sorcar *et al.*<sup>61</sup> deposited Cu and Pt over reduced blue-titania by the photodeposition method to improve the yield of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. Photoconversion of CO<sub>2</sub> using 1 wt% of Cu–0.35 wt% of Pt modified blue titania generated CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> with a rate of 3.0 mmol g<sup>-1</sup> and 0.15 mmol g<sup>-1</sup> in 6 h under artificial sunlight illumination with 1% solar to fuel efficiency (SFE) and 86% AQE, respectively. The catalyst was found to be stable for 60 h (Fig. 13a). FTIR spectra of the catalyst recorded after

photocatalytic CO<sub>2</sub> conversion showed characteristic signals corresponding to CH<sub>3</sub>; this indicated that CH<sub>3</sub> was the intermediate formed during the catalytic reaction (Fig. 13b). They claimed that the Cu nanoparticles provided sites for CO<sub>2</sub> adsorption, while the Pt effectively prevented electron–hole recombination. The improvement of photocatalytic activity was attributed to the synergistic effect between charge separation and transfer from Pt to Cu and the enhanced adsorption of CO<sub>2</sub> by the presence of both oxygen defects and Cu sites.

**4.1.3 High energy particle: H<sub>2</sub> plasma treatment.** Yan *et al.*<sup>62</sup> synthesized defective TiO<sub>2</sub> by hydrogen plasma treatment at 150 °C using P25 TiO<sub>2</sub>. The concentration of defects was varied by varying the plasma treatment time for 30 s, 1 min, 3 min, 5 min, and 20 min and the sample was referred to as H–TiO<sub>2</sub>-x where x is plasma treatment time. It was found that the absorption in the visible region increases with an increase in the time of plasma treatment. This was also evident from the color change of the sample from white to black (Fig. 14a). The increase in disordered layer thickness was observed from 0 to 2 nm while increasing the plasma treatment time from 30 s to 20

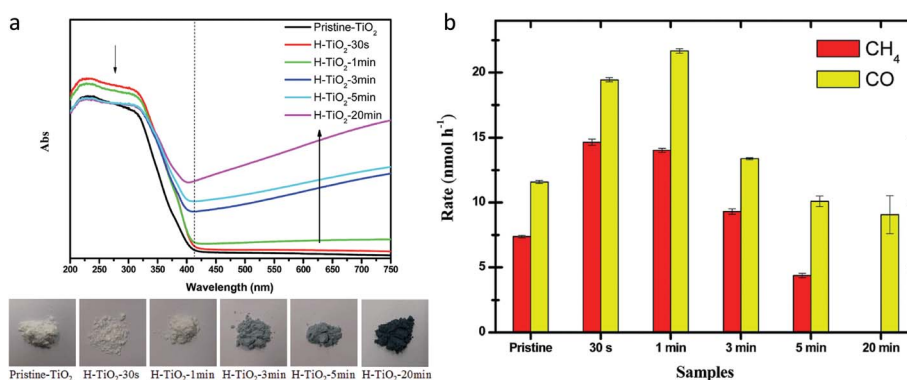


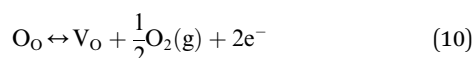
Fig. 14 (a) DRS spectra and the photograph of the samples with increasing plasma treatment time and (b) photocatalytic CO<sub>2</sub> conversion using hydrogenated samples under solar light illumination (reproduced from ref. 62 with permission from the Royal Society of Chemistry, copyright 2014).



min. The 1 min plasma-treated sample showed the highest CH<sub>4</sub> and CO generation at a rate of 14.03 and 21.67 nmol h<sup>-1</sup> using 90 mg of the catalyst under solar light illumination, respectively (Fig. 14b).

## 4.2 Defect generation by annealing in an oxygen-deficient atmosphere

**4.2.1 Annealing in an inert (Ar, He or N<sub>2</sub>) atmosphere.** One of the ways to generate the oxygen vacancy in TiO<sub>2</sub> is by thermal treatment in an oxygen-deficient environment such as an He, Ar, or N<sub>2</sub> atmosphere, or vacuum. The generation of oxygen vacancies at a high temperature can be elucidated by the following reversible reaction using standard Kröger-Vink notation:<sup>33</sup>



where O<sub>o</sub>, V<sub>o</sub>, [V<sub>o</sub>] and p(O<sub>2</sub>) refer to lattice oxygen, oxygen vacancy, concentration of oxygen vacancies and oxygen pressure, respectively.

The equilibrium constant (*K*) of the above reaction can be given as follows:

$$K = [\text{V}_o]n^2p(\text{O}_2)^{(1/2)} \quad (11)$$

Rearranging the equation in terms of the concentration of oxygen vacancies can give the following:

$$[\text{V}_o] = Kn^{-2}p(\text{O}_2)^{-(1/2)} \quad (12)$$

This equation indicates that the concentration of oxygen vacancies will increase with a decrease in oxygen pressure. Thus, thermal treatment in the oxygen-deficient atmosphere facilitates the generation of oxygen vacancies.<sup>33</sup>

Liu *et al.*<sup>63</sup> compared the photocatalytic activity of defective and defect-free anatase, rutile and brookite polymorphs of TiO<sub>2</sub>. They introduced defects in the polymorphs by heating them in the flow of He gas for 1.5 h at 220 °C. It was found that heating in the presence of He produces oxygen vacancies and Ti<sup>3+</sup> ions on the surface of the anatase and brookite form while it is negligible in the case of the rutile phase. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies

revealed that the pristine TiO<sub>2</sub> could not activate the CO<sub>2</sub>, as no formation of the CO<sub>2</sub><sup>-</sup> intermediate occurred over it. Different intermediates were spotted over anatase and brookite forms. The anatase phase formed predominantly CO<sub>2</sub><sup>-</sup> as one of the intermediates, whereas brookite showed the formation of both CO<sub>2</sub><sup>-</sup> and HCOOH species. It was observed that water adsorption was favored over the brookite surface. Only in the absence of water, characteristics bands of CO<sub>2</sub><sup>-</sup> species appeared and the concentration of these species increased with an increase in illumination time, confirming that the CO<sub>2</sub><sup>-</sup> species reacted immediately with water to form CO during light irradiation. Also, they found that the brookite phase was more photo-catalytically active as a lower amount of energy was required to produce the oxygen vacancy on its surface as compared to the anatase and rutile phases by using this synthesis protocol. Total production of CO and CH<sub>4</sub> was found to be 18.9 μmol g<sup>-1</sup> in 6 h under solar light illumination using the defective brookite TiO<sub>2</sub> polymorph in the presence of water vapor. CO was found to be the major product of CO<sub>2</sub> conversion.

Further research was carried out by Xin *et al.*<sup>64</sup> to synthesize the defects over brookite nanosheets of TiO<sub>2</sub>, by an oxidation-based hydrothermal method using TiH<sub>2</sub> as a titanium precursor, followed by post-annealing at different temperatures, 300, 500 and 700 °C, in the presence of a N<sub>2</sub> flow. They found that with an increase in calcination temperature, the (concentration of Ti<sup>3+</sup> decreases) powder becomes brown, black and light grey. The crystallinity of samples also increased with increasing calcination temperature. The fading of color of the sample annealed at 700 °C was attributed to the difficulty in the diffusion of Ti<sup>3+</sup> with improved crystallinity resulting in a lower concentration of defect centers. The sample annealed at 500 °C with the highest concentration of 0.7 × 10<sup>20</sup> spins mol<sup>-1</sup> of Ti<sup>3+</sup> showed CH<sub>4</sub> and CO generation at a rate of 11.9 and 23.5 μmol g<sup>-1</sup> h<sup>-1</sup> under visible light illumination, respectively. The improvement in the activity was attributed to the Ti<sup>3+</sup> ion concentration and light absorption properties of the catalyst.

Zhao *et al.*<sup>65</sup> reported the generation of the oxygen vacancy by annealing in a vacuum. To prevent the oxidation of Cu metal, the TiO<sub>2</sub> precursor was coated over Cu metal nanoparticles and annealed in a vacuum (referred as Cu@TiO<sub>2</sub>). They observed that the oxygen vacancies were created as a result of annealing

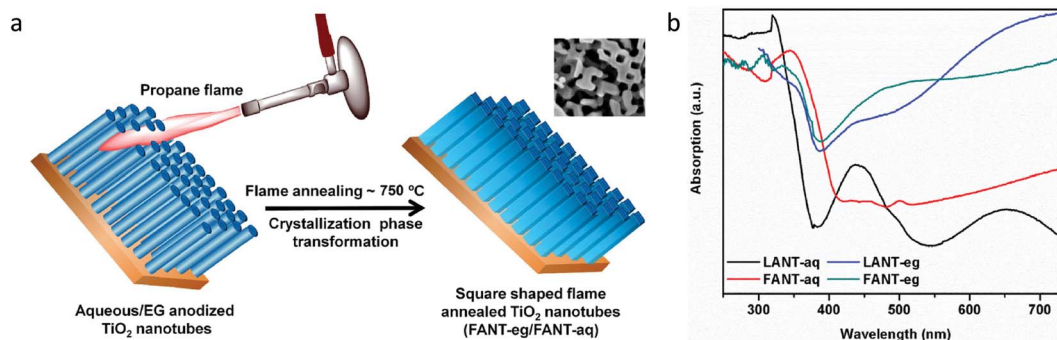


Fig. 15 (a) Synthesis protocol for the generation of oxygen vacancies using propane flame treatment (inset shows TEM image of square-shaped TiO<sub>2</sub> nanotubes after treatment with propane flame) and (b) DRS absorption spectra of LANT-aq, LANT-eg, FANT-aq and FANT-eg samples (reproduced from ref. 66 with permission from Elsevier, copyright 2019).



in a vacuum and their amount increased with an increase in Cu content. The presence of Cu nanoparticles helped form the oxygen vacancies in  $\text{TiO}_2$  via metal-oxide interactions. This also resulted in improved visible light absorption of  $\text{Cu@TiO}_2$ . The highest CO and  $\text{CH}_4$  production at a rate of 48.5 and  $8 \mu\text{mol g}^{-1}$  in 6 h was observed using  $\text{Cu@TiO}_2$  (4 wt% Cu), which was 1.4 times higher than the black  $\text{TiO}_2$  under visible light illumination. The improvement in activity was attributed to the enhancement of adsorption of  $\text{CO}_2$ , light absorption and separation of charge carriers revealed by the transient photocurrent measurements.

**4.2.2 Flame reduction method.** A flame operates under hydrocarbon-rich and oxygen-deficient conditions, thus providing a reducing atmosphere containing CO and  $\text{H}_2$ . The annealing of  $\text{TiO}_2$  in the reducing atmosphere of a flame generates oxygen vacancies in  $\text{TiO}_2$ . The flame reduction method offers several advantages, such as high temperature and fast heating rate, allowing the creation of  $V_{\text{O}}$  in less than a minute. Kar *et al.*<sup>66</sup> synthesized defective  $\text{TiO}_2$  nanotubes by the flame reduction method. In this work, they synthesized defective  $\text{TiO}_2$  nanotubes by electrochemical anodization of the Ti electrode in the aqueous and non-aqueous based electrolyte, followed by annealing in the high-temperature flame of a propane torch (750 °C) for 2 min (Fig. 15a). The sample synthesized using the aqueous solution and non-aqueous solution before flame annealing was referred to as LANT-aq and LANT-eg and after flame annealing referred to as FANT-aq and FANT-eg, respectively. They observed that the circular LANT-aq and LANT-eg nanotubes transformed into the square-shaped nanotubes (as shown in Fig. 15a inset) after heating using a propane flame. FANT-aq showed a pure rutile phase while FANT-eg showed a mixture of anatase and rutile phase. The phase transformation, along with thermal stresses during flame annealing at high temperature resulted in the transformation of nanotubes from circular to square-shaped morphology. The square-shaped flame annealed nanotubes showed a higher density of electromagnetic hot spots for visible light and stronger absorption in the UV region than regular nanotubes calcined in the furnace. The presence of  $\text{Ti}^{3+}$  was confirmed by XPS and EPR studies. Both the flame annealed nanotubes showed the highest light absorption in the visible region due to

the generation of localized  $\text{Ti}^{3+}$  states (Fig. 15b). The FANT-aq and FANT-eg showed methane generation at a rate of 156.5 and  $9.5 \mu\text{mol g}^{-1} \text{h}^{-1}$ , respectively. The improvement of activity was attributed to the enhanced light absorption in visible light due to the presence of  $\text{Ti}^{3+}$ , square morphology, and the presence of both anatase and rutile phases with the (110) plane.

### 4.3 Using organic reducing agents

Tu *et al.*<sup>67</sup> synthesized the  $\text{TiO}_2/\text{graphene}$  (referred to as Gx- $\text{TiO}_2$  where  $x = 0, 1, 2, 5$  wt% of graphene) hybrid using the simultaneous reduction-hydrolysis method using ethylenediamine and water as a solvent in the hydrothermal treatment. They observed the formation of  $\text{Ti}^{3+}$  and reduction of graphene from graphene oxide by treatment with ethylenediamine. The light absorption increases with an increase in graphene content, as shown in Fig. 16a. The dispersion of  $\text{TiO}_2$  prohibited the restacking of the sheets of the graphene. The nanocomposite with 2 wt% graphene shows the highest rate of 8 and  $16.8 \mu\text{mol g}^{-1} \text{h}^{-1}$  of methane and ethane, respectively (Fig. 16b). Initially, the yield of ethane increased with an increase in graphene content. On further increase in graphene content to more than 2 wt%, a decrease in activity was observed which could be attributed to the hindering of light absorption of  $\text{TiO}_2$  due to the presence of excess graphene. They attributed the generation of ethane to the synergistic effect between surface  $\text{Ti}^{3+}$  sites and graphene. Matching energy levels of the d-orbital of  $\text{TiO}_2$  and  $\pi$  orbital of graphene and formation of the Ti-O-C bond between graphene and  $\text{TiO}_2$  results in d to  $\pi$  orbital overlap; this makes the transfer of the electron from the CB of  $\text{TiO}_2$  to graphene possible upon light illumination. This transferred electron could help reduce  $\text{CO}_2$  adsorption on the surface. No ethane formation was observed over P25; hence they proposed that electron-rich graphene could stabilize  $\cdot\text{CH}_3$  radicals and thus help in the formation of methane as well as ethane by coupling of the  $\cdot\text{CH}_3$  radical.

### 4.4 Metallothermic reduction

The metallothermic reduction method to generate defects in  $\text{TiO}_2$  is easier, safer, and cost-effective as compared to the  $\text{H}_2$  reduction method carried out at high pressure and

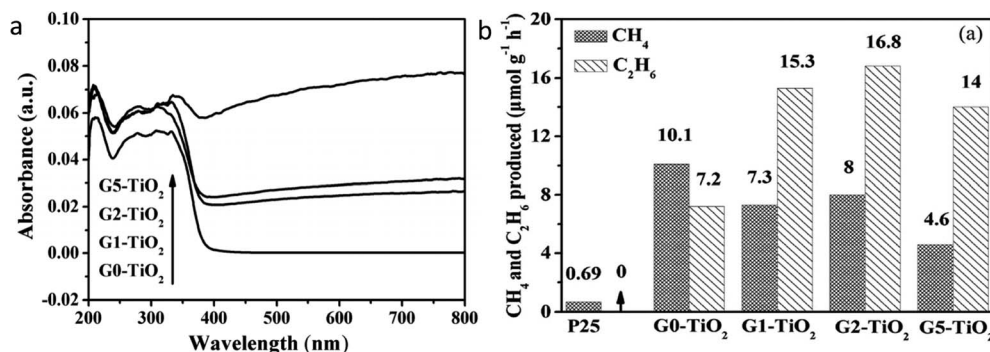


Fig. 16 (a) UV-visible DRS spectrum of Gx- $\text{TiO}_2$  ( $x = 0, 1, 2$  and  $5$  wt% of graphene) samples and (b) comparison of photocatalytic activity of Gx- $\text{TiO}_2$  samples in the presence of water vapor (reproduced from ref. 67 with permission from Wiley, copyright 2013).





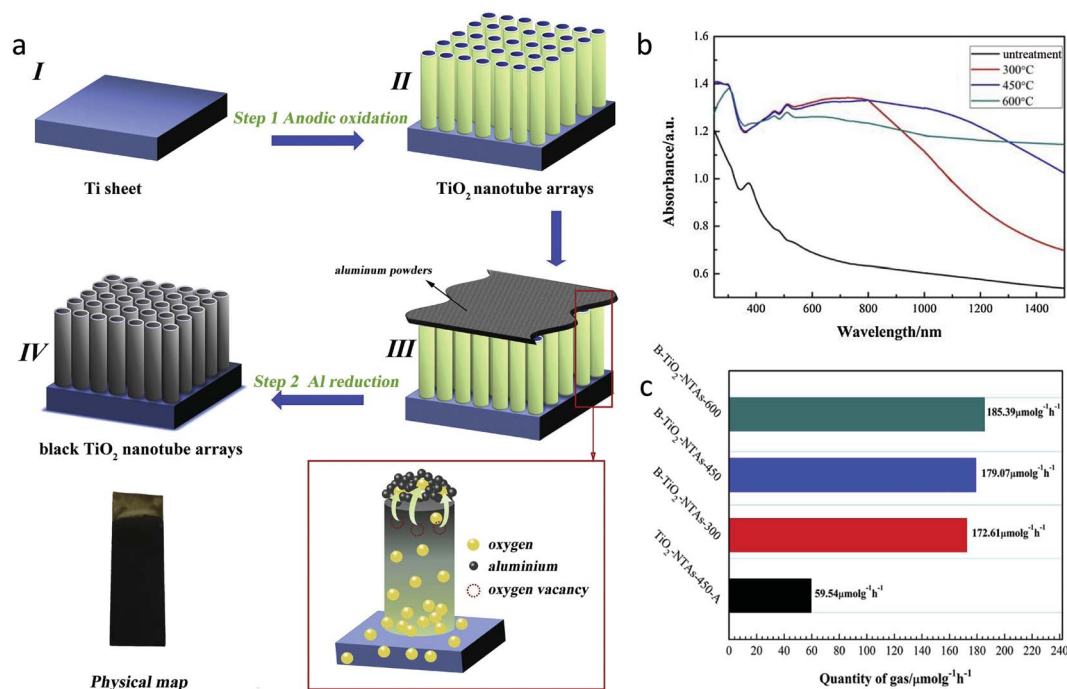


Fig. 17 (a) Schematic of synthesis procedure for the black TiO<sub>2</sub> nanotube array, (b) UV-visible DRS spectra of the sample annealed at different temperatures and (c) photocatalytic CO<sub>2</sub> conversion using different samples under visible light illumination (reproduced from ref. 70 with permission from Elsevier, copyright 2020).

temperature. According to the Ellingham diagram, Al, Mg, and Li possess lower negative potential, and thus can be potential candidates for the reduction of TiO<sub>2</sub>.<sup>68</sup> In this method, these metals act as a reducing agent to capture lattice oxygen effectively.

**4.4.1 Aluminothermic reduction.** Yin *et al.*<sup>69</sup> used Al metal for the generation of defects along with a defective core-shell structure with a crystalline core surrounded by an amorphous layer. They synthesized TiO<sub>2</sub>@TiO<sub>2-x</sub> using a two-zone furnace in which Al and TiO<sub>2</sub> were placed in a different zone and evacuated to a pressure <0.5 Pa. Al was heated at 800 °C, whereas the temperature of TiO<sub>2</sub> was varied from the 300–500 °C to study the impact of the oxygen defect (V<sub>O</sub>) and disordered shell on the photocatalytic activity of TiO<sub>2-x</sub>. It was observed that with an increase in temperature from 400 (referred to as 400-TiO<sub>2-x</sub>) to 500 °C (referred to as 500-TiO<sub>2-x</sub>), the amorphous layer thickness increased from 1–2 to 2–3 nm. Also, the oxygen defects and Ti<sup>3+</sup> increased with an increase in heating temperature, as confirmed by EPR. With an increase in defects, the absorption in the visible region enhanced with a marked change in color of the sample from blue to black. The CO<sub>2</sub> temperature-programmed reduction profile showed that the amount of CO<sub>2</sub> adsorbed over 500-TiO<sub>2-x</sub> was more than that of pristine TiO<sub>2</sub>. The photocatalytic CO<sub>2</sub> conversion was evaluated at 2 bar CO<sub>2</sub> pressure under different sources of light. The highest CH<sub>4</sub> generation at a rate of 14.3 μmol g<sup>-1</sup> h<sup>-1</sup> with 74% selectivity was found using 500-TiO<sub>2-x</sub> under simulated solar light. The 500-TiO<sub>2-x</sub> catalyst showed considerable methane yield under visible and IR light illumination, whereas pristine TiO<sub>2</sub> did not

show any activity under similar photocatalytic conditions. They found that the photothermal effect was not very pronounced as the photocatalytic activity at 50 °C was lower than the activity evaluated at room temperature. Increased oxygen defects and Ti<sup>3+</sup>, narrowed bandgap, and pronounced surface electronic modification contributed positively to the enhancement of photocatalytic activity.

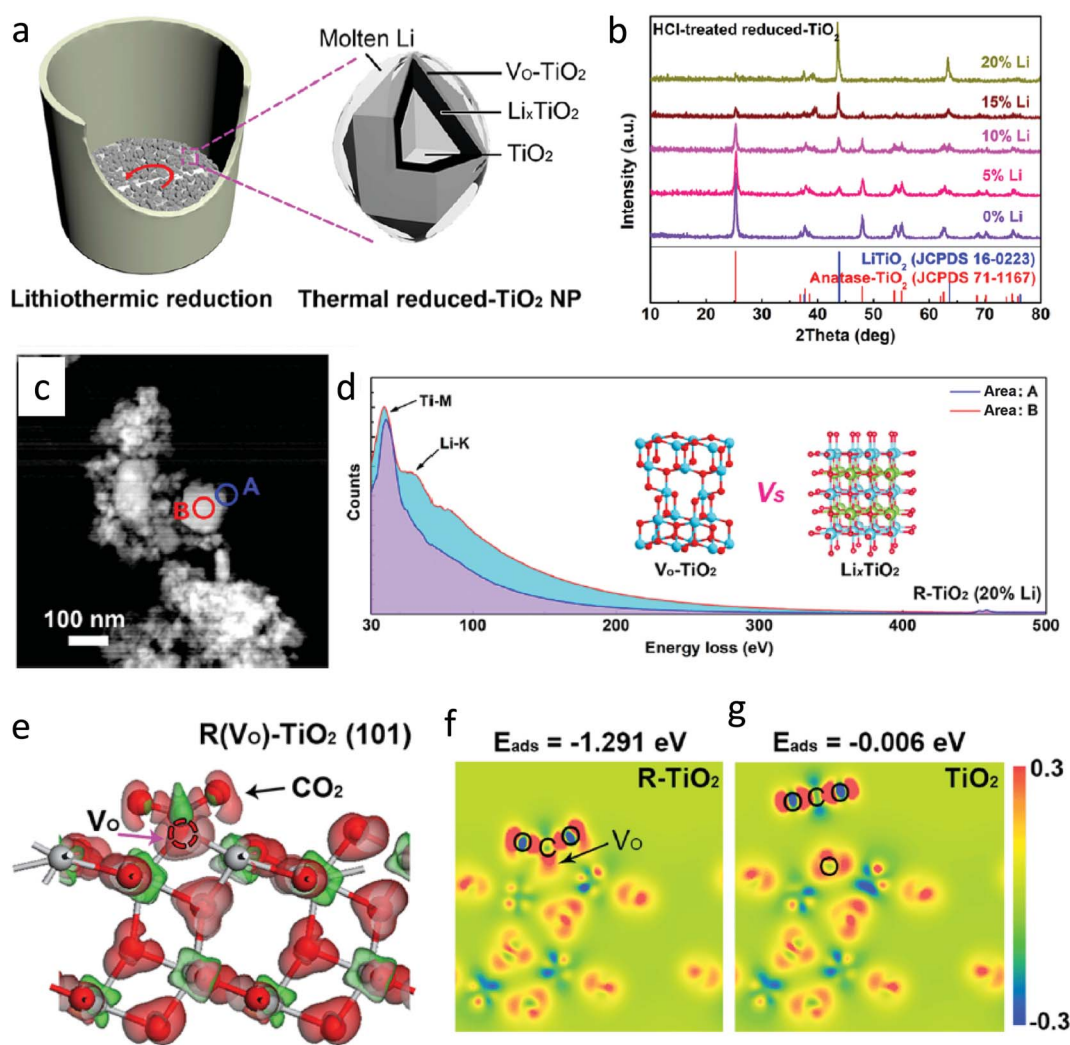
Also, the oxygen vacancies in TiO<sub>2</sub> were induced by thermal treatment of a mixture of aluminum powder and TiO<sub>2</sub>. Gao *et al.*<sup>70</sup> synthesized black TiO<sub>2</sub> nanotube arrays (B-TiO<sub>2</sub> NTAs) by annealing TiO<sub>2</sub>-NTAs wrapped with Al powder in an argon atmosphere at temperatures of 250, 300, 450, and 600 °C (Fig. 17a). The obtained samples were named B-TiO<sub>2</sub> NTAs-*x*, where *x* is the temperature. No doping of Al in TiO<sub>2</sub> was observed. The presence of a high concentration of oxygen vacancies introduced by the aluminothermic reduction process and the resultant Ti<sup>3+</sup> centres creates a defect energy level below the CB of TiO<sub>2</sub>; thus, B-TiO<sub>2</sub> NTAs exhibited strong visible light absorption as compared to TiO<sub>2</sub> NTAs (Fig. 17b). The concentration of oxygen vacancy defects was increased with an increase in temperature. The formed oxygen vacancies could act as electron traps; hence B-TiO<sub>2</sub> NTAs showed a lower charge recombination rate than TiO<sub>2</sub> NTAs. To know the effect of oxygen vacancies on CO<sub>2</sub> conversion, they also synthesized NTAs-450-A by annealing TiO<sub>2</sub> NTAs at 450 °C in the air. It was observed that B-TiO<sub>2</sub> NTA samples exhibited better performance in photocatalytic reduction of CO<sub>2</sub> than TiO<sub>2</sub> NTAs-450-A. Among the synthesized photocatalysts, B-TiO<sub>2</sub> NTAs-600 demonstrated the



best performance under visible light irradiation with a CO yield of  $185.39 \mu\text{mol g}^{-1} \text{h}^{-1}$ , which could be due to the presence of a large amount of oxygen vacancies in  $\text{TiO}_2$  NTAs, lower charge carrier recombination, and abundant sites for the photocatalytic  $\text{CO}_2$  reduction (Fig. 17c). The catalyst was 95% active for  $\text{CO}_2$  reduction even after five cycles of testing.

**4.4.2 Lithiothermic reduction.** In this method, defects can be generated at a relatively lower temperature as compared to that required using Al or Mg metal. Li metal is very reactive because of its lower negative potential.<sup>71</sup> Recently, Wang *et al.*<sup>72</sup> generated oxygen defects in anatase  $\text{TiO}_2$  nanoparticles using a lithiothermic reduction approach (Fig. 18a), where they used molten Li (at  $200^\circ\text{C}$ ) to create defects. They performed the reduction of the anatase phase of  $\text{TiO}_2$ , by varying the ratio of Li/ $\text{TiO}_2$  from 0–20 wt% to synthesize oxygen-deficient R- $\text{TiO}_2$  nanoparticles. The color of the sample changed from white to gray to black with an increase

in Li/ $\text{TiO}_2$  ratio. They observed that in the lithiothermic reduction method, along with the introduction of oxygen defects, lithium ions also get incorporated into the lattice of  $\text{TiO}_2$ . At a higher ratio of Li/ $\text{TiO}_2$ , a cubic phase of  $\text{LiTiO}_2$  was observed (Fig. 18b). The bandgap varied from 3.3 to 2.4 eV for the different oxygen-deficient R- $\text{TiO}_2$  nanoparticles. The presence of oxygen deficiency and  $\text{Ti}^{3+}$  species was confirmed from EPR spectra of the R- $\text{TiO}_2$  samples. Electron energy loss spectroscopy (EELS) spectra recorded at the edges and center showed that edges were deficient of Li whereas the presence of Li was observed at the center of the nanoparticle (Fig. 18c and d). 1 wt% Pt decorated R- $\text{TiO}_2$  obtained using 5 wt% Li/ $\text{TiO}_2$  ratio showed  $\text{CH}_4$  and  $\text{CO}$  at a rate of 8.85 and  $3.49 \mu\text{mol g}^{-1}$  in 8 h under UV-visible light illumination, respectively. Charge difference distribution over the (101) plane of anatase phase of  $\text{TiO}_2$  showed that the oxygen defects act as a center for the  $\text{CO}_2$  adsorption and activation. The  $\text{CO}_2$  adsorption



**Fig. 18** (a) Synthesis of defective  $\text{TiO}_2$  by lithiothermic reduction, (b) XRD spectra of samples synthesized by varying the amount of Li, (c) HAADF-TEM image of R- $\text{TiO}_2$  (20% Li), (d) EELS spectra recorded at the edge position A and center position B; inset shows the atomic structure of oxygen-deficient  $\text{TiO}_2$  and cubic  $\text{LiTiO}_2$ , (e) charge difference of the  $\text{CO}_2$  molecule adsorbed on the surface of the (101) plane for anatase phase of R- $\text{TiO}_2$  (gray: Ti atom, red: O atom), and (f and g) differential charge density after  $\text{CO}_2$  adsorption (reproduced from ref. 72 with permission from the American Chemical Society, copyright 2020).



energy was found to be  $-1.291$  eV over defect sites of  $\text{R-TiO}_2$  lower than on the bare  $\text{TiO}_2$  ( $-0.006$  eV) (Fig. 18e-g). This further confirmed the role of defects in  $\text{CO}_2$  activation and conversion.

## 5. Defect generation by morphology and facet engineering

Facet engineering is one of the aspects adopted to improve charge separation and thus enhanced photocatalytic  $\text{CO}_2$  conversion. The particular facet of the crystal possesses unique electronic properties due to the specific atomic arrangement and coordination, which may affect the adsorption of the reactant, stabilization of intermediates and desorption of the product.  $\text{TiO}_2$  with different facets has been reported to carry out different oxidation and reduction reactions on different facets. Generally, the hydrothermal method is adapted to synthesize faceted  $\text{TiO}_2$  along with the introduction of  $\text{Ti}^{3+}$  vacancies or oxygen defects.

It was observed that not only the presence of defects but also the particular morphology assists in improving the yield of photocatalytic  $\text{CO}_2$  conversion. Sasan *et al.*<sup>73</sup> reported self-doped rutile  $\text{TiO}_2$  ( $\text{Ti}^{3+}\text{-TiO}_2$ ) with facets synthesized using the

hydrothermal method in the presence of HCl. Fig. 19a shows the SEM images of the  $\text{Ti}^{3+}\text{-TiO}_2$  sample.  $\text{Ti}^{3+}$  concentration in self-doped  $\text{TiO}_2$  was reported to be  $\approx 4.5 \mu\text{mol g}^{-1}$ . They claimed the formation of  $\text{Ti}^{3+}$  in bulk as the XPS did not show any peak corresponding to  $\text{Ti}^{3+}$ , whereas EPR showed the presence of  $\text{Ti}^{3+}$  (Fig. 19b). To improve the activity of self-doped  $\text{TiO}_2$ , Pd and Cu were photodeposited (referred to as  $\text{Cu}^{\text{I}}/\text{Pd}/\text{Ti}^{3+}\text{-TiO}_2$ ) and evaluated for its potential for  $\text{CH}_4$  generation from  $\text{CO}_2$  and water in the presence of visible light. Fig. 19c shows the TEM image of  $\text{Cu}^{\text{I}}/\text{Pd}/\text{Ti}^{3+}\text{-TiO}_2$ , which showed the presence of the co-catalyst on the  $\{110\}$  facets. This confirmed that the photogenerated electrons accumulated preferentially at the  $\{110\}$  facets than the  $\{111\}$  facets. The generation of  $\sim 1 \mu\text{mol g}^{-1} \text{h}^{-1}$   $\text{CH}_4$  was observed under visible light illumination (Fig. 19d). To evaluate the impact of the shape and morphology, self-doped  $\text{TiO}_2$  was synthesized by the combustion method.  $\text{CH}_4$  productivity of  $\text{Ti}^{3+}\text{-TiO}_2$  synthesized by the hydrothermal method was 2.5 times more than that of the sample synthesized by the combustion method and improvement in activity assigned to the structural features like morphology and facets. The electrons and holes were trapped at different facets such as  $\{111\}$  and  $\{110\}$  of the rutile  $\text{TiO}_2$  phase, respectively, thus resulting in improved separation of charge carriers and photocatalytic activity.

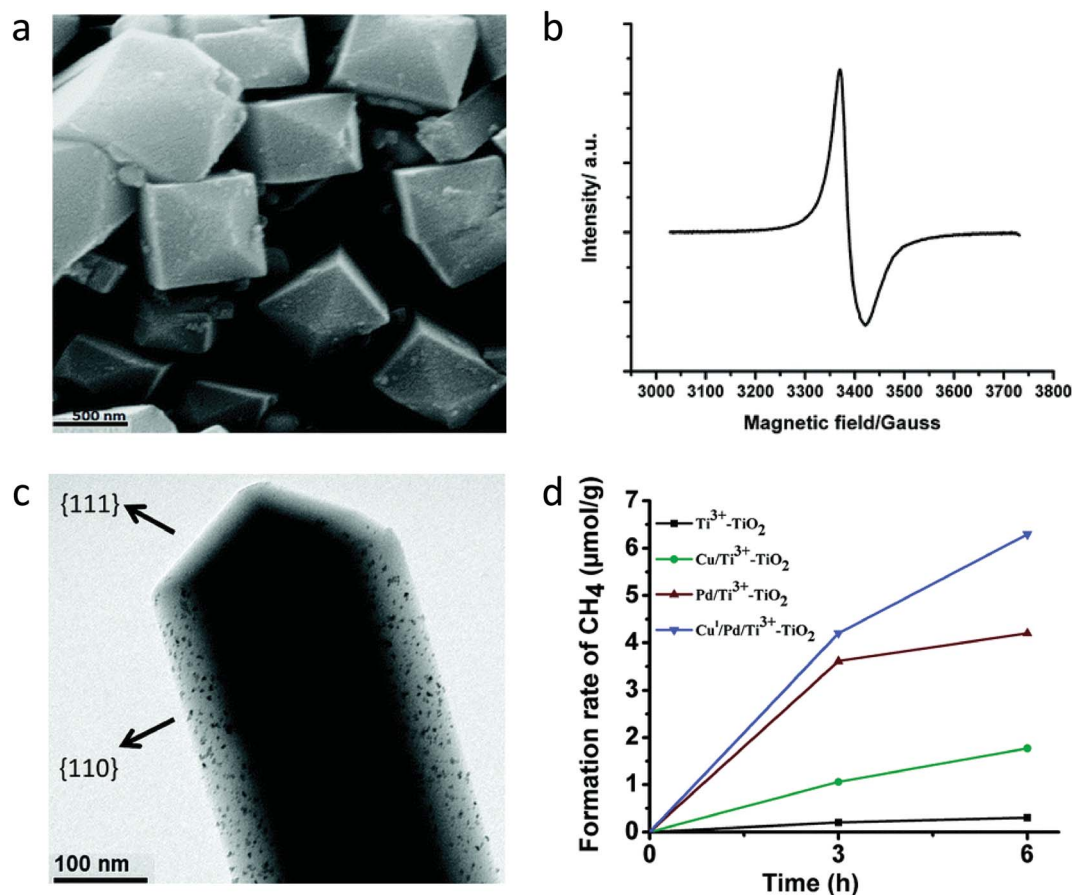


Fig. 19 (a) SEM image of the  $\text{Ti}^{3+}\text{-TiO}_2$  sample and (b) EPR spectra of the  $\text{Ti}^{3+}\text{-TiO}_2$  sample recorded at 100 K, (c) TEM images of the  $\text{Cu}^{\text{I}}/\text{Pd}/\text{Ti}^{3+}\text{-TiO}_2$  sample, and (d) comparison of photocatalytic  $\text{CO}_2$  conversion using different samples (reproduced from ref. 73 with permission from the Royal Society of Chemistry, copyright 2015).





It was observed that the sample synthesized by hydrothermal treatment using HF showed the incorporation of fluoride ions into the lattice of  $\text{TiO}_2$  because of its smaller size. The presence of this fluoride ion induces the disordered layer, which further assists in preventing the  $\text{Ti}^{3+}$  oxidation in the air.<sup>74</sup> Fang *et al.*<sup>74</sup> synthesized deep blue colored reduced  $\text{TiO}_{2-x}$  via a one-step hydrothermal process using HCl and the  $\text{Ti}(\text{III})\text{Cl}_3$  precursor. During synthesis, a small amount of HF was also added, which resulted in the introduction of a disordered layer, increase in the content of the anatase phase of  $\text{TiO}_2$  and structural morphology with the  $\{101\}$  and  $\{001\}$  facets. The samples were referred to as  $\text{TiO}_{2-x}$  followed by the amount of HF added. The presence of fluoride ions was verified by XPS and HRTEM-EDS. EDS elemental mapping further confirmed that fluoride ions were homogeneously dispersed in the catalyst. Because of the size and charge of fluoride ions, the transformation of the anatase to the rutile phase gets prohibited. The light absorption in the visible region increased with an increase in fluorination and showed the highest absorption for  $\text{TiO}_{2-x-0.5}$  (Fig. 20a). This light absorption could be due to the presence of  $\text{Ti}^{3+}$  and oxygen vacancies. The presence of  $\text{Ti}^{3+}$  ions was also confirmed by the EPR spectra and showed the presence of  $24.6 \times 10^{19}$  spins per g in  $\text{TiO}_{2-x-0.50}$ , which was nearly 14 000-fold more as compared to the pristine  $\text{TiO}_2$  (Fig. 20b and c). Fig. 20d and e show the HR-TEM image of the  $\text{TiO}_{2-x-0.5}$  sample and shows the presence of the  $\{101\}$  and  $\{001\}$  facets.

The presence of the disordered layer of 1–2 nm on the surface of  $\text{TiO}_{2-x}$  induced by the fluoride atoms prevents the oxidation of  $\text{Ti}^{3+}$  ions. The presence of facets promotes the separation of electrons and holes as they prefer to accumulate at the  $\{101\}$  and  $\{001\}$  facets, respectively. Photocatalytic  $\text{CO}_2$

conversion carried out in the absence of the cocatalyst and under simulated solar light illumination generated  $\text{CH}_4$  and CO. The selectivity for  $\text{CH}_4$  evolution increased from 51.7% to 83.4% after fluorination (Fig. 20f). The improved photocatalytic performance was attributed to the enhanced solar light absorption by the presence of the  $\text{Ti}^{3+}$  ion, improved activation of  $\text{CO}_2$  by the induced oxygen vacancies and the slow recombination rate because of migration of photogenerated charges on different facets.

Similarly, Liu *et al.*<sup>75</sup> synthesized  $\text{TiO}_2$  with co-exposed facets of  $\{001\}$  and  $\{101\}$  by the hydrothermal method using titanium isopropoxide and a small amount of HF. Defects were created by heating a  $\text{TiO}_2$  and  $\text{NaBH}_4$  mixture at 300 °C. The highest yield for CO generation obtained was  $54.5 \mu\text{mol g}^{-1}$  in 5 h under UV-visible light with an AQE of 0.31%. The improved activity is attributed to the electron transfer between the  $\{001\}$  and  $\{101\}$  planes and enhanced light absorption due to the formation of the  $\text{Ti}^{3+}$  states within a bandgap of  $\text{TiO}_2$ . *In situ* DRIFTS studies confirmed that the presence of  $\text{Ti}^{3+}$  along with co-exposed facets of  $\{001\}$ – $\{101\}$  helped in the activation and conversion of  $\text{CO}_2$ .

Similarly, Liu *et al.*<sup>76</sup> synthesized ultrathin nanosheets with a thickness of  $\sim 0.8$  nm (approximately two atomic layers thick) of  $\text{TiO}_2$  with abundant facets by the hydrothermal method using ethylene glycol. EPR and XPS studies indicated that the concentration of  $\text{Ti}^{3+}$  increased after irradiation with UV-visible light. Pt deposited ultrathin  $\text{TiO}_2$  exhibited excellent photocatalytic activity for the conversion of  $\text{CO}_2$  into  $\text{CH}_4$  and CO with a yield of 66.4 and  $54.2 \mu\text{mol g}^{-1} \text{h}^{-1}$ , respectively. The improved photocatalytic activity was attributed to the increased surface area and defect sites, which assisted in the charge transfer to well-dispersed Pt nanoparticles and reduced the

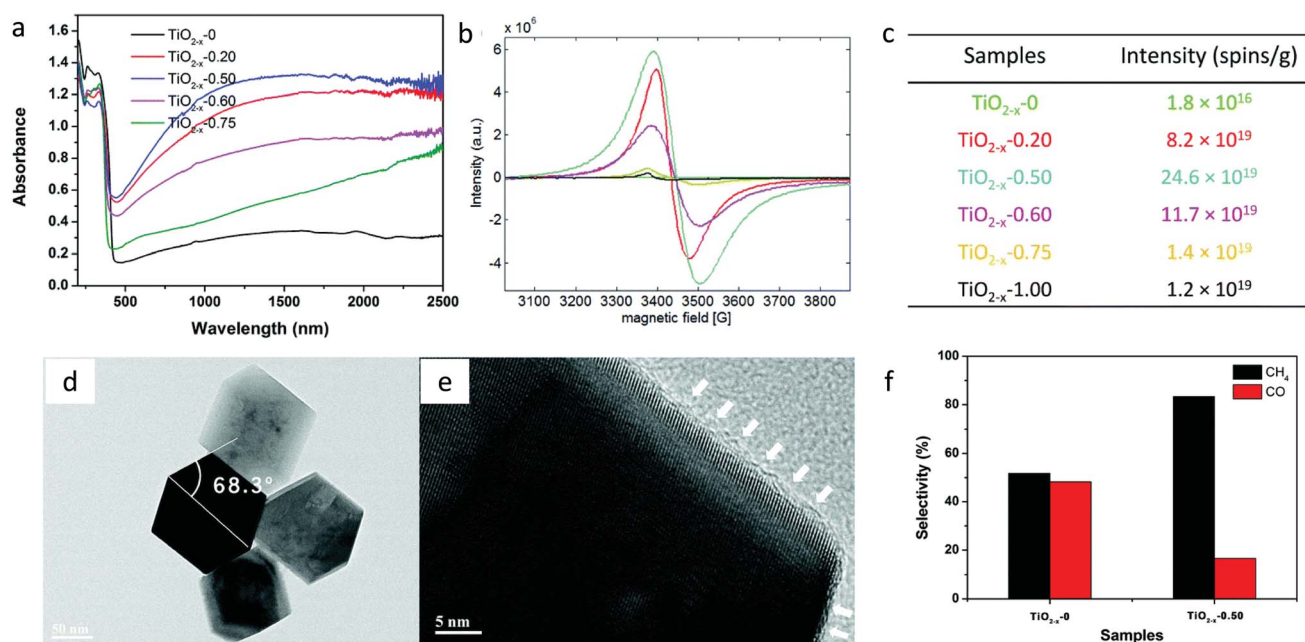


Fig. 20 (a) DRS absorption spectra, (b) EPR spectra and (c) the spin intensity of reduced  $\text{TiO}_2$  samples, (d) HRTEM image of  $\text{TiO}_{2-x-0.50}$ , (e) disordered layers on the surface of  $\text{TiO}_{2-x}$  marked with white color arrows and (f) selectivity for  $\text{CH}_4$  and CO generation using  $\text{TiO}_{2-x-0}$  and  $\text{TiO}_{2-x-0.50}$  in the absence of the cocatalyst and under simulated solar light (reproduced from ref. 74 with permission from the Royal Society of Chemistry, copyright 2017).





recombination of charge carriers, and the synergy between metal and support helped in the adsorption of  $\text{CO}_2$ .

It is difficult to generate a defective layer over the particular facets of the photocatalyst by the methods discussed above and, hence, to study its impact on photocatalytic  $\text{CO}_2$  conversion. Recently, Shi *et al.*<sup>77</sup> adopted a mild reducing condition to study the role of the formation of the defective layer, particularly on the  $\{001\}$  facets of  $\text{TiO}_2$  nanocrystals. The synthesis was carried out in a two-step reduction process *viz.*, the first involves the solvothermal method using  $\text{TiO}_2$ ,  $\text{NaBH}_4$  and glycol and the second step involves calcination under Ar flow at  $400^\circ\text{C}$ . Fig. 21a–c shows HRTEM images of the  $\text{TiO}_2$  homojunction formed after reduction treatment, showing a truncated octahedral bipyramid consisting of the  $\{101\}$  facets on the side and the  $\{001\}$  facets on top and bottom. HRTEM images indicated that the defective layer forms only on the  $\{001\}$  facets and not on the  $\{101\}$  facets. They observed the formation of a heterojunction between the defective layer, interface layer and the crystalline core. HAADF images showed a disordered layer on the  $\{001\}$  facets (Fig. 21d and e). The EELS spectra were recorded at different depths to know the distribution of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  species on the  $\{001\}$  facets (Fig. 21f). Until the depth of 2 nm, the characteristic signals of  $\text{Ti}^{3+}$  appeared, confirming its presence in the defective layer. In between 2 and 3 nm, the presence of both  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  appears, confirming their co-occurrence in the interface layer. After 3 nm depth, the existence of  $\text{Ti}^{4+}$  in the crystalline layer was observed. EELS spectra confirmed the presence of  $\text{Ti}^{3+}$  in the defective and interface

layer of thickness nearly 2 and 1 nm, respectively. *In situ* DRIFTS study performed in the dark and in the presence of  $\text{CO}_2$  saturated with water vapor further confirmed that  $\text{CO}_2$  was activated by forming  $\text{CO}_2^{\cdot-}$  species on the surface, which was easy to reduce further. Methane was produced at a rate of  $2.49\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$  with 100% selectivity under UV light ( $\lambda = 365\ \text{nm}$ ), in the absence of a cocatalyst. The catalyst was found to be stable even after 60 h of a run. The holes are supposed to accumulate on the  $\{001\}$  surface, but they observed that due to the formation of the electron-rich defective layer, the reduction of  $\text{CO}_2$  has occurred over the  $\{001\}$  facets and oxidation over the  $\{101\}$  facets.

Similarly, Qingli *et al.*<sup>78</sup> synthesized a porous black  $\text{TiO}_2$  film by hydrothermally treating a Ti plate in  $\text{H}_2\text{O}_2$  solution. The oxygen-deficient nature of the black  $\text{TiO}_2$  film was confirmed by the EDX. They monitored photocatalytic  $\text{CO}_2$  conversion using simulated sunlight in the presence of moist  $\text{CO}_2$  with the production of  $\text{CO}$  and  $\text{CH}_4$  at a rate of 115 and  $12\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$  respectively.

An attempt was also made to further enhance the light absorption by using the light trapping property of the hollow microstructure synthesized by the hydrothermal method. Liu *et al.*<sup>79</sup> synthesized the porous fluorinated  $\text{TiO}_2$  hollow microstructure (referred to as THMs) with exposed  $\{001\}$  facets and induced defects by hydrothermal treatment using  $\text{Ti}(\text{SO}_4)_2$  and  $\text{NH}_4\text{F}$ . Au was photodeposited on THMs by varying its amount from 0, 0.5, 1, 2 and 4 wt% and referred to as  $\text{Au}_x/\text{THMs}$  where  $x$  is the weight ratio of Au to Ti. They found that photodeposition of Au on the THMs increases both the oxygen vacancy and  $\text{Ti}^{3+}$ ,

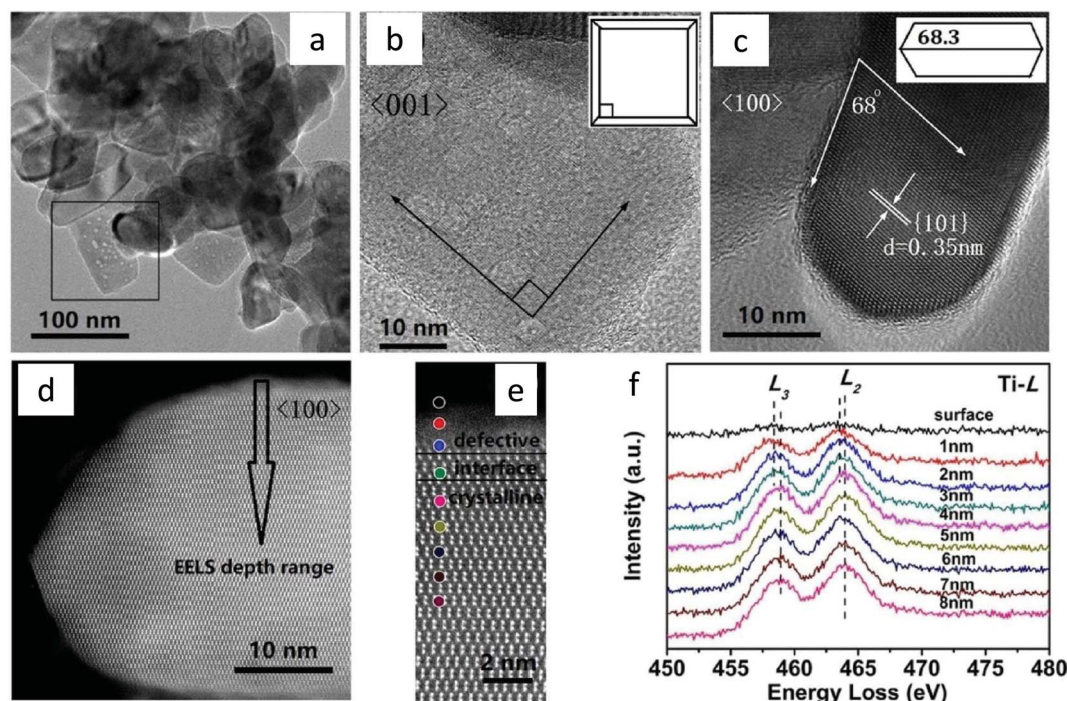


Fig. 21 (a) TEM image of the  $\text{TiO}_2$ -homojunction, HRTEM image recorded from (b)  $\langle 001 \rangle$  orientation, inset shows the model of truncated octahedral bipyramid projected along  $\langle 001 \rangle$  direction, and (c)  $\langle 100 \rangle$  orientation inset shows the model of truncated octahedral bipyramid projected along  $\langle 100 \rangle$  direction, (d) HAADF-STEM image recorded from  $\langle 100 \rangle$  orientation, (e) position for signal collection for EELS spectra, (f) Ti-L spectra recorded at the different positions marked with colored dots in (e) (reproduced from ref. 77 with permission from Wiley, copyright 2019).



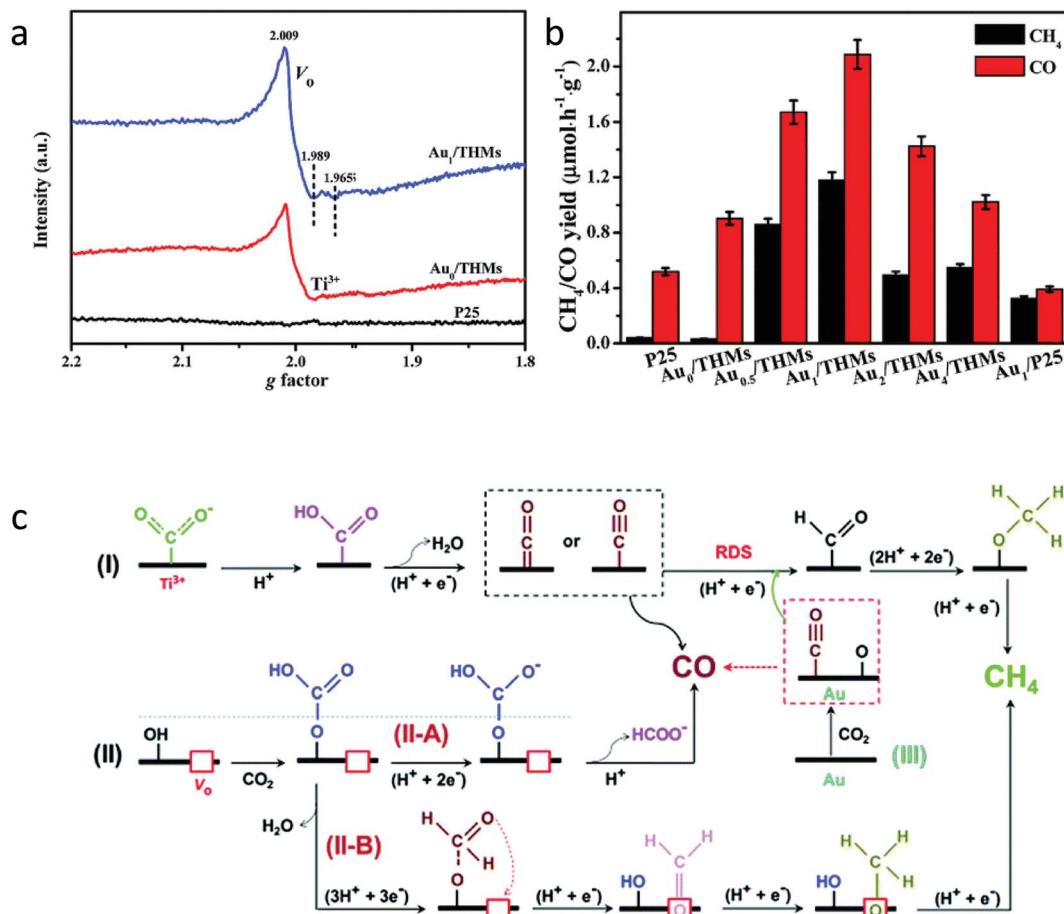


Fig. 22 (a) EPR spectra of P25, Au<sub>0</sub>/THMs, and Au<sub>1</sub>/THMs. (b) photocatalytic CO<sub>2</sub> conversion over different samples under full-spectrum light illumination and (c) probable mechanism pathway for CO<sub>2</sub> to CH<sub>4</sub> conversion (reproduced from ref. 79 with permission from the Royal Society of Chemistry, copyright 2018).

which further helps adsorb and activate the CO<sub>2</sub> molecule (Fig. 22a). The formation of Ti-F species, surface Ti<sup>3+</sup> and oxygen vacancies helps in trapping the surface photogenerated charge carriers, thus reducing surface recombination. The improved light absorption was attributed to the light trapping effect of the hollow sphere and surface plasmon resonance (SPR) effect of the Au nanoparticles. The photocatalytic activity for CO<sub>2</sub> conversion enhanced due to improved charge separation as a result of the Schottky junction between Au and TiO<sub>2</sub> and the {001}/{101} facet junction and increased CO<sub>2</sub> adsorption due to the strong affinity of Au nanoparticles to CO<sub>2</sub> as well as the presence of surface Ti<sup>3+</sup> and V<sub>O</sub> sites. Methane formation was favored over the Au<sub>1</sub>/THMs due to the strong affinity of CO to Au, which restricted its escape from the surface and helped to further hydrogenate the surface-bound CO to form methane. The maximum yield for CH<sub>4</sub> and CO was 1.19 and 2.10 μmol g<sup>-1</sup> h<sup>-1</sup> under UV-visible light irradiation, respectively, using Au<sub>1</sub>/THMs (Fig. 22b). *In situ* DRIFTS studies performed using Au<sub>1</sub>/THMs revealed that even in the absence of light, species like monodentate and bidentate carbonate, bicarbonate, carboxylate (CO<sub>2</sub><sup>-</sup>), and carbon monoxide were formed. CO<sub>2</sub><sup>-</sup> species were formed as a result of the presence of oxygen defects and Ti<sup>3+</sup> sites. Under LED light illumination, the species like

bicarbonate, CO<sub>2</sub><sup>-</sup> and CO depleted and new species like formate, formaldehyde, dioxyethylene and methoxy groups appeared and became stronger with time. They proposed the possible pathways to generate CO and CH<sub>4</sub> (Fig. 22c): (i) a surface Ti<sup>3+</sup> (or oxygen vacancy (V<sub>O</sub>))-bound CO<sub>2</sub><sup>-</sup> activated reaction pathway, (ii) a surface hydroxyl (OH)-bound HCO<sub>3</sub><sup>-</sup> derived reaction pathway and (iii) Au-bound CO initiated hydrogenation to produce CH<sub>4</sub>.

Another approach was adapted by Yin *et al.*<sup>80</sup> for the synthesis of hydrogenated blue H-TiO<sub>2-x</sub> by a facile low-temperature solvothermal method using Li-dissolved ethanediamine. During the solvothermal reaction, the generated Li species and [H] atom after mixing of Li metal and ethanediamine were capable of reducing TiO<sub>2</sub> by introducing surface defects and intercalated H. The sample was referred to as H-TiO<sub>2-x-y</sub> where y represents the amount of Li in mg. It was observed that the thickness of the disordered layer increases with an increase in the Li content, *i.e.* it changed from 2–3 nm for H-TiO<sub>2-x-200</sub> to 4–6 nm for H-TiO<sub>2-x-300</sub> (Fig. 23A). <sup>1</sup>H NMR spectra of the samples showed the presence of protons in a different environment. It was observed that during the solvothermal process, more H atoms were incorporated at the bridging sites in the amorphous layer (Fig. 23B). The kinetic



isotope effect studies indicated that the breaking of the C–O bond of CO<sub>2</sub> was the rate-determining step in photocatalytic CO<sub>2</sub> conversion rather than the O–H bond of H<sub>2</sub>O. Fig. 23C shows the *in situ* DRIFTS performed in the dark as well as under light illumination to study the reaction intermediates. The amount of the different carbonate species increases with an increase in illumination time over the surface of H–TiO<sub>2-x</sub>. The *in situ* DRIFTS measurements confirmed the formation of the intermediate of CO<sub>2</sub><sup>-</sup> which indicated that CO<sub>2</sub> gets adsorbed and activated on the surface of defective H–TiO<sub>2-x</sub>. CO<sub>2</sub> conversion into methane at a rate of 16.2 and 2.7 μmol h<sup>-1</sup> g<sup>-1</sup> with a selectivity of 75 and 77% were observed using H–TiO<sub>2-x</sub>

200 under solar light and visible light illumination (400–780 nm), respectively. It was found that the increase of thickness of the disorder layer to 4–6 nm in H–TiO<sub>2-x</sub>-300 was not favorable for the transport of photo-generated charge carriers, which resulted in low photocatalytic activity.

## 6. Defect generation during synthesis, doping and composite formation

The formation of defect during the synthesis of the catalyst and its application for the CO<sub>2</sub> conversion is discussed in this

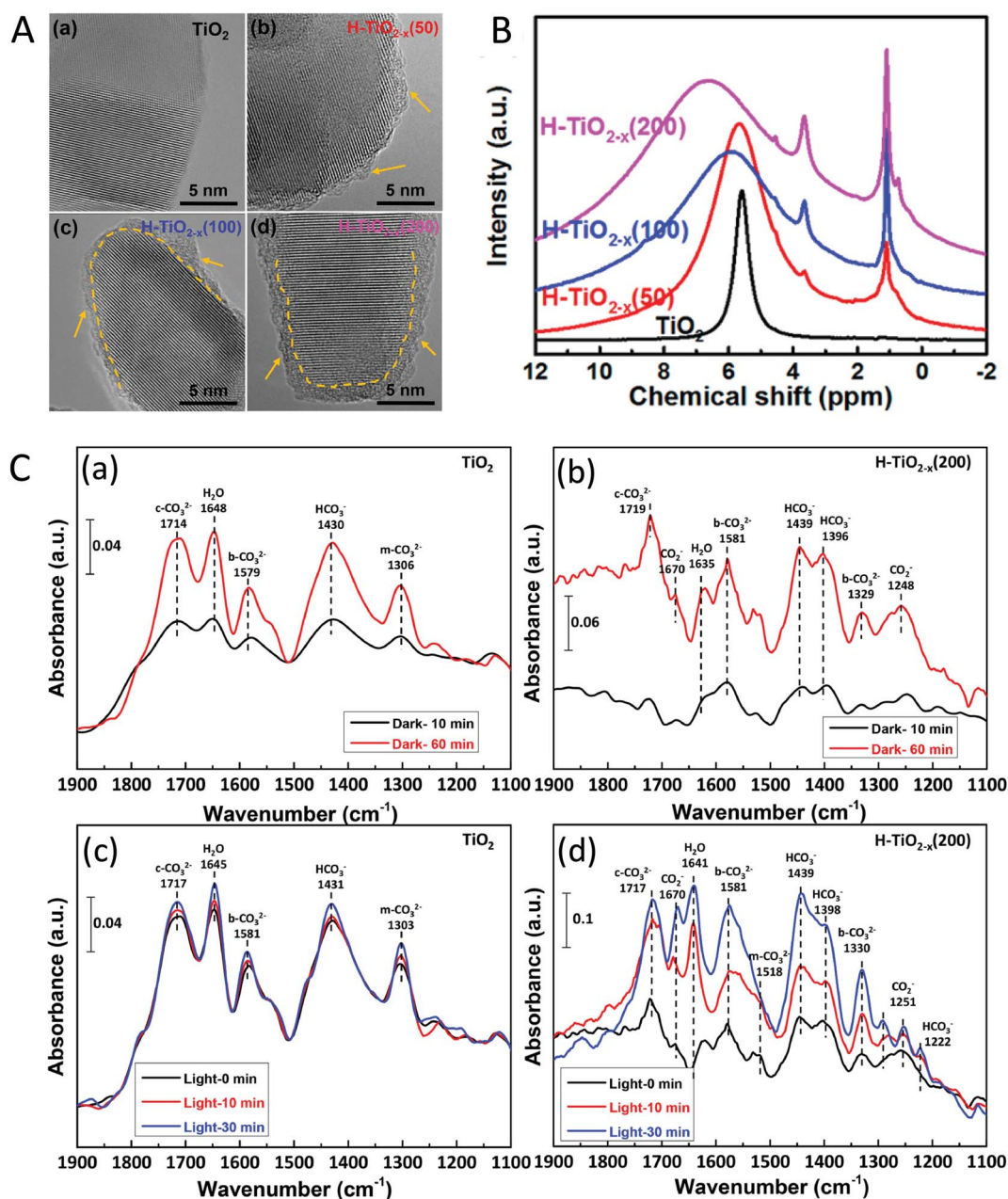


Fig. 23 (A) HRTEM images of the TiO<sub>2-x</sub> with different amounts of Li, (B) <sup>1</sup>H NMR spectra of the defective blue H–TiO<sub>2-x</sub> samples, (C) *in situ* DRIFTS spectra monitored in the dark for (a) TiO<sub>2</sub> and (b) H–TiO<sub>2-x</sub>-200 and after shining light for (c) TiO<sub>2</sub> and (d) H–TiO<sub>2-x</sub>-200 (reproduced from ref. 80 with permission from the American Chemical Society, copyright 2018).





section. The defects were also found to generate during the photodeposition process. Zhu *et al.*<sup>81</sup> studied the impact of defects generated during photodeposition of Cu<sub>2</sub>O. They synthesized the nanosheets of TiO<sub>2</sub> with facets of {001} by the hydrothermal method and Cu<sub>2</sub>O was deposited over it by the photodeposition method (referred to as Cu-TiO<sub>2-x</sub>, where x is the wt% of Cu species). During *in situ* photodeposition, along with Cu deposition, oxygen vacancies were also generated on the surface of TiO<sub>2</sub> nanosheets. The EPR spectra revealed that the intensity of V<sub>O</sub> after deposition of Cu<sub>2</sub>O increased, whereas the intensity of Ti<sup>3+</sup> decreased significantly (Fig. 24A). The decrease in Ti<sup>3+</sup> signal indicated that the Cu<sup>2+</sup> adhered to the Ti<sup>3+</sup> sites where it was reduced to Cu<sup>1+</sup> by accepting an electron from Ti<sup>3+</sup>. Fig. 24A(b) indicated that after the introduction of CO<sub>2</sub>, the oxygen defects decreased, whereas the Ti<sup>3+</sup> remains the same. This further confirmed that the V<sub>O</sub> acts as CO<sub>2</sub> adsorption centers and the formation of CO<sub>2</sub><sup>•-</sup> sites on the surface of the Cu-TiO<sub>2-1</sub>. The presence of Cu<sub>2</sub>O increases the alkalinity and forms oxygen defects (V<sub>O</sub>), thus leading to improvement of adsorption of CO<sub>2</sub> over Cu-TiO<sub>2-1</sub> as compared to pristine TiO<sub>2</sub> (Fig. 24B).

*In situ* FTIR spectra recorded under light illumination showed that the intensity of the CO<sub>2</sub><sup>•-</sup> species increases with an increase in light illumination (Fig. 24C). The decrease in the water absorption band indicated its consumption during the reaction. Methane yield was found to be dependent on the concentration of Cu<sub>2</sub>O. The highest methane yield of 8.68 μmol g<sup>-1</sup> h<sup>-1</sup> was observed with 100% selectivity using 1 wt% of Cu(I) species under simulated solar light illumination and in the presence of CO<sub>2</sub> and H<sub>2</sub>O vapor (Fig. 24D). On further increase

in the Cu<sub>2</sub>O amount, active species decreased due to its aggregation. Surface V<sub>O</sub> and Cu<sup>1+</sup> act as active centers for the conversion of CO<sub>2</sub> into methane. The enhancement of photocatalytic activity was attributed to high CO<sub>2</sub> adsorption capacity, high electron mobility, and high concentration of V<sub>O</sub>. Based on the experimental results, they proposed a plausible mechanism for methane production, as shown in Fig. 24E. CO<sub>2</sub><sup>•-</sup> was formed by accepting the electron from V<sub>O</sub> site. The photo-generated electron in the presence of atomic hydrogen was used for the reduction of CO<sub>2</sub><sup>•-</sup> species to give methane over the Cu<sup>1+</sup> sites of Cu-TiO<sub>2-x</sub>.

Lan *et al.*<sup>82</sup> reported the defects induced during the loading of Cu. They synthesized a series of ultrafine highly crystalline metallic Cu nanoparticles deposited TiO<sub>2</sub> *via* a solvothermal method using alcohol (referred to as Cu/TiO<sub>2</sub>). The defects induced by the introduction of Cu during the synthesis decreased the bandgap of Cu/TiO<sub>2</sub> (Fig. 25a). They found that CO was the only product formed during photocatalytic CO<sub>2</sub> reduction using Cu/TiO<sub>2</sub>. The 0.5 wt% Cu/TiO<sub>2</sub> catalyst produced 32.5 μmol g<sup>-1</sup> h<sup>-1</sup> of CO, which was 5.2 times higher as compared to pure TiO<sub>2</sub> under irradiation of UV-visible light (Fig. 25b). The high activity and selectivity could be attributed to the oxygen vacancies in Cu/TiO<sub>2</sub> catalysts. Importantly, the Cu/TiO<sub>2</sub> catalyst stopped producing hydrogen after 2 h of light irradiation, whereas CO yield increased continuously with irradiation time. DFT calculation showed that the adsorption energy of CO on the Cu surface was much higher than that of H<sub>2</sub> (Fig. 25c). Hence, with increasing reaction time, the accumulated CO species occupied the Cu surface and prevented the access of H ions to the Cu surface, resulting in the suppression



Fig. 24 (A) (a) EPR spectra of TiO<sub>2</sub> and Cu-TiO<sub>2-1.0</sub> samples recorded under vacuum at 77 K in the dark and after solar light illumination, (b) EPR spectra of the Cu-TiO<sub>2-1.0</sub> catalyst in the presence of air and CO<sub>2</sub>, (B) CO<sub>2</sub> adsorption isotherm of TiO<sub>2</sub> and Cu-TiO<sub>2-1.0</sub> samples, (C) *in situ* FTIR spectra recorded in the presence of CO<sub>2</sub> and H<sub>2</sub>O, (a) raw Cu-TiO<sub>2-1</sub> sample (b) after 30 min in the dark, (c) after 30 min of light illumination and (d) after 50 min of light illumination, (D) comparison of the CH<sub>4</sub> yield generated using different catalysts under simulated solar light, and (E) plausible reaction mechanism for CO<sub>2</sub> conversion using Cu-TiO<sub>2-x</sub>. (reproduced from ref. 81 with permission from the Royal Society of Chemistry, copyright 2015).





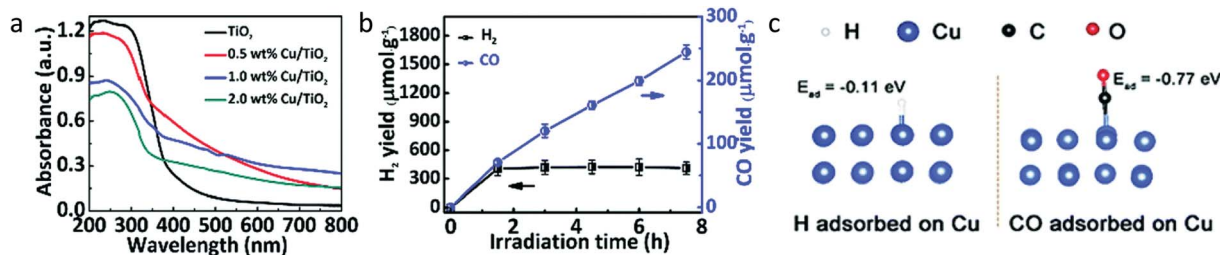


Fig. 25 (a) UV-vis DRS of different samples, (b) time profile for the generation of products, CO and H<sub>2</sub> using 0.5 wt% Cu/TiO<sub>2</sub> photocatalyst, and (c) by use of DFT, calculation of adsorption energy of H<sub>2</sub> and CO on the Cu surface (reproduced from ref. 82 with permission from the Royal Society of Chemistry, copyright 2019).

of hydrogen evolution. However, the yield of CO generation was found to decrease in a sample having a Cu content more than 1 wt%. This was due to the aggregation of Cu and the light-shielding caused by the presence of excess Cu on the surface.

The generation of oxygen defects after heteroatom doping into the TiO<sub>2</sub> lattice and its effect on photocatalytic CO<sub>2</sub> conversion were studied by Pham *et al.*<sup>83</sup> They synthesized Ag and Cu co-doped TiO<sub>2</sub> over honeycombed structured polyurethane (referred to as Ag@Cu-TiO<sub>2</sub>/PU). Co-doping with 2 wt% Ag and 4 wt% Cu (referred to as 2Ag@4Cu/TiO<sub>2</sub>/PU) resulted in a higher Ti<sup>3+</sup>/Ti<sup>4+</sup> ratio than the single doped Ag or Cu (6 wt% Ag or Cu@TiO<sub>2</sub>/PU). This indicated that the co-doping of Ag and Cu further enhanced Ti<sup>3+</sup> and oxygen vacancies, as evident from XPS analysis. Enhanced absorption of visible light, separation of the electron and hole and adsorption of CO<sub>2</sub> due to the presence of defects resulted in the enhancement of the total photocatalytic yield of 2Ag@4Cu/TiO<sub>2</sub>/PU under visible light illumination. The total product yield of CH<sub>4</sub>

and CO was found to be 880 and 550 μmol g<sup>-1</sup> in 6 h using 2Ag@4Cu/TiO<sub>2</sub>/PU, respectively. They also observed a slight improvement in the CH<sub>4</sub> and CO production yield at a rate of 933 and 588 μmol g<sup>-1</sup> in 6 h using co-doped 2 wt% Cu and 4 wt% V-TiO<sub>2</sub>/PU under visible light illumination.<sup>84</sup>

Similarly, Wang *et al.*<sup>85</sup> synthesized cobalt doped ordered mesoporous TiO<sub>2</sub> by a multicomponent self-assembly process (referred to as Co-OMT-*x*, OMT stands for ordered mesoporous TiO<sub>2</sub>; the molar ratio of Co/Ti varied from 0.002 to 0.2; *x* = 1–8 corresponds to molar ratio of Co/Ti 0.002, 0.005, 0.01, 0.025, 0.05, 0.10, 0.15, and 0.20). The maximum CO<sub>2</sub> conversion was found at 0.025 molar ratio of Co/Ti, with a yield of CO and CH<sub>4</sub> at a rate of 1.94 and 0.09 μmol g<sup>-1</sup> h<sup>-1</sup>, respectively (Fig. 26a). The greater selectivity for CH<sub>4</sub> formation was observed when the molar ratio of Co/Ti was 0.2. This improvement in selectivity with an increase in the Co content was attributed to the formation of the nanocomposite of Co<sub>3</sub>O<sub>4</sub>/doped Co-TiO<sub>2</sub> and increase in oxygen vacancies. As a result of doping of Co, the CB

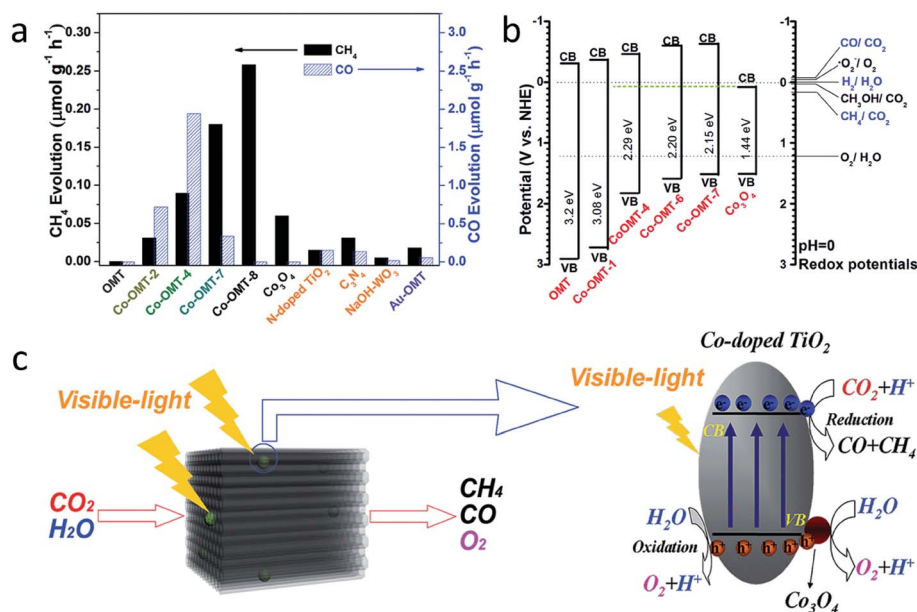


Fig. 26 (a) Comparison of photocatalytic CO<sub>2</sub> conversion using different samples, (b) valence band and conduction band position in different samples, (c) schematic representation of photocatalytic CO<sub>2</sub> conversion over Co-doped mesoporous ordered TiO<sub>2</sub> (reproduced from ref. 85 with permission from the Royal Society of Chemistry, copyright 2015).



and VB shifted upward, resulting in the decrease in bandgap with an increase in Co content as shown in Fig. 26b. Fig. 26c shows the schematic illustration of the proposed mechanism for CO<sub>2</sub> conversion.

Different precursors of Ti can be used for the generation of inherent oxygen vacancies. Yaghoubi *et al.*<sup>86</sup> synthesized TiO<sub>2</sub> using the peroxy-titanium complex and found the generation of defects during the synthesis. The obtained crystalline TiO<sub>2</sub> was composed of a mixed phase of anatase, rutile and brookite. The VB and CB of mixed-phase TiO<sub>2</sub> were determined with the help of UPS and inverse photoemission spectroscopy (IPES), respectively (Fig. 27a and b). The bandgap determined by the above two techniques was 3.8 eV higher than that determined using DRS (3.1 eV as depicted in Fig. 27c) due to the high threshold energy required to create an unbound e<sup>-</sup> and h<sup>+</sup> pair. UPS spectra show that the edge corresponds to midgap states at 1.7 eV below the Fermi level *i.e.* at 2.2 eV from the conduction band edge, which was also elucidated by the Urbach tail in the UV-visible DRS spectrum (Fig. 27c). XPS and ICP-OES were performed to rule out the possibility of extended absorption due to doping with heteroatoms. The formation of the mid-gap

states within the bandgap was due to the presence of oxygen defects and Ti<sup>3+</sup> and not because of heteroatom doping. The presence of midgap states was responsible for the absorption in the visible region. The mechanism for photocatalytic CO<sub>2</sub> conversion was proposed (Fig. 27d), where illumination of the TiO<sub>2</sub> with the photon of energy equal to and greater than 2.2 eV excited the electron from midgap state to the CB where the reduction of CO<sub>2</sub> takes place. The hole in the mid-gap states oxidizes water to give a proton. The catalyst was active for CO<sub>2</sub> conversion under both solar light and visible light illumination. The mixed-phase TiO<sub>2</sub> showed CO and CH<sub>4</sub> yield at a rate of 1357 and 360 ppm g<sup>-1</sup> in 6 h under visible light illumination, which was 6.75 and 7.66 times better as compared to P25 TiO<sub>2</sub>, respectively. The total quantum yield was found to be of 0.0289% in the region of 250–564 nm.

Han *et al.*<sup>87</sup> synthesized the defective truncated bi-pyramidal structure with co-exposed {101} and {001} facets of anatase TiO<sub>2</sub> (referred to as TiO<sub>2</sub>-B) using TiB<sub>2</sub> as the precursor by one-step hydrothermal treatment. To further improve the charge separation, nanosheets of SnS<sub>2</sub> were loaded over defective TiO<sub>2</sub>-B (referred to as SnS<sub>2</sub>/TiO<sub>2</sub>-B). XPS studies indicated that the

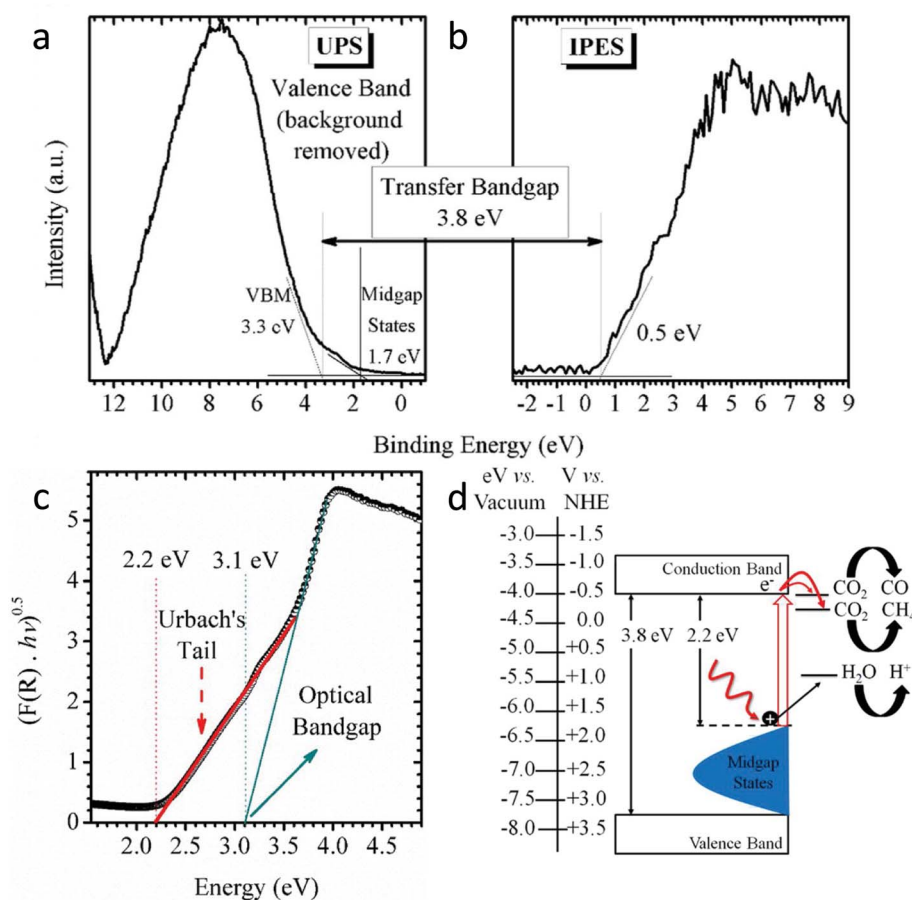


Fig. 27 Valence band and conduction band of TiO<sub>2</sub> nanoparticles determined using (a) UPS and (b) IPES spectra and (c) plot of Kubelka–Munk Function vs. energy derived from the UV-visible DRS spectrum of TiO<sub>2</sub>. The green line denotes the optical bandgap, whereas the red line shows Urbach's tail. (d) Schematic representation of the electronic structure of TiO<sub>2</sub> in combination with a suggested diagram for photocatalytic CO<sub>2</sub> conversion. The blue region shows the presence of extended localized states within the bandgap resulting in the absorption in the visible region (reproduced from ref. 86 with permission from the American Chemical Society, copyright 2015).



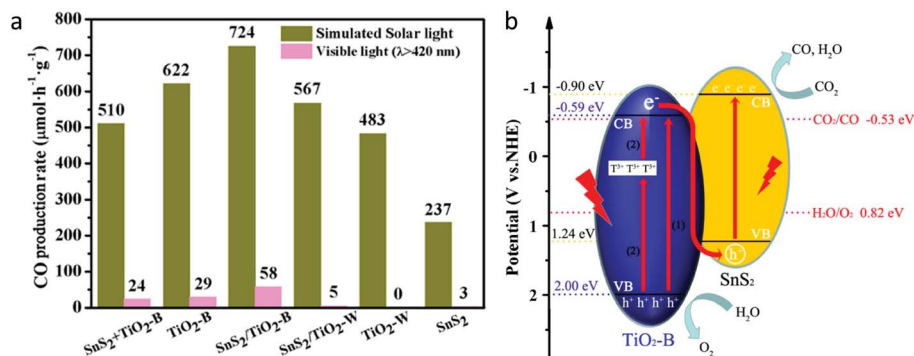


Fig. 28 (a) Comparison of the yield of CO produced by photocatalytic CO<sub>2</sub> conversion using SnS<sub>2</sub>/TiO<sub>2</sub>-B under simulated solar light and visible light and (b) schematic for the Z-scheme mechanism of separation of photogenerated charge carriers (reproduced from ref. 87 with permission from MDPI, copyright 2019).

oxygen vacancies were maintained well even after the formation of the composite with SnS<sub>2</sub> nanosheets. The improved light absorption and adsorption and activation of the CO<sub>2</sub> molecule due to the presence of defects in TiO<sub>2</sub> and enhanced separation of charge carriers as a result of the formation of the Z-scheme heterojunction between TiO<sub>2</sub> and SnS<sub>2</sub> nanosheets improved the photocatalytic performance of the sample. The highest CO production was observed at a rate of 58 μmol g<sup>-1</sup> h<sup>-1</sup> with a selectivity of 96.3% under visible light irradiation (Fig. 28a). In the Z-scheme mechanism, the electron from the CB of TiO<sub>2</sub>-B gets transferred to the hole in the VB of SnS<sub>2</sub> (Fig. 28b). The electron present in the CB of SnS<sub>2</sub> was then used for the conversion of the CO<sub>2</sub> to CO.

Another strategy adopted by Shi *et al.*<sup>88</sup> was to construct a heterojunction between TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> to separate the photogenerated charge carriers and improve the activity. They synthesized the 0D/2D heterojunctions of oxygen defect rich TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> (referred to as γTiO<sub>2-x</sub>-MCN) by *in situ* two-step pyrolysis of NH<sub>2</sub>-MIL-125(Ti) and melamine. HR-TEM images revealed that the 5 nm quantum dots of TiO<sub>2</sub> were homogeneously distributed on the surface of the nanosheets of g-C<sub>3</sub>N<sub>4</sub>. XPS and EPR showed the existence of Ti<sup>3+</sup> and oxygen vacancies in γTiO<sub>2-x</sub>-MCN. The *g*-value for the unpaired electron of g-C<sub>3</sub>N<sub>4</sub> and oxygen vacancies of TiO<sub>2</sub> is similar. On comparison of the EPR spectra of the TiO<sub>2</sub>-MCN (synthesized by one-step pyrolysis mixing of TiO<sub>2</sub> and melamine), which was devoid of oxygen vacancies, MCN (g-C<sub>3</sub>N<sub>4</sub> synthesized by thermal pyrolysis of melamine) and γTiO<sub>2-x</sub>-MCN revealed that the increase in intensity in γTiO<sub>2-x</sub>-MCN could be attributed to the existence of oxygen defects of TiO<sub>2</sub> rather than an unpaired electron in g-C<sub>3</sub>N<sub>4</sub>. The charge transfer that occurs from 2D-g-C<sub>3</sub>N<sub>4</sub> to 0D-TiO<sub>2</sub> in less than 1 ps was revealed by the transient photoluminescence and femtosecond and nanosecond pumped-probe transient absorption spectra. CO<sub>2</sub> adsorption of γTiO<sub>2-x</sub>-MCN (8–10 cm<sup>3</sup> g<sup>-1</sup>) was ten times higher than that of MCN (0.8 cm<sup>3</sup> g<sup>-1</sup>). The presence of oxygen defects enhanced both absorption of light in the visible region and the CO<sub>2</sub> adsorption. The photocatalytic performance was studied in the presence of an acetonitrile/triethanolamine mixture and Co(bpy)<sub>3</sub><sup>2+</sup> as the cocatalyst in the presence of visible light. CO generation at

a rate of 388.9 μmol g<sup>-1</sup> using 2TiO<sub>2-x</sub>/MCN was observed to be five times higher than that of MCN (75.3 μmol g<sup>-1</sup>) in 5 h. The significant improvement in activity of TiO<sub>2-x</sub>/MCN was attributed to the enhanced visible light absorption, CO<sub>2</sub> adsorption, large surface area and efficient charge separation due to the formation of an interface between TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. After absorption of light, the electron from g-C<sub>3</sub>N<sub>4</sub> transfers to the conduction band of TiO<sub>2-x</sub> where the conversion of CO<sub>2</sub> to CO takes place in the presence of the electron mediator Co(bpy)<sub>3</sub><sup>2+</sup>. A hole is generated on TiO<sub>2-x</sub> transfer to g-C<sub>3</sub>N<sub>4</sub> where it gets removed by oxidation of triethanolamine, and this efficient transfer of the electron and hole pair across the heterojunction resulted in the effective separation of charge carriers.

Feng *et al.*<sup>89</sup> reported the formation of Ti<sup>3+</sup> ions while depositing the MgO layer over porous TiO<sub>2</sub> by atomic layer deposition (ALD). Porous TiO<sub>2</sub> was synthesized using the metal-organic framework MIL-125 as the Ti precursor. Five layers of MgO deposited by the ALD showed four times higher photocatalytic yield than porous TiO<sub>2</sub> and 21 times better than P25. Uniform distribution of MgO over porous TiO<sub>2</sub> generated the active site for CO<sub>2</sub> reduction by increasing the amount of Ti<sup>3+</sup> species on the surface and hydroxyl groups bonded to Mg and also helped in reduction of the surface photogenerated charge recombination rate by passivating the surface states of porous TiO<sub>2</sub>. With an increase in ALD cycles to more than five, photocatalytic activity for CO generation decreased due to the reduced contact of adsorbed CO<sub>2</sub> with TiO<sub>2</sub>. The photocatalytic activity was found to be higher for the ALD deposited MgO than that from the wet impregnation (WI) method. This was due to the high concentration of Ti<sup>3+</sup> and oxygen defects in the case of MgO deposited by the ALD method.

## 7. Conclusions and future directions

The defect engineering in TiO<sub>2</sub> has raised tremendous interest in the scientific community and different protocols based on reduction and oxidation strategies have been introduced for the synthesis of oxygen vacant/Ti<sup>3+</sup> induced TiO<sub>2</sub>. This review discussed various ways for the introduction of defects such as oxygen vacancies and Ti<sup>3+</sup> generation and their impact on



photocatalytic CO<sub>2</sub> conversion. The formation of the disordered layer and concentration of defects play an important role in determining the product yield and selectivity in photocatalytic CO<sub>2</sub> conversion. Defects significantly narrowed the bandgap, which resulted in improved absorption in the visible region. In addition, the defects provided the sites to bind and activate the CO<sub>2</sub> into CO<sub>2</sub><sup>•-</sup>, which is much easier to reduce further and thus enhance the CO<sub>2</sub> conversion yield.

The point defects in TiO<sub>2</sub> were generated by different synthesis methods such as treatment under a hydrogen atmosphere, inert gas (Ar, He, or N<sub>2</sub>), using a reducing agent, hydrogen plasma treatment, metallothermic reduction, doping with a heteroatom, *etc.* Although there are different methods reported in the literature, several of them required harsh conditions, hazardous chemicals, and costly and complex procedures or equipment. Therefore, the development of a low temperature, cost-effective and scalable process is needed for its practical application.

Thermal treatment in the presence of hydrogen gas at ambient pressure was found to be useful not only for the generation of defects but also to reduce the metal ion into metal nanoparticles and also to clean the surface of the catalyst. Also, it was observed that the product yield and selectivity depend on the particle size and degree of hydrogenation. Smaller particles of TiO<sub>2</sub> dispersed over the silica support showed a higher degree of reduction than the large particles. It was also observed that the presence of an oxygen vacancy could alter the dispersion of metal nanoparticles and thus affect the photo-thermo-catalytic activity. The decoration of the surface of the defective TiO<sub>2</sub> with chemical species like thiocyanate passivates the defects and also induces the electric field at the interface, which helped in the separation of charge carriers.

Defect generation using hydrides like NaBH<sub>4</sub> is one of the safe and easiest ways for the generation of a reductive atmosphere. Also, the generation of defects in the presence of He, N<sub>2</sub>, Ar and vacuum was also reported. The concentration of vacancies generated after thermal treatment in an inert atmosphere was dependent on the partial pressure of oxygen. By using the flame reduction method, defects can be induced within a minute because of the faster heating rate and high temperature of the flame. The metallothermic reduction method is a cost-effective method as compared to the high pressure and temperature hydrogenation method. In this method, metals such as Al, Mg, Li and Zn were used as a reducing agent to capture lattice oxygen effectively. By using lithiothermic reduction, defects can be generated at room temperature.

In all the reduction methods, the concentration of defects was found to increase with an increase in the amount of reducing agent. Also, the enhancement in light absorption was observed with an increase in the concentration of defects. But a similar trend was not observed for the photocatalytic activity. Hence the optimum amount of defects is needed to get a better yield.

Along with the defects, the presence of particular facets was also found to impact the CO<sub>2</sub> conversion yield. Facet engineering was found to be effective for the separation of charge carriers at different facets. Shi *et al.*<sup>77</sup> generated disorder layers only on particular facets using mild reducing conditions and

found that the chemical reactions on the facets were altered. The holes are supposed to accumulate at the {001} surface, but they observed that due to the formation of the electron-rich defective layer, the reduction of CO<sub>2</sub> occurred over the {001} facets and oxidation over the {101} facets. Along with the generation of oxygen vacancies or Ti<sup>3+</sup> in TiO<sub>2</sub>, attempts were also made to improve the charge carrier separation by facet selective deposition of metal nanoparticles, doping with heteroatoms like Co, Cu, *etc.*, Z-scheme heterojunction formation with visible light active semiconductors like SnS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, and surface decoration with chemical species like thiocyanate, which helped induce an electric field and passivated the surface defects.

This review also discusses the theoretical aspects of the formation of different products. Theoretical studies revealed that the formaldehyde pathway is most preferred in the case of both defective and non-defective TiO<sub>2</sub>, while the carbene pathway is not favored over the defective TiO<sub>2</sub> due to the formation of energetically unfavourable <sup>•</sup>C intermediates.

The photocatalytic CO<sub>2</sub> conversion yield of defective TiO<sub>2</sub> is summarized in Table 1. It is difficult to compare the yield as the reaction conditions reported by the different research groups were different. Also, the expression of the product yield in terms of μmol g<sup>-1</sup> h<sup>-1</sup> is inappropriate as it does not account for the intensity of the light source, photons falling on the reactor system, illumination area, *etc.* Also, it is difficult to extrapolate the yield in terms of per gram of catalyst as the yield does not vary linearly with the catalyst amount. Catalyst dispersion also plays a crucial role in determining the yield of the product.

There are several unknowns and challenges not yet addressed in this field. The nature and concentration of the defects and how they are helping in the improvement of photocatalytic activity are still not well understood. The defects created by adopting different synthetic methods have different physical and chemical properties and thus, assessment of the exact reason responsible for the enhancement of photocatalytic activity is another challenge. More information on structural distortion needs to be acquired using various *in situ* spectroscopy techniques. This will be helpful to rationalize the design of the photocatalyst. Efforts to produce C<sub>2</sub> and higher products by utilizing the advantages provided by the defects present on the surface of TiO<sub>2</sub> are needed. Recent work by Chen *et al.*<sup>90</sup> who reported the activation of CO<sub>2</sub> over defective Bi<sub>2</sub>O<sub>3</sub> for the production of the dimethyl carbonate using methanol, and Polshettiwar *et al.*<sup>91</sup> who reported activation of CO<sub>2</sub> using defective dendritic fibrous nanosilica (DFNS) without any metal sites, could be a way forward for defect engineering in other catalytic materials.

The catalyst's stability is another critical issue as the strong adsorption of the intermediate species at defect sites may deactivate the catalyst. Adsorption of reactants and desorption of products are important factors. Therefore, the removal of the products generated during the reaction is necessary to further prevent their oxidation into CO<sub>2</sub> or other products by accepting a hole. One of the ways to improve the adsorption and desorption kinetics is by carrying out the photothermal reactions where the CO<sub>2</sub> conversion can be performed at a slightly higher temperature than room temperature. The high temperature may hamper the adsorption of CO<sub>2</sub>, but temperature





optimization can result in the desired results where desorption as well as adsorption could be possible.

Along with tailoring of defects in TiO<sub>2</sub>, designing a specific photoreactor is also equally important in the view of efficient removal of the products as well as effective utilization of light falling on the system. A monolith photoreactor design holds promise for better product yields.<sup>92</sup>

Overall, defect engineering in TiO<sub>2</sub> is a potential approach for the production of value-added products and chemicals from photocatalytic CO<sub>2</sub> conversion by utilizing solar energy.

## Conflicts of interest

There are no conflicts to declare.

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