



## REVIEW

[View Article Online](#)  
[View Journal](#) | [View Issue](#)Cite this: *Nanoscale Adv.*, 2020, 2, 930

# Metal/semiconductor interfaces in nanoscale objects: synthesis, emerging properties and applications of hybrid nanostructures

Michael Volokh  and Taleb Mokari \*

Hybrid nanostructures, composed of multi-component crystals of various shapes, sizes and compositions are much sought-after functional materials. Pairing the ability to tune each material separately and controllably combine two (or more) domains with defined spatial orientation results in new properties. In this review, we discuss the various synthetic mechanisms for the formation of hybrid nanostructures of various complexities containing at least one metal/semiconductor interface, with a focus on colloidal chemistry. Different synthetic approaches, alongside the underlying kinetic and thermodynamic principles are discussed, and future advancement prospects are evaluated. Furthermore, the proved unique properties are reviewed with emphasis on the connection between the synthetic method and the resulting physical, chemical and optical properties with applications in fields such as photocatalysis.

Received 19th November 2019  
Accepted 4th February 2020

DOI: 10.1039/c9na00729f

[rsc.li/nanoscale-advances](http://rsc.li/nanoscale-advances)

## 1. Introduction

Today, different nano-sized objects are synthesized, manipulated, characterized, and utilized in a plethora of scientific and technological applications. Every B.Sc. student in chemistry, physics, and most branches of engineering has heard of 'nano' objects such as carbon nanotubes or quantum dots (QD). Colloidal QDs are considered a masterpiece of modern nanoscience. The development of the hot-injection method<sup>1</sup> in 1993 allowed studying the unique optical properties of QDs, since the surfactant-assisted precision synthetic method gives controlled surface chemistry with narrow size distributions and uniform morphologies.<sup>2</sup> The QD, which is a quantum-confined semiconductor nanocrystal, is just one excellent example of the rapid progress of this relatively new field of science, from the theoretical description of quantum-confinement, which explains the unique photophysical properties, to other calculated physical properties,<sup>3</sup> through different applications in electronic and optoelectronic devices,<sup>4</sup> to commercialization in displays and bio-labeling, which are already on the market.<sup>5</sup>

With available pathways for the controlled synthesis of various shapes, sizes, and compositions of nanoscale objects (see for example reviews by van Embden *et al.*<sup>6</sup> and Hyeon and co-workers<sup>7–9</sup> on various colloidal synthetic methods), scientists looked for ways to combine two (or more) nano-objects into hybrid nanostructures (HNS) and potentially obtain materials with new properties. Continuing with the QD example, varying the deposition of a second semiconductor crystal on the existing

QD results in a hybrid semiconductor/semiconductor (SC/SC) interface; some synthesized examples include core/(multi) shell,<sup>10–18</sup> yolk/shell<sup>19–21</sup> and heterodimers (usually two or more quasi-spherical shapes forming a heterojunction<sup>22–24</sup> as well as acorn-style structures<sup>25</sup>). When the QD serves as a seed for an anisotropic structure such as a rod,<sup>26</sup> tetrapod<sup>26,27</sup> or octapod,<sup>28</sup> more complex structures result,<sup>29</sup> where the seed (junction) and arm are different SCs. Obviously, if the starting material is anisotropic (*e.g.*, nano-rod, -wire, -belt, -ribbon, -sheet, -pyramid)<sup>6,30,31</sup> or even branched,<sup>32</sup> other hybrid SC/SC nanostructures (possibly with mixed dimensionalities) result—ranging from simple heterostructures through rod-in-rod, dumbbells, dot-in-rod and graded shells,<sup>33</sup> to 'double' QD fixed in a rod with unique optoelectronic properties.<sup>34</sup> The examples thus far focused on the SC/SC interface, but a vast body of knowledge has been acquired on interfacing a SC with a metal (M)—these hybrid nanostructures (HNSs) are the topic of this review—and we will begin with discussion of binary systems in Section 2. For detailed analysis of the electronic coupling between a semiconductor, a metal and variable (insulating) interfaces, we refer the reader to the thorough review by Vilan and Cahen.<sup>35</sup>

Both shape and size dictate the electronic structure in metals<sup>36</sup> and in semiconductors due to different quantum-confinement effects.<sup>37</sup> Noteworthy, many electronic and optical properties of nanocrystals result not only from dimensionality and size but also from surface properties.<sup>38</sup> Formation of an HNS could result in a mere combination of the individual material's properties (fluorescence, magnetism, plasmonic response, catalytic activity and so forth). However, usually, new properties arise from both the modifications at the surface of the original constituents and the newly formed interface,

Department of Chemistry, Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva 8410501, Israel. E-mail: [mokari@bgu.ac.il](mailto:mokari@bgu.ac.il)



It is impossible to provide an adequate classification of all possible property combinations, yet a useful generalization would be to classify the metal and semiconductor roles. The intrinsic role of a metal (or a bimetallic compound) can be classified, as common for metal NPs,<sup>52</sup> into plasmonic (*e.g.*, Cu, Ag, Au), magnetic (Fe, Ni, Co), and catalytic properties (*e.g.*, Pt-group metals). To these roles, we can add the electronic properties of the metal, which are intimately connected to the semiconductor—specifically, electrical conductivity and Fermi level ( $E_F$ ). In the case of the semiconductor, the most important property is usually the bandgap ( $E_g$ ), which defines the material and its optical absorption, though the entire electronic structure (*i.e.*, density of states) is important for planning an applicable M/SC interface: Fermi level, doping, band positions and expected defect levels, carrier diffusion length, fluorescence yield and even plasmonic response due to defects in semiconductors (*e.g.*, vacancies in copper sulfide and impurity doping in metal oxides).<sup>53</sup>

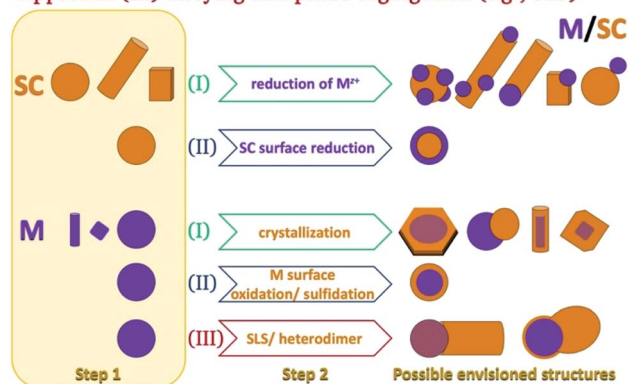
This basic thermodynamic principle,<sup>54</sup> alongside kinetic control over the number of available nucleation sites and precursors, allows interfacing two materials. Fig. 1 schematically depicts the conventional two-step approaches for the formation of SC/M and M/SC interfaces. One can divide the syntheses according to the first material employed: semiconductor or metal. When the first material is a semiconductor, the subsequent metal domain formation is usually performed by reducing a metal cation—either using a photo-assisted process (Section 2.1.1) or chemically (Section 2.1.2). This is approach (I), where a reduction of metal from the solution

## Nanoscale Adv., 2020, 2, 930–961 | 931

## Approach (I) nucleation over pre-formed structure

## Approach (II) partial transformation of a pre-formed structure

## Approach (III) alloying and phase segregation (e.g., SLS)



**Fig. 1** Schematic options to form nanoscale colloidal-phase heterostructures using a starting semiconductor (SC, orange) or metal (M, purple) structure. Approach (I): nucleation of M over SC or SC over M; approach (II): partial transformation of the first structure (reduction at the surface of a binary SC's cation to the metal or surface transformation of a metal into a semiconductor (e.g., oxidation or sulfidation)); approach (III): precipitation out of a metal-alloy core, which either forms a heterodimer or a nanorod via a solid-liquid-solid (SLS) mechanism, where the SC precursors are dissolved in the metal tip (alloying) and precipitate out of it, resulting in the formation of an M/SC interface.

results in nucleation and growth on the SC. The other option, approach (II), is a partial chemical reduction of the SC at the surface of the nanocrystal, resulting in metal coating or domains. This is a relatively rare synthetic approach with a starting SC (e.g.,  $\text{Cu}_2\text{O}$  into  $\text{Cu}_2\text{O}/\text{Cu}^0$ ).<sup>55</sup>

The colloidal approaches for the synthesis of metal NPs (as the anchor for a subsequent SC growth) are dominated by chemical reduction both in aqueous and organic-solvent environments. The most prominent example is the citrate-assisted reduction of gold from  $\text{Au}(\text{III})$  to  $\text{Au}^0$ , but alcohols, amines,<sup>56</sup> etc. are also common reducing agents. Noticeable alternatives include the use of metal carbonyl complexes, where the metal's oxidation state is 0.<sup>57</sup> To stabilize the resulting metallic NPs, the typical surfactants are long-chain organic molecules, polymers (e.g., PVP), and micelles (formed using hexadecyl-trimethylammonium bromide, CTAB, in an aqueous environment for example).

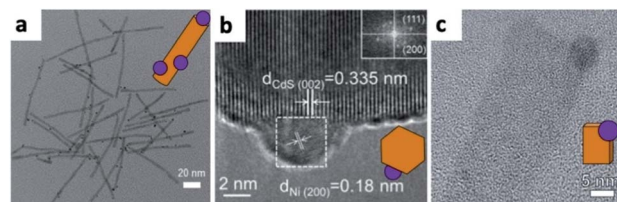
The metal can serve as the seed for growth of SC crystals (approach (I), discussed in Section 2.1.3), as the substrate for chemical transformations (approach (II), e.g., surface oxidation and sulfidation, discussed in Section 2.1.4), or as the catalyst for a solution-liquid-solid (SLS) growth (approach (III), Section 2.1.5).

**2.1.1 Photodeposition of metals on semiconductor nanostructures.** When using a SC nanostructure, one can nucleate a metal crystal on its surface by reduction. The reduction can be induced either chemically (Section 2.1.2) or photochemically (this section). Illuminating a semiconductor and using the excited electrons to reduce an existing metal-containing

molecule in the surrounding solution is a photodeposition method. The Weller group deposited silver on ZnO nanorods (NRs) in an ethanediol/water (2 : 1 v/v) mixture.<sup>58</sup> Alivisatos and co-workers have shown photodeposition of Pt on CdS and CdSe-CdS core-shell NRs in toluene.<sup>59</sup> The control over the number of Pt NPs per rod (a wide distribution in the 0–6 range) proved to be hard, with the best control achieved on well-passivated CdSe-CdS NRs, where most NRs contained a single Pt domain, close to the CdSe core. Others have deposited different metals on various semiconductors of diverse shapes.<sup>60</sup> Recently, photodeposition in ionic liquids has been carried out by Hill and co-workers, who have shown non-selective deposition of Pt, Au and Ag on CdSe-CdS NRs with similar results to the common amine-capped colloidal synthesis in toluene (Fig. 2a).<sup>61</sup>

Carbone *et al.* have used UV light in 9 : 1 v/v  $\text{CHCl}_3$  : ethanol (EtOH) to achieve controlled reduction of gold on the tips of CdS and CdSe(core)@(shell)CdS NRs.<sup>62</sup> The advantage of this method is that the EtOH acts as an electron donor, reacting with the photogenerated holes in the semiconductor, thus allowing the photogenerated electron in the rod to reduce a gold cation. This method allowed the synthesis of large Au domains on CdSe@CdS or CdS NR tips and nano-dumbbells. The fact that the large domain formation is selective at one tip is a significant synthetic achievement since photodeposition is not usually selective. By measuring the absorption peak location stemming from the metal domain's plasmonic response, transmission electron microscopy (TEM) analysis and controlled addition of a gold precursor, the authors deduce that the mechanism is mainly through selective drift of the photogenerated electrons towards the gold tip (forming, at first, alongside other Au domains), which enhances further reduction of the large metal tip, acting as an electron sink.

Fernando *et al.* have shown that gold readily photodeposits on ZnO at high-energy sites as facet edges and corners when the capping ligand is a labile amine, but when a more strongly bound dodecanethiol (DDT) is used, the deposition is quenched.<sup>63</sup> Furthermore, since the deposition rate depends on the interfacial electron transfer from the ZnO to the cationic gold complex, changing the solvent could determine whether multiple small Au domains are formed, or fewer larger Au

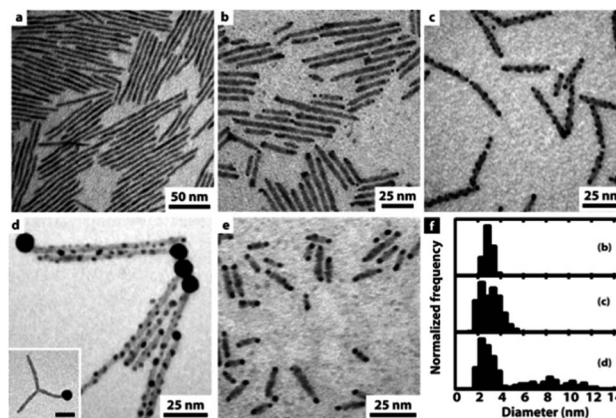


**Fig. 2** Examples of metal photodeposition on SCs. (a) Pt/CdSe-CdS NRs via a non-selective Pt domain photodeposition reaction carried out in an ionic liquid, adapted from ref. 61, Creative Commons Attribution 4.0 International Public License, published by Beilstein-Institut, copyright 2019. (b) Ni/CdS NCs, adapted with permission from ref. 67, American Chemical Society, copyright 2016. (c) Ni/CdS nanosheets, adapted with permission from ref. 68, American Chemical Society, copyright 2015.



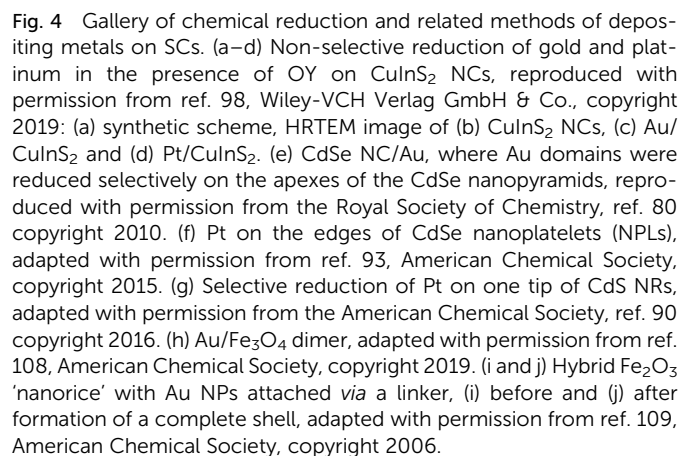


Further investigation of a similar system of CdS NRs showed an interesting strategy to control the amount and location of the gold NPs—the reduction takes place on defect sites at the nanorod's surface, thus controlled etching allowed exposing



This procedure, adapted from a  $\text{Ni}_x\text{Pt}_{1-x}$  synthesis,<sup>77</sup> also allowed the formation of bimetallic tips (*i.e.*, PtCo and PtNi) when the other metal precursors are present in the system prior to injection.<sup>76,78</sup> The choice of stabilizers is responsible for the metal (or bimetallic) tip—with the OA : OY combination being responsible for the spherical single-crystalline nature while the diol is mainly responsible for the reduction. Schlicke *et al.* have shown that a Pt-tipped CdS NR can be transformed in a subsequent step into a faceted metallic tip, by introduction of CO(g) to the growth solution in benzyl ether.<sup>79</sup> The CO served a dual role—it reduced the  $\text{Pt}(\text{acac})_2$  on the pre-formed Pt-tip and also dictated the final {100} faceted tip morphology.

Other metals such as cobalt were deposited on CdSe NRs by heating a solution of an organometallic Co-precursor in toluene in the presence of lauric acid and hexadecylamine under a reducing  $H_2$  atmosphere.<sup>101</sup> When a multielement SC is desired, an attractive synthetic path is the use of single-source

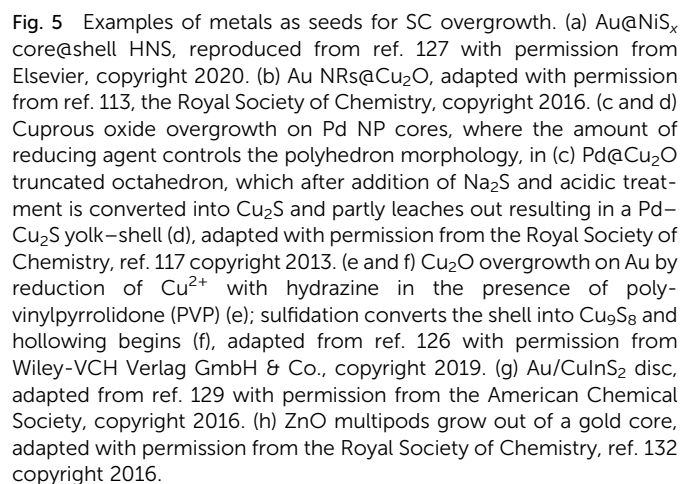


An alternative approach, which circumvents using organometallic precursors is the protocol by Yang *et al.*,<sup>82</sup> where different aqueous metal salt solutions are mixed with an ethanolic solution of a long chain amine (*i.e.*, DDA), which allows transfer of the metal cation to an organic phase. They have used this to synthesize metal NPs, metal-sulfide SC nanocrystals, as well as metal-sulfide-metal HNSs. Such a multi-phase approach for metal NP synthesis has since been expanded for deposition of metals on non-sulfide-based SCs such as Pt-CeO<sub>2</sub>.<sup>104</sup> An



### 2.1.3 Metal NPs as seeds for growth of semiconductors.

Additional optical response tuning can be achieved through formation of hollow centers in a HNS, *e.g.*, Au@Cu<sub>2</sub>O core@-shell,<sup>120</sup> selective oxidation of Au NRs@Cu<sub>2</sub>O,<sup>121</sup> formation of a selective gap between the outer metal core and internal Cu<sub>2</sub>O shell in Au NR@Ag@Cu<sub>2</sub>O HNSs<sup>121</sup> and controlled formation of gaps in an Au-Cu<sub>2</sub>O yolk-shell system.<sup>122</sup> For further information regarding the various LSPR (localized surface plasmon resonance) influences of the M-Cu<sub>2</sub>O and related M-metal oxide systems with emphasis on the facet-dependent properties



of a binary semiconductor to its metal, when the transformation is performed on a metallic ‘reactant’, *e.g.*, formation of Cu(0) particles over Cu<sub>2</sub>O films for CO<sub>2</sub> reduction purposes,<sup>134</sup> and cyclic voltammetry in the presence of Cl<sup>−</sup> anions producing a chloride-stabilized biphasic Cu–Cu<sub>2</sub>O electrocatalyst from Cu<sub>2</sub>O.<sup>135</sup>

A partial oxidation can take place on various starting morphologies: for example, different spherical NPs,<sup>136</sup> and nanowires (NWs, such as copper into cuprous oxide forming 1D Cu@Cu<sub>2</sub>O NWs).<sup>137</sup> As discussed by Cozzoli and co-workers,<sup>138</sup> centrosymmetric M-SC core-shell systems are most common with transition-metal cores (*e.g.*, Co, Fe, Cu) as they are easily oxidized. Several notable examples are mentioned herein: metallic copper NPs dispersed in hexane are oxidized under ambient conditions to form a Cu<sub>2</sub>O shell (the thickness of which depends on the elapsed time);<sup>139</sup> this technique can be expanded to more complex starting NPs such as Cu@Ag—in which case, the benefit was the introduction of strain into the resulting Cu<sub>2</sub>O shell due to similarity with the Ag core's crystal structure;<sup>140</sup> Pt-Co core-shell NPs can be oxidized to Pt-CoO by blowing an O<sub>2</sub>/Ar 1 : 4 v/v mixture into the solution at 455 K;<sup>141</sup> Co is especially prone to oxidation as surface oxidation occurs even when the synthesis is carried out using standard air-free techniques.<sup>142</sup> The study of metallic NP oxidation has consequences both on the synthetic opportunities of HNS design but also on the stability of NPs in applications and as an indirect characterization technique, as demonstrated by Ustarroz *et al.*, who studied the electrochemical oxidation of Ag NPs, which can result in dissolution (stripping).<sup>143</sup>

As was briefly mentioned in the previous section (Section 2.1.3, and will be discussed again in Section 2.3), sulfidation (also known as sulfurization) can transform a metal or a metal-oxide into a metal-sulfide, sometimes forming a void. It is, however, possible to partly convert a metal surface into its sulfide, thus forming a M-metal-sulfide HNS. For example, transforming a Cd metal core, on which ZnO NPs were grown, into a ZnO-CdS@Cd HNS;<sup>144</sup> in this example—by treatment with Na<sub>2</sub>S(aq). Moreover, if a second metal shell is formed on the first M core before sulfidation, a complete conversion of the former leads to HNS formation, for example, Au/Ag NRs can transform into different Au NR core/(complete, corner-opened or end-opened) Ag<sub>2</sub>S shell HNSs.<sup>145</sup>

Schaak and co-workers have designed bimetallic AuCu NPs, which were converted to Au-Cu<sub>2</sub>S when heated under bubbling oxygen in the presence of an OY surfactant and sulfur.<sup>146</sup> This is an excellent demonstration of M-SC dimer formation without direct nucleation of an SC on the surface of the metal. In this case, depicted in Fig. 6, the dimer undergoes a chemically induced phase-segregation, where the copper transforms into a Cu<sub>2</sub>S SC. About 80% chemical yield is achieved, while only 3% of the particles seen in the TEM images are non-hybrid Cu<sub>2</sub>S NPs, which the authors suggest formed either through a dewetting process of the HNS or by a reaction of the sulfur with a dissolved Cu-complex. The role of oxygen is to activate the transformation—probably by forming some kind of intermediate oxide. The authors have also checked whether an alternative mechanism of partial dissolution and reprecipitation is

As was depicted in approach (II) in Fig. 1, HNSs can be formed by partial chemical transformation of the starting material. The two most common paths are oxidation and sulfidation of a metal (surface) to form metal/metal-oxide or metal/metal-sulfide interfaces, respectively, and partial (surface) reduction

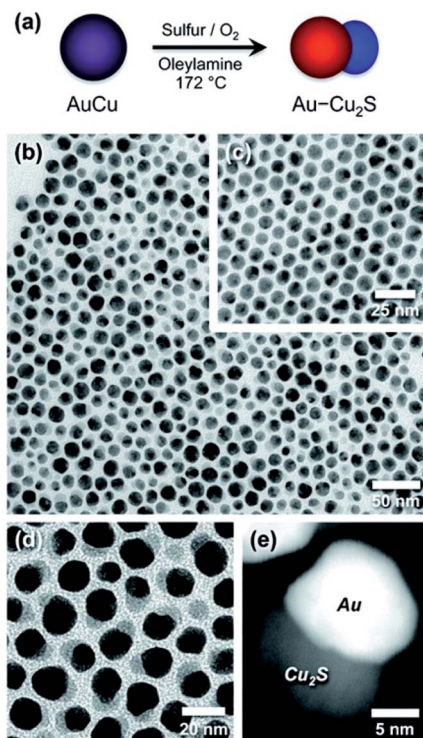


Fig. 6 Chemically induced phase-segregation mechanism for the synthesis of Au–Cu<sub>2</sub>S heterodimers. In this mechanism the sulfidation does not partially convert the metal core—as depicted in approach (II) in Fig. 1—rather the bimetallic precursor phase-segregates into a dimer, with concurrent sulfidation of the copper into Cu<sub>2</sub>S, i.e., combination of approach (III) in Fig. 1 and sulfidation. (a) Synthetic path scheme, TEM of (b) dimers, (c) AuCu NPs before synthesis, (d) higher-magnification of dimers, and (e) dark-field image. Reproduced with permission from ref. 146, American Chemical Society, copyright 2012.

involved. Upon reacting Au NPs with copper and sulfur precursors, Au–Cu<sub>2</sub>S HNSs were formed but with yield *ca.* 16%—this different low yield suggests that the phase-segregation mechanism is the major reaction path.<sup>146</sup>

Silver is especially popular as the metal transformed into Ag<sub>2</sub>S.<sup>147,148</sup> Han and co-workers, for example, formed various M–Ag metallic heterodimers (where M = Pd, Au, Pt). In a subsequent step, in the presence of PVP (polyvinylpyrrolidone) and Na<sub>2</sub>S the silver was sulfidized, resulting in a M–SC heterodimer.<sup>147</sup> This effect can also happen unintentionally, as in the case of Ag NWs, which are sulfidized under environmental conditions.<sup>149</sup>

Furthermore, addition of another reactive precursor containing a different element can also form a ternary sulfide as demonstrated by van Embden *et al.*, who have used a ‘one-pot’ organic-phase synthesis (S coming from CS<sub>2</sub>, and DDT being the solvent) to form either core/shell or heterostructures of Ag/Ag<sub>8</sub>GeS<sub>6</sub>.<sup>150</sup>

A binary semiconductor can also be partially reduced to the metallic element it contains to form a SC/M interface. From the electronic structure point-of-view, even a reduction of few atoms due to charging (*e.g.*, Cd<sup>0</sup> in a cadmium chalcogenide) has significant influence as it forms a trap.<sup>151</sup> On a larger scale, an

ammonia electrosynthesis catalyst was prepared by reduction of iron oxyhydroxide to form a core-shell  $\alpha$ Fe–Fe<sub>3</sub>O<sub>4</sub> hybrid by annealing under a reducing H<sub>2</sub>(g) environment.<sup>152</sup> Another interesting related example is the formation of a bimetallic thin layer in a HNS: Peng and co-workers have shown that for Pt/Fe<sub>3</sub>O<sub>4</sub> core/shell triangular nanoprisms, an interfacial iron-platinum layer is formed.<sup>153</sup> This serves as an epitaxial layer, and is therefore important as a possible synthetic tool to allow formation of heterojunctions using partial reduction of the SC.

Such an approach was also used to form hybrid bimetallic CdNi decoration of CdS NRS: in the first step CdS NRS were partially chemically reduced by dispersing calcined NR powder in an aqueous NaBH<sub>4</sub> solution; subsequently, a photo-deposition procedure on CdS/Cd NRS was performed in an ethanolic solution of nickel chloride salt, resulting in CdNi decoration of CdS NRS.<sup>154</sup> Aqueous-phase reduction using NaBH<sub>4</sub> was used to form a complex Ag/AgBr/BiVO<sub>4</sub> photocatalyst.<sup>155</sup> First, AgBr was precipitated over hydrothermally prepared BiVO<sub>4</sub> microspheres from a solution of Ag<sup>+</sup>(aq) and Br<sup>–</sup>(aq). Then, silver NPs were deposited over the AgBr domains by reduction of silver cations. In such a mechanism the solubility product of the AgBr determines the available concentration of silver for the reduction step, effectively transforming an AgBr NP into an Ag/AgBr dimer.<sup>155</sup>

**2.1.5 Solution–liquid–solid (SLS).** The SLS growth mechanism (approach (III) in Fig. 1) was first reported by Buhro and co-workers for the growth of III–V semiconductor whiskers from indium.<sup>156</sup> It has been expanded since for the formation of a wide variety of 1D (usually NW semiconductor) structures, *e.g.*, Ge, Si, InAs and other ME (M = In, Ga; E = N, P, As) as well as metal-sulfides MS (M = Pb, Cd) through the use of SSPs with controlled aspect ratios and monodisperse diameters.<sup>157–163</sup> The SLS mechanism involves: (i) a reaction of metallo-organic precursors in a hot solution (the solution phase), usually initiated by a thermal decomposition; (ii) semiconductor components, which are formed from the precursor reaction, dissolve inside molten metal nanodroplets (the liquid phase) until supersaturation is achieved; (iii) the semiconductor crystal (the solid phase) starts to precipitate out of the metal. As the feed of new atomic components into the metal droplet is sustained, the supersaturation conditions are maintained, and the semiconductor continues to precipitate out. Since the activation barrier for semiconductor crystallization is lower at the liquid–solid interface, the precipitation of the semiconductor tends to preferentially proceed at this juncture, leading to 1D growth behavior. As a result, the SLS process usually results in 1D structures such as nanowires and nanorods. The metal nanodroplets play two mechanistic roles—they catalyze both the decomposition of the precursors at the solution–liquid interface and the semiconductor growth (precipitating out of the droplet) by functioning as a crystallization solvent.<sup>164</sup> A strong correlation was found between the diameter of the metal droplet and the diameter of the growing NW (*e.g.*, Au droplet and PbS NW).<sup>164</sup> Therefore, the mean size of the metal nanocatalysts and their size monodispersity are crucial. SLS-grown CdSe NWs (from a Bi catalyst) can act as the nucleation sites for further metal deposition (overgrowth) of metal or binary-metal





As was described for these M/ZnO systems, there is a large mismatch between the lattice distances, which prevents formation of complete anisotropic core-shell systems. One way to circumvent this limitation is using a hydrothermally prepared coating of TiO<sub>2</sub> over Ag NW cores, which allows deposition of multiple ZnO NPs as the sheath.<sup>170</sup> Since Ag NWs have potential application as the main ingredient of conductive transparent (flexible) electrodes, such hybrids are of much interest, and simple deposition techniques (spin coating and mild thermal annealing) were used to this end to form ZnO NP/Ag NW composite mesh over polyethylene terephthalate (PET) as an example.<sup>171</sup> Since the outcome is attachment based on random physical interactions without controlled interfaces, we will not discuss this synthetic approach further.

Figure 1 consists of four panels (A, B, C, D) showing cryo-electron micrographs of actin filaments. Panels A, B, and C show actin filaments with various bound proteins. Panel D shows a single actin filament with a 100 nm scale bar.

This journal is © The Royal Society of Chemistry 2020

To achieve a metallic gold shell over CdSe dihexagonal pyramidal nanostructures, Meyns *et al.* have used wurtzite CdSe NCs as the seeds for a modified AuCl<sub>3</sub> reduction procedure.<sup>80</sup> They have reacted the NCs in the presence of OY and an Au(III) complex resembling Au(III)-DDAB (specifically, AuCl<sub>3</sub> with *n*-dodecyltrimethylammonium bromide, DTAB). Under these reaction conditions, the OY surfactant is a mild reducing agent and a thin (partial) amorphous gold shell was formed around the CdSe NCs. When irradiated under a TEM electron beam, this shell transformed into Au dots on the vertices of the NC. This observation demonstrates several important lessons: (i) it

For further discussion of the factors governing the formation of heterostructures *vs.* multi-component mixing, *i.e.*, formation of solid solutions during synthesis, we refer the reader to a review by Jeong and co-workers.<sup>174</sup>

Nanoscale Adv., 2020, 2, 930–961 | 939

This journal is © The Royal Society of Chemistry 2020



This class of materials are treated in this review as semiconductors due to the similarity in the synthetic methods to other binary and ternary semiconductors as demonstrated in the work of Shavel and co-workers who have synthesized various colloidal TMPs of different aspect ratios.<sup>240</sup>

## Nanoscale Adv., 2020, 2, 930–961 | 941

This journal is © The Royal Society of Chemistry 2020

Significant progress has been achieved by the Schaak group which has used heterodimers (as shown in Fig. 10) as the precursors for development of a wide array of complex inorganic nanostructures with a consecutive-step chemical

An additional option to obtain a complex heterojunction-containing colloidal structure is attachment of different structures in the system as discussed in the review by Buck and Schaak,<sup>51</sup> followed by fusion. This is usually achieved by controlled elimination of stabilizing agents, which favors controlled aggregation, for example using iodine to 'weld'



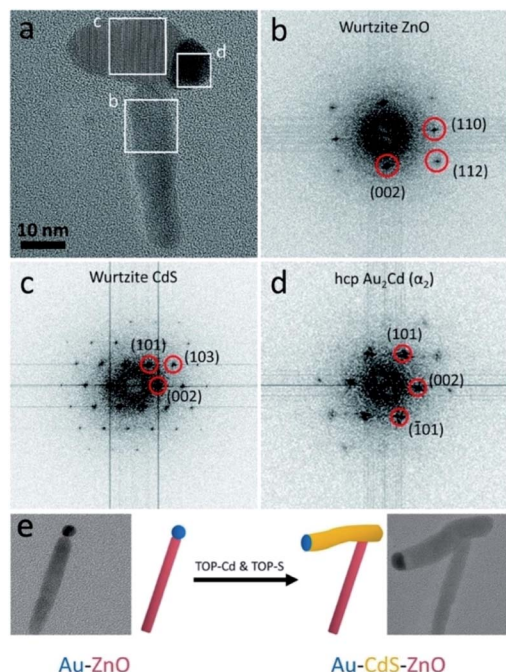


Fig. 11 Ternary hybrid system using an SLS mechanism. (a) High-resolution TEM image of Au–CdS–ZnO with marked areas for fast-Fourier transform (FFT) analysis: (b) from the ZnO, (c) from the CdS, (d) from the Au–Cd. (e) Synthetic scheme and TEM images: Au–ZnO NR formed using the seeded growth approach is reacted with Cd- and S-complexes to insert a CdS domain. Reproduced from ref. 266 with permission from the Royal Society of Chemistry, copyright 2017.

different Au-(multiple) tipped nanostructures as reported by Manna and co-workers.<sup>267</sup>

The ability to form three-component systems can also be used as an intermediate synthetic pathway to achieve two-component products, where the third component acts as a protective layer—to be removed during synthesis. This was reported using a polymer by Xia and co-workers for formation of bimetallic Au–M (M = Ag, Pd, Pt) NPs,<sup>268</sup> and also in an all-inorganic system by Chen and co-workers, where a silica is protecting a gold core, *i.e.*, an Au–SiO<sub>2</sub> dumbbell is reacted with another metal, which cannot conformally coat the Au-core due to the existence of the SiO<sub>2</sub> mask.<sup>269</sup>

This allowed formation of Pd–Au and Pt–Au dimers, as well as Pt–Pd–Au trimers, where dendritic Pt domains were deposited on the Pd, before removal of the protective silica layer from the terminal gold NP. Silica is popular as a hard template that can be removed, as demonstrated in the formation of Pt–Fe<sub>3</sub>O<sub>4</sub> HNS encapsulated in N-doped carbon hollow spheres by embedding the dumbbell in silica and polydopamine, which after carbonization and silica removal resulted in a yolk-shell morphology.<sup>270</sup> Naya *et al.* have used ZnO, which dissolves under mild conditions to form a ‘nanoegg’ shape, of half-cut Au(core)–CdS(shell).<sup>271</sup>

### 3.2 Complex (higher-order) systems

In addition to increasing the complexity (*e.g.*, morphology, number of components and functionalities) of a single colloidal

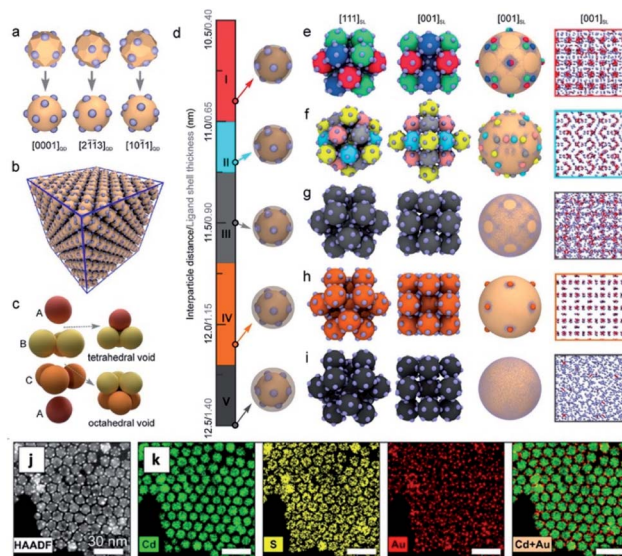


Fig. 12 Self-assembly into superlattices from patchy quantum dot-gold hetero-structural nanocrystals without inherent anisotropy. The top part shows simulation of gold NPs on different facets of wurtzite QD hosts with varying interparticle distance adjusted by the ligand shell (surfactant chain-length) and the resulting unit cells: (a) satellite configurations of polyhedral and spherical models, (b) packing into a superlattice with a face-centered cubic (fcc) arrangement of individual patchy NCs, (c) illustration of the voids formed within the fcc lattice, (d) illustration of the five different orientational orders observed in the MD simulation, where the semitransparent gray highlight presents the length of the passivating ligand shell, (e–i) the different orientational order of the structures presenting different projections and a snapshot (right column) highlighting the contacts in red. The bottom part shows experimental high-angle annular dark-field scanning TEM (HAADF STEM) image (j) and the corresponding EDS elemental mapping of CdS polyhedra (9.7 ± 0.5 nm)/Au-satellites (2.2 ± 0.3 nm) HNSs after self-assembly (k), where Cd, S and Au are presented in green, yellow and red, respectively, and the rightmost frame shows the overlay of Cd and Au. Adapted from ref. 39 with permission from the American Chemical Society, copyright 2019.

nanostructure, the different domains constituting an ensemble of HNSs can be used to form complex high order systems such as 3D superlattices and other arrangements on substrates. Much progress has been achieved in using self-assembly for these purposes. For example, Chen and co-workers could successfully demonstrate it using pressure-induced interparticle fusion<sup>272</sup> and more recently<sup>39</sup> using patchy Au QDs coupled to interparticle distance control *via* variation of the passivating ligand shell to self-assemble them into different superlattices using NPs without an inherent anisotropy (Fig. 12). The same group also reported how patchy gold domains on CdS–Au<sub>2</sub>S Janus NPs migrate and coalesce to form CdS–AuS–Au hetero-trimers upon pressure-treatment.<sup>273</sup>

Integration into 2D predetermined patterns can also be achieved using the attraction of metal domains of the HNS to metal anchor points on a substrate (Fig. 13). Such integration was exemplified with Au/CdS NRs/Au nano-dumbbells forming ‘nanolithographic docking’ using the chemical affinity of dithiol molecules to AuPd nanodots on a Si substrate and the Au domains of the HNS.<sup>274</sup>



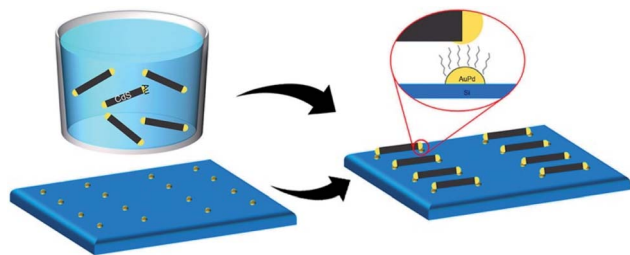


Fig. 13 CdS-Au nano-dumbbells self-assemble on pre-fabricated AuPd NPs on a Si substrate ('nanolithographic docking').<sup>274</sup> Reproduced with permission from the American Chemical Society, copyright 2018.

## 4. Properties and applications

To utilize the unique properties of HNSs in many applications they must be connected to an external circuit when the electric response is required either as an input or an output, including sensing, photovoltaics, (photo)electrocatalysis and so forth. Since an electric signal is transported *via* metallic connectors, there are three common approaches to connect an HNS to an external electrode: (i) direct synthesis of the SC part on a metallic substrate as was discussed with the nickel foam examples in Section 2.2; (ii) deposition of a metal over a SC structure—a possible configuration for photovoltaic devices, where an active layer of semiconductor(s) is sandwiched between a transparent conductive oxide and metal electrodes;<sup>275</sup> (iii) using the metal part of the HNS itself to serve as the anchoring point to an external macroscale measuring system, for example by connecting a metal to a nano-scale p-n junction. To achieve the latter, lithographic techniques as demonstrated in a recent report by Duan and co-workers<sup>186</sup> are most common. As these three approaches are less suitable for colloidal HNSs they are mostly outside the scope of this review. Instead, we focus in this section on the utilization of the phenomena arising from the formation of colloidal HNSs in dispersion for (photo)catalytic, photoelectronic and some biomedical applications. Of note is that the solid-state Photovoltaic devices section (Section 4.3) deals with deposited HNS dispersions, which constitute the photoactive layer itself.

For practical utilization of HNSs, the source of the favorable novel properties must be identified. Coupling a metal to a semiconductor can be beneficial for catalysis (Section 4.1) and can improve the light absorption through a plasmonic mechanism or improve the generated charge-carrier dissociation kinetics from the semiconductor—both mechanisms are elaborated in the photocatalysis subsection (Section 4.2).

The formation of a M/SC interface in a colloidal HNS solution also increases the conductance of individual NPs, as exemplified for CdSe NR/Au.<sup>276</sup> Such phenomena can be used for characterization of multicomponent SC nanostructures using variants of probe microscopy<sup>277</sup> on the one hand, and for providing a high-chemical yield method to connect metallic domain(s) on various NPs for further integration<sup>276</sup> on the other hand. The latter is an alternative to the more traditional metal deposition through nanolithography, for integration into

nanoelectronics as was demonstrated by the Alivisatos group.<sup>278</sup> The exact mechanism of conductance enhancement in HNSs is still not fully understood and may change from system to system. Possible contributions (sometimes parallel) may stem from a lower Schottky barrier (shown in single NP measurements<sup>276</sup> and CdSe/Au nano-dumbbells, which form linked networks),<sup>279</sup> percolation of metallic domains, and different M-SC electronic coupling phenomena (including photoconduction in Pt-CdSe monolayers<sup>280</sup>) as discussed by Mahler *et al.*, who conclude that the most likely explanation in the case of CdSe NPLs/Au is tunneling events between metal tips with little contribution (if any) from electronic states of the SC.<sup>70</sup>

### 4.1 Catalysis

An interesting example of interface engineering has been recently shown by Zhu *et al.*, who have used galvanic replacement to partially exchange Cu NPs into Cu@Ag NPs alongside partial oxidation of the Cu to Cu<sub>2</sub>O.<sup>140</sup> Control over the oxidation allowed formation of a thin layer (3–6 atomic layers) of Cu<sub>2</sub>O, which induced compressive strain at the NPs' surface, which was demonstrated as beneficial for the catalytic transformation of aniline into azobenzene (oxidation). Another common model reaction to test SC/M systems is the (photo)reduction of 4-nitrophenol (4-NP) to 4-aminophenol in the presence of sodium borohydride (NaBH<sub>4</sub>),<sup>117</sup> which was recently shown to take place on the catalyst's surface—adsorbed 4-NP molecules are reduced using electrons from the catalyst and protons coming from the protic solvent (water, alcohol, *etc.* but not directly from BH<sub>4</sub><sup>−</sup>).<sup>281</sup>

The oxygen reduction reaction (ORR) is a reaction in the field of batteries (Li-O<sub>2</sub> batteries, for example)<sup>282</sup> and fuel cells,<sup>283</sup> where an electrocatalyst (most commonly a precious metal) is responsible for the transformation of O<sub>2</sub> into H<sub>2</sub>O (in the case of Pt(100) the ORR is performed *via* the oxygen dissociation mechanism).<sup>284</sup> Using the interaction between the metal-oxide support and the metal,<sup>285–288</sup> the energetics of the catalyst can be improved. Meng *et al.* have epitaxially grown Pt on single-crystal CuO NRs for this purpose.<sup>285</sup> They have loaded a carbon cloth with fcc CoO NRs with pyramidal facets, which served as the nucleation centers for epitaxially grown fcc Pt NPs (~7% lattice mismatch) using magnetron sputtering followed by annealing to achieve crystallization.

The reported Pt/CoO configuration results in electron donation from the oxide to the metal, which tunes the d-band structure of Pt in the hybrid system downwards, and results in favorable intermediate adsorption.<sup>289</sup> This is an elegant demonstration of the electronic charge transfer into a metallic catalyst, which improves its catalytic efficiency. As pointed out by Wang *et al.*, this is only one contribution to ORR activity and other effects such as particle size, crystal facets and lattice strain have a critical impact, which is usually hard to decouple from the charge transfer effect in hybrid structures (either M-support or M-M).<sup>289</sup> Further advancement is expected when the metal-oxide support is doped, which can improve its conductivity, stability of the active electrochemical and specific surface areas, as well as tuning of the energy alignment with the metal catalyst.<sup>283</sup>



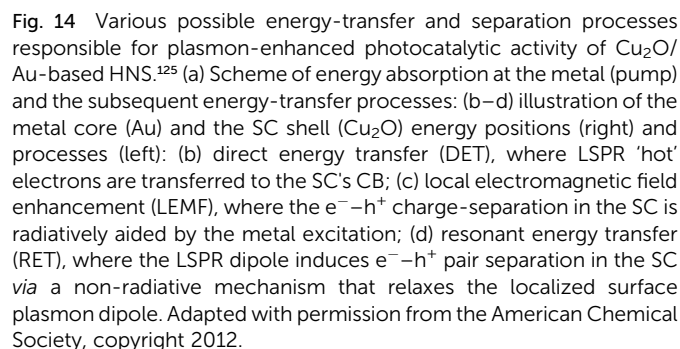
## 4.2 Photocatalysis

Pradhan and co-workers have shown how the incorporation of Sb ions into a bismuth sulfide NR matrix improves light

The plasmonic mechanism is very appealing since this mechanism results in an experimentally improved absorption cross-section of the metallic domain relative to the purely geometric one<sup>309</sup> (which is relatively low for small colloidal NPs). The metal can thus photo-enhance catalytic reactions,<sup>310</sup> with an adjacent wide bandgap SC or insulator (a stable oxide) acting as a support. For example, the Linic group has shown the photocatalytic activity of alumina-supported silver nanostructures towards oxidation reactions.<sup>311</sup> They have ascribed the plasmonic effect manifestation in the form of an electron transfer to antibonding orbitals of oxygen in the adsorbed reactants. Many others have used a variety of metal-metal-oxide combinations; some recent examples include Ag<sup>312</sup> or Rh<sup>313</sup> nanocubes supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, different Au NPs supported or coated on TiO<sub>2</sub>,<sup>314,315</sup> SiO<sub>2</sub>,<sup>316,317</sup> or both (*i.e.*, Au@SiO<sub>2</sub>@TiO<sub>2</sub>),<sup>318</sup> as well as multi-metal combinations as Al antenna-Ir NPs on an

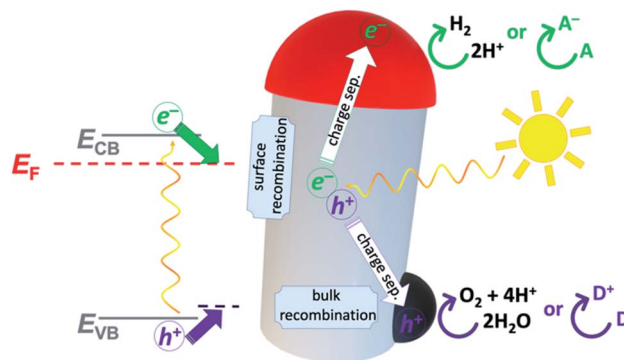


One of the consequences of the plasmonic response is local heat generation through electron-phonon scattering,<sup>318</sup> which has made a distinct contribution to successful photocatalytic CO<sub>2</sub> methanation of Rh/TiO<sub>2</sub>, for example.<sup>318</sup> It has been suggested recently that the catalytic activity of the generated ‘hot-electrons’, *i.e.*, non-thermal charge carriers in the metallic nanoparticles (which are responsible for the photocatalytic



The metal as an electron sink is the other common way to imbue enhanced photocatalytic properties to an absorbing SC nanostructure. The two most commonly reported photocatalytic applications are: (i) light-induced heterogeneous catalysis, mostly performed in a solution, where the colloidal HNSs are suspended, and (ii) photoelectrochemical cell (PEC) setups, where the HNSs are deposited on a photoanode or a photocathode. Colloidal-phase photocatalytic reactions are mainly

As these examples show, a metal domain is beneficial for dye degradation since it attracts photoexcited electrons, and then these electrons may generate hydroxyl and superoxide radicals, which then attack the dyes. To this end, a good practice is to measure not only photodegradation kinetics but also to detect the radicals using methods such as electron paramagnetic resonance (EPR) and a spin trapping agent such as 5,5-

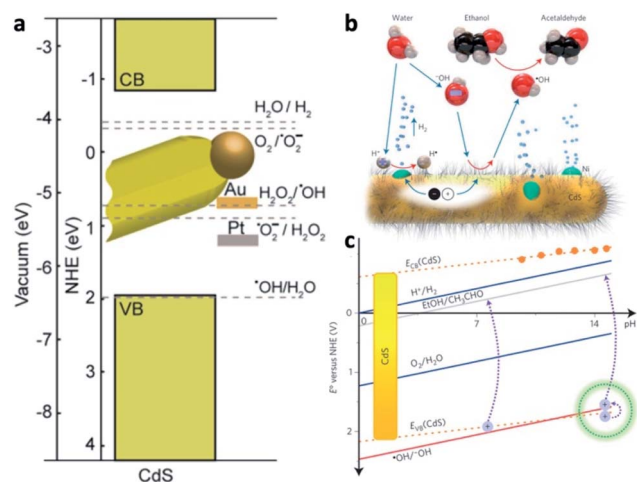


dimethyl-1-pyrroline-N-oxide (DMPO).<sup>168</sup> It is important to stress that especially in the case of the common MB dye, decoloration can result from reversible photoreduction to the leucomethylene blue form,<sup>86,342</sup> which is different from complete degradation (*via* a photooxidative path).<sup>343</sup> MB can also be degraded from an alcoholic solution, where a catalytic amount can be dispersed even in an organic solvent (*e.g.*, Au-Cu<sub>2</sub>S in hexane degrades MB in hexane).<sup>146</sup> Related reactions, which provide further physical insight, are site-specific dye transformations. For example, Ha *et al.* have used an Au-CdS NR HNS to transform an amplex red dye (non-fluorescent) into resorufin (fluorescent) in the presence of H<sub>2</sub>O<sub>2</sub>. This work demonstrated the ability to distinguish between the charge carriers (h<sup>+</sup> and e<sup>-</sup>), which are generated from distinct excitations, namely the gold metal domain, which is excited at its plasmonic resonance wavelength and the CdS SC, which is excited at its shorter-wavelength first excitonic band edge.<sup>344</sup> Since the product is fluorescent, high-resolution localized imaging became possible. In a related report, fluorescent ATTO dyes were used to probe energy transfer and charge separation mechanisms.<sup>345</sup>

## Nanoscale Advances

Another aspect to the role of the metal as an electron sink is that it might reduce electron-hole recombination, thus facilitating oxidation reactions, where the hole ‘attacks’ the oxidized species on the SC’s surface. Such an example is the oxidation of benzyl alcohol by a  $\text{TiO}_2/\text{Pd}$  hybrid in water.<sup>337</sup>

Many additional variations to the cadmium chalcogenide NR/M system were attempted to improve the stability and increase catalytic efficiencies—including variation of the NR’s dimensions, CdSe@CdS seeded NRs, variation of tip size,



Nanoscale Adv., 2020, 2, 930–961 | 949



This journal is © The Royal Society of Chemistry 2020

#### 4.4 Biomedical applications

The tunable properties of HNSs make them candidates for various biomedical applications ranging from bioimaging to active phototherapeutic materials (a representative example will be the previously discussed 'classic' system of CdSe seed@CdS NR/Au NPs).<sup>383</sup> The main concern regarding nanomaterials and the limiting factor for their application, in general, is their toxicity; much progress is being achieved recently in this respect for all kinds of nanomaterials.<sup>384</sup> One possible cure is using heavy-metal-free materials, with significant progress achieved, for example, in SC NR-related systems.<sup>385</sup>

Cheng *et al.* have shown a photothermal effect in a Bi<sub>2</sub>S<sub>3</sub> NR/Au NP system, where bismuth sulfide absorbs a near-infrared (NIR) signal (808 nm laser) and the non-radiative recombination is enhanced *via* the decorating gold NPs, as shown in Fig. 17.<sup>386</sup> Other examples include SiO<sub>2</sub>/Au/Fe<sub>3</sub>O<sub>4</sub> multi-shell structures for photothermal treatment of breast cancer cells and magnetic stimuli functionality for MRI.<sup>387</sup>

Related reported systems also include other hybrids with insulators or double hydroxides, such as core-shell Au NRs in Al and Mg hydroxides<sup>388</sup> and Au NRs partially embedded in silica (Au-SiO<sub>2</sub> Janus particle with the Au NR partially exposed) that show improved infrared response for photo-triggered drug delivery alongside improved loading.<sup>389</sup> Another advancement was reported by Jiang and co-workers, who have synthesized a material with a strong response in the second NIR window (they measured light penetration at 1064 nm) using Au/Cu<sub>9</sub>S<sub>5</sub> HNS, where both the metal and the semiconductor have an LSPR response.<sup>390</sup> A related spherical core@shell Au@Cu<sub>2-x</sub>E (E = S, Se) was demonstrated by Zhu *et al.*, where the coupling of the plasmonic response of the core and the shell was responsible for high extinction coefficient at 808 nm.<sup>391</sup>

Huang and co-workers have used the combination of facet-dependent absorption and a plasmonic response to tune photothermal effects of a simple Au-Cu<sub>2</sub>O system.<sup>113</sup> Sun *et al.* have recently shown a very high photothermal anticancer activity with sub-stoichiometric tungsten trioxide (WO<sub>2.9</sub>) NRs, which exhibit partial metallic character.<sup>392</sup>

It is envisioned that this kind of systems can be further enhanced by an HNS formation and other modifications such as cation intercalation (*e.g.*, NH<sub>4</sub><sup>+</sup>).<sup>393</sup> Biocompatible magnetic domain-containing HNSs are also promising due to their possible magnetic-controllable catch and release, as demonstrated for Au- and FePt-Fe<sub>3</sub>O<sub>4</sub> heterodimers,<sup>394</sup> and multimodal imaging using M/Fe<sub>3</sub>O<sub>4</sub>.<sup>108</sup>

## 5. Perspective

This review presents the synthesis and applications of diverse types of colloidal hybrid metal-semiconductor nanostructures reported over the last several years. One of the significant challenges in this field is the ability to design and increase the functionality of the single nanostructure. The recent advances in the development of multifunctional materials by interfacing multiple types of materials within a single nanoparticle entity are truly promising but still challenging and have to be further explored. Controlling the properties and the functionalities of nanostructures requires primarily a comprehensible knowledge of the material interfacing mechanism of the sought-after hybrid nanostructure. Thankfully, due to the enormous combinations of diverse hybrid nanomaterials, the scientific community has gained a better insight into the thermodynamic and kinetic parameters, which influence the formation and growth of the hybrid nanomaterials, on the road to develop new multi-component systems with increasing complexity.

Further mechanistic elucidation is expected in the near future with the wide-spreading use of advanced electron microscopy techniques. Liquid-phase *in situ* TEM that allows continuous monitoring has made a significant progress in the elucidation of various metallic NP formation<sup>395–397</sup> and transformation,<sup>398,399</sup> as well as other inorganic materials.<sup>400–405</sup> Other related fields such as superlattice self-assembly from NPs are also treated.<sup>406</sup> Though some studies dealing with HNSs exist,<sup>407,408</sup> we envision that a more extensive application of these techniques would thrive, mainly when applied to lower-temperature reactions and some technical limitations (see, for example, a tutorial by De Yoreo and co-workers)<sup>409</sup> are solved.

Another aspect of characterization is the new information gained using aberration-corrected TEM or STEM: the atomic resolution was already applied to gain mechanistic insight for questions such as SC growth kinetics,<sup>410</sup> structural evolution by atom diffusion,<sup>411</sup> surface reconstruction,<sup>185</sup> composition and bonding in multilayer or multivalent oxides,<sup>412</sup> crystal structures of growing 1D materials from metallic catalysts (though usually in gas-phase syntheses),<sup>413,414</sup> defects in 2D materials,<sup>415</sup> liquid metal/metal-nitride interfaces<sup>416</sup> and structural changes on the atomic level of SC NRs/M tips.<sup>417</sup> We expect that its use would expand and allow further understanding of reaction intermediates.

Additionally, advanced analytical microscopy techniques coupled to the microscope will shed light on optical and optoelectronic properties.<sup>418</sup> Advances in electron energy loss spectroscopy (EELS, used in STEM),<sup>419</sup> in particular, could give further insight on the connection between composition (*e.g.*, doping levels, oxidation states)<sup>420</sup> and electronic structure

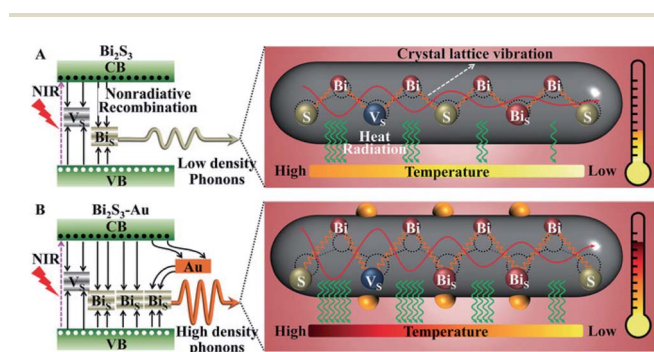


Fig. 17 Schematic photothermal mechanism of (A) Bi<sub>2</sub>S<sub>3</sub> NRs and (B) Bi<sub>2</sub>S<sub>3</sub>/Au HNSs. On the left side an energy diagram shows the SC band edge absorption, vacancy levels and possible gold incorporation are translated into phonons (crystal lattice vibrations, depicted on the right side) that generate the heat. Reproduced from ref. 386 with permission from Wiley-VCH Verlag GmbH & Co., copyright 2018.



SLS	Solution-liquid-solid
SSP	Single-source precursor
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TM	Transition-metal
TMP	Transition-metal phosphide
VB	Valance band
vdW	van der Waals
VLS	Vapor-liquid-solid

## Chemicals and reagents

acac	Acetylacetonate
DDA	Dodecylamine
DDAB	Didodecyltrimethylammonium bromide
DDT	Dodecanethiol
DTAB	<i>n</i> -Dodecyltrimethylammonium bromide
EtOH	Ethanol
MB	Methylene blue
MeCN	Acetonitrile
MO	Methyl orange
MPA	Mercaptopropionic acid
MUA	Mercaptoundecanoic acid
4-NP:	4-Nitrophenol
OA	Oleic acid
OY	Oleylamine
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PVP	Polyvinylpyrrolidone
RhB	Rhodamine B
Rh6G	Rhodamine 6G

## Conflicts of interest

## List of abbreviations

CB	Conduction band
e <sup>-</sup>	Electron
fcc	Face-centered cubic
h <sup>+</sup>	Hole
HAADF	High-angle annular dark field
HER	Hydrogen evolution reaction
HNS	Hybrid nanostructure
ITO	Indium tin oxide
LSPR	Localized surface plasmon resonance
M	Metal
NC	Nanocrystal
NF	Nickel foam
NIR	Near-infrared
NPL	Nanoplate or nanoplatelet
NR	Nanorod
NW	Nanowire
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PCE	Photon-to-electron conversion efficiency
PEC	Photoelectrochemical cell
QD	Quantum dot
rt	Room temperature (25 °C)
SC	Semiconductor

## References

- 1 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706–8715.
- 2 M. V. Kovalenko, L. Manna, A. Cabot, Z. Hens, D. V. Talapin, C. R. Kagan, V. I. Klimov, A. L. Rogach, P. Reiss, D. J. Milliron, P. Guyot-Sionnest, G. Konstantatos, W. J. Parak, T. Hyeon, B. A. Korgel, C. B. Murray and W. Heiss, *ACS Nano*, 2015, **9**, 1012–1057.
- 3 Y. Hong, Y. Wu, S. Wu, X. Wang and J. Zhang, *Isr. J. Chem.*, 2019, **59**, 661–672.
- 4 C. R. Kagan, E. Lifshitz, E. H. Sargent and D. V. Talapin, *Science*, 2016, **353**, aac5523.
- 5 D. V. Talapin and E. V. Shevchenko, *Chem. Rev.*, 2016, **116**, 10343–10345.
- 6 J. van Embden, A. S. R. Chesman and J. J. Jasieniak, *Chem. Mater.*, 2015, **27**, 2246–2285.
- 7 J. Lee, J. Yang, S. G. Kwon and T. Hyeon, *Nat. Rev. Mater.*, 2016, **1**, 16034.
- 8 S. G. Kwon and T. Hyeon, *Small*, 2011, **7**, 2685–2702.
- 9 J. Park, J. Joo, S. G. Kwon, Y. Jang and T. Hyeon, *Angew. Chem., Int. Ed.*, 2007, **46**, 4630–4660.



## Nanoscale Advances

- This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



- 65 E. R. Wacławik and D. V. Golberg, *Langmuir*, 2018, **34**, 7334–7345.
- 66 Y. Ge, T. Wang, M. Zheng, Z. Jiang and S. Wang, *Nanotechnology*, 2019, **30**, 315702.
- 67 X. Chen, W. Chen, P. Lin, Y. Yang, H. Gao, J. Yuan and W. Shangguan, *Catal. Commun.*, 2013, **36**, 104–108.
- 68 Z. Chai, T.-T. Zeng, Q. Li, L.-Q. Lu, W.-J. Xiao and D. Xu, *J. Am. Chem. Soc.*, 2016, **138**, 10128–10131.
- 69 M. Zhukovskiy, P. Tongying, H. Yashan, Y. Wang and M. Kuno, *ACS Catal.*, 2015, **5**, 6615–6623.
- 70 T. Simon, N. Bouchonville, M. J. Berr, A. Vaneski, A. Adrović, D. Volbers, R. Wyrwich, M. Döblinger, A. S. Susha, A. L. Rogach, F. Jäckel, J. K. Stolarczyk and J. Feldmann, *Nat. Mater.*, 2014, **13**, 1013–1018.
- 71 B. Mahler, L. Guillemot, L. Bossard-Giannesini, S. Ithurria, D. Pierucci, A. Ouerghi, G. Patriarche, R. Benbalagh, E. Lacaze, F. Rochet and E. Lhuillier, *J. Phys. Chem. C*, 2016, **120**, 12351–12361.
- 72 A. Manzi, T. Simon, C. Sonnleitner, M. Döblinger, R. Wyrwich, O. Stern, J. K. Stolarczyk and J. Feldmann, *J. Am. Chem. Soc.*, 2015, **137**, 14007–14010.
- 73 T. Mokari, *Science*, 2004, **304**, 1787–1790.
- 74 T. Mokari, C. G. Sztrum, A. Salant, E. Rabani and U. Banin, *Nat. Mater.*, 2005, **4**, 855–863.
- 75 T. Mokari, R. Costi, C. G. Sztrum, E. Rabani and U. Banin, *Phys. Status Solidi*, 2006, **243**, 3952–3958.
- 76 A. E. Saunders, I. Popov and U. Banin, *J. Phys. Chem. B*, 2006, **110**, 25421–25429.
- 77 S. E. Habas, P. Yang and T. Mokari, *J. Am. Chem. Soc.*, 2008, **130**, 3294–3295.
- 78 K. Ahrenstorf, O. Albrecht, H. Heller, A. Kornowski, D. Görlitz and H. Weller, *Small*, 2007, **3**, 271–274.
- 79 B. D. Yuhas, S. E. Habas, S. C. Fakra and T. Mokari, *ACS Nano*, 2009, **3**, 3369–3376.
- 80 H. Schlick, D. Ghosh, L.-K. Fong, H. L. Xin, H. Zheng and A. P. Alivisatos, *Angew. Chem., Int. Ed.*, 2013, **52**, 980–982.
- 81 M. Meyns, N. G. Bastus, Y. Cai, A. Kornowski, B. H. Juárez, H. Weller and C. Klink, *J. Mater. Chem.*, 2010, **20**, 10602.
- 82 T. Okuhata, Y. Kobayashi, Y. Nonoguchi, T. Kawai and N. Tamai, *J. Phys. Chem. C*, 2015, **119**, 2113–2120.
- 83 J. Yang, E. Sargent, S. Kelley and J. Y. Ying, *Nat. Mater.*, 2009, **8**, 683–689.
- 84 I. R. Franchini, G. Bertoni, A. Falqui, C. Giannini, L. W. Wang and L. Manna, *J. Mater. Chem.*, 2010, **20**, 1357–1366.
- 85 M. Dalmases, M. Ibáñez, P. Torruella, V. Fernández-Altable, L. López-Conesa, D. Cadavid, L. Piveteau, M. Nachttegaal, J. Llorca, M. L. Ruiz-González, S. Estradé, F. Peiró, M. V. Kovalenko, A. Cabot and A. Figuerola, *Chem. Mater.*, 2016, **28**, 7017–7028.
- 86 X. Yu, A. Shavel, X. An, Z. Luo, M. Ibáñez and A. Cabot, *J. Am. Chem. Soc.*, 2014, **136**, 9236–9239.
- 87 P. S. Dilsaver, M. D. Reichert, B. L. Hallmark, M. J. Thompson and J. Vela, *J. Phys. Chem. C*, 2014, **118**, 21226–21234.
- 88 A. Ganai, P. S. Maiti, L. Houben, R. Bar-Ziv and M. Bar Sadan, *J. Phys. Chem. C*, 2017, **121**, 7062–7068.
- 89 X. Yu, R. Du, B. Li, L. Liu and Y. Zhang, *J. Phys. Chem. C*, 2017, **121**, 6712–6720.
- 90 E. A. Hernández-Pagán, A. D. P. Leach, J. M. Rhodes, S. Sarkar and J. E. Macdonald, *Chem. Mater.*, 2015, **27**, 7969–7976.
- 91 P. Rukenstein, A. Teitelboim, M. Volokh, M. Diab, D. Oron and T. Mokari, *J. Phys. Chem. C*, 2016, **120**, 15453–15459.
- 92 Y. Nakibli, Y. Mazal, Y. Dubi, M. Wächter and L. Amirav, *Nano Lett.*, 2018, **18**, 357–364.
- 93 B. Li, Y. Zhang, R. Du, L. Gan and X. Yu, *Langmuir*, 2016, **32**, 11639–11645.
- 94 S. Naskar, A. Schlosser, J. F. Miethe, F. Steinbach, A. Feldhoff and N. C. Bigall, *Chem. Mater.*, 2015, **27**, 3159–3166.
- 95 H. Chauhan, Y. Kumar, J. Dana, B. Satpati, H. N. Ghosh and S. Deka, *Nanoscale*, 2016, **8**, 15802–15812.
- 96 S. Naskar, F. Lübckemann, S. Hamid, A. Freytag, A. Wolf, J. Koch, I. Ivanova, H. Pfnür, D. Dorfs, D. W. Bahnemann and N. C. Bigall, *Adv. Funct. Mater.*, 2017, **27**, 1604685.
- 97 Q. Li, F. Zhao, C. Qu, Q. Shang, Z. Xu, L. Yu, J. R. McBride and T. Lian, *J. Am. Chem. Soc.*, 2018, **140**, 11726–11734.
- 98 H. Fridman, L. Tian, K. Shreth, M. Volokh and T. Mokari, *Front. Mater.*, 2020, **6**, 345.
- 99 S.-Y. Tang, H. Medina, Y.-T. Yen, C.-W. Chen, T.-Y. Yang, K.-H. Wei and Y.-L. Chueh, *Small*, 2019, **15**, 1803529.
- 100 E. P. Lazareva, V. F. Kozlovskii, R. B. Vasiliev and A. M. Gaskov, *Russ. J. Inorg. Chem.*, 2018, **63**, 642–646.
- 101 Y. Ben-Shahar, F. Scotognella, I. Kriegel, L. Moretti, G. Cerullo, E. Rabani and U. Banin, *Nat. Commun.*, 2016, **7**, 10413.
- 102 J. Maynadié, A. Salant, A. Falqui, M. Respaud, E. Shaviv, U. Banin, K. Soullantica and B. Chaudret, *Angew. Chem., Int. Ed.*, 2009, **48**, 1814–1817.
- 103 A. B. Ghosh, N. Saha, A. Sarkar, A. K. Dutta, J. Satra and B. Adhikary, *Dalton Trans.*, 2018, **47**, 1071–1081.
- 104 O. Kluge, I. J.-L. Plante, M. Diab, M. Volokh, A. Teitelboim and T. Mokari, *J. Mater. Chem. C*, 2015, **3**, 4657–4662.
- 105 Q. Tan, C. Du, Y. Sun, G. Yin and Y. Gao, *J. Mater. Chem. A*, 2014, **2**, 1429–1435.
- 106 T. Bala, A. Singh, A. Sanyal, C. O'Sullivan, F. Laffir, C. Coughlan and K. M. Ryan, *Nano Res.*, 2013, **6**, 121–130.
- 107 L. J. Zhang, R. Zheng, S. Li, B. K. Liu, D. J. Wang, L. L. Wang and T. F. Xie, *ACS Appl. Mater. Interfaces*, 2014, **6**, 13406–13412.
- 108 S. Das, B. Satpati, H. Chauhan, S. Deka, M. K. Ghosal, C. S. Gopinath and T. Bala, *RSC Adv.*, 2016, **6**, 14658–14665.
- 109 J. Zeng, M. Gong, D. Wang, M. Li, W. Xu, Z. Li, S. Li, D. Zhang, Z. Yan and Y. Yin, *Nano Lett.*, 2019, **19**, 3011–3018.
- 110 H. Wang, D. W. Brandl, F. Le, P. Nordlander and N. J. Halas, *Nano Lett.*, 2006, **6**, 827–832.
- 111 M. Chang, M. Wang, Y. Chen, M. Shu, Y. Zhao, B. Ding, Z. Hou and J. Lin, *Nanoscale*, 2019, **11**, 10129–10136.
- 112 C. Kuo, T. Hua and M. H. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 17871–17878.
- 113 W. Wang, L. Lyu and M. H. Huang, *Chem. Mater.*, 2011, **23**, 2677–2684.

- 113 H. Wang, K. Yang, S. Hsu and M. H. Huang, *Nanoscale*, 2016, **8**, 965–972.
- 114 S. Rej, H. Wang, M.-X. Huang, S. Hsu, C. Tan, F. Lin, J.-S. Huang and M. H. Huang, *Nanoscale*, 2015, **7**, 11135–11141.
- 115 K. Yang, S. Hsu and M. H. Huang, *Chem. Mater.*, 2016, **28**, 5140–5146.
- 116 C.-F. Hsia, C.-H. Chang and M. H. Huang, *Part. Part. Syst. Charact.*, 2018, **35**, 1800112.
- 117 N. Meir, I. Jen-La Plante, K. Flomin, E. Chockler, B. Moshofsky, M. Diab, M. Volokh and T. Mokari, *J. Mater. Chem. A*, 2013, **1**, 1763–1769.
- 118 H. Jing, N. Large, Q. Zhang and H. Wang, *J. Phys. Chem. C*, 2014, **118**, 19948–19963.
- 119 C. Kuo and M. H. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 12815–12820.
- 120 B. Lu, A. Liu, H. Wu, Q. Shen, T. Zhao and J. Wang, *Langmuir*, 2016, **32**, 3085–3094.
- 121 S. Zhang, R. Jiang, Y. Guo, B. Yang, X.-L. Chen, J. Wang and Y. Zhao, *Small*, 2016, **12**, 4264–4276.
- 122 L. Zhang, D. A. Blom and H. Wang, *Chem. Mater.*, 2011, **23**, 4587–4598.
- 123 M. H. Huang, *Small*, 2019, **15**, 1804726.
- 124 J. Li, S. K. Cushing, J. Bright, F. Meng, T. R. Senty, P. Zheng, A. D. Bristow and N. Wu, *ACS Catal.*, 2013, **3**, 47–51.
- 125 S. K. Cushing, J. Li, F. Meng, T. R. Senty, S. Suri, M. Zhi, M. Li, A. D. Bristow and N. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 15033–15041.
- 126 C. Tao, L. An, J. Lin, Q. Tian and S. Yang, *Small*, 2019, **15**, 1903473.
- 127 Y. Lv, S. Duan, Y. Zhu, H. Guo and R. Wang, *Chem. Eng. J.*, 2020, **382**, 122794.
- 128 S. Javaid, Y. Li, D. Chen, X. Xu, Y. Pang, W. Chen, F. Wang, Z. Shao, M. Saunders, J.-P. Veder, G. Jia and F. Jones, *J. Phys. Chem. C*, 2019, **123**, 10604–10613.
- 129 B. K. Patra, S. Khilari, D. Pradhan and N. Pradhan, *Chem. Mater.*, 2016, **28**, 4358–4366.
- 130 F. Vita, C. Innocenti, A. Secchi, F. Albertini, V. Grillo, A. Fiore, P. D. Cozzoli and C. de Julián Fernández, *J. Mater. Chem. C*, 2018, **6**, 12329–12340.
- 131 J. F. S. Fernando, M. P. Shortell, K. C. Vernon, E. A. Jaatinen and E. R. Waclawik, *Cryst. Growth Des.*, 2015, **15**, 4324–4330.
- 132 D. Zeng, P. Gong, Y. Chen, Q. Zhang, Q. Xie and D.-L. Peng, *Nanoscale*, 2016, **8**, 11602–11610.
- 133 T. R. Gordon and R. E. Schaak, *Chem. Mater.*, 2014, **26**, 5900–5904.
- 134 C. W. Li and M. W. Kanan, *J. Am. Chem. Soc.*, 2012, **134**, 7231–7234.
- 135 S. Lee, D. Kim and J. Lee, *Angew. Chem., Int. Ed.*, 2015, **54**, 14701–14705.
- 136 M. Verelst, T. O. Ely, C. Amiens, E. Snoeck, P. Lecante, A. Mosset, M. Respaud, J. M. Broto and B. Chaudret, *Chem. Mater.*, 1999, **11**, 2702–2708.
- 137 W. Liu, L. Chen, L. Cui, J. Yan, S. Zhang and S. Shi, *J. Mater. Chem. A*, 2019, **7**, 15089–15100.
- 138 M. Casavola, R. Buonsanti, G. Caputo and P. D. Cozzoli, *Eur. J. Inorg. Chem.*, 2008, 837–854.
- 139 L.-I. Hung, C.-K. Tsung, W. Huang and P. Yang, *Adv. Mater.*, 2010, **22**, 1910–1914.
- 140 X. Zhu, H. Rong, X. Zhang, Q. Di, H. Shang, B. Bai, J. Liu, J. Liu, M. Xu, W. Chen and J. Zhang, *Nano Res.*, 2019, **12**, 1187–1192.
- 141 Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai and P. A. Alivisatos, *Science*, 2004, **304**, 711–714.
- 142 J. B. Tracy, D. N. Weiss, D. P. Dinega and M. G. Bawendi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 064404.
- 143 J. Ustarroz, M. Kang, E. Bullions and P. R. Unwin, *Chem. Sci.*, 2017, **8**, 1841–1853.
- 144 X. Wang, G. Liu, L. Wang, Z.-G. Chen, G. Q. M. Lu and H.-M. Cheng, *Adv. Energy Mater.*, 2012, **2**, 42–46.
- 145 F. Nan, S. Liang, J.-H. Wang, X.-L. Liu, D.-J. Yang, X.-F. Yu, L. Zhou, Z.-H. Hao and Q.-Q. Wang, *Adv. Opt. Mater.*, 2014, **2**, 679–686.
- 146 N. E. Motl, J. F. Bondi and R. E. Schaak, *Chem. Mater.*, 2012, **24**, 1552–1554.
- 147 S. U. Lee, J. W. Hong, S. Il Choi and S. W. Han, *J. Am. Chem. Soc.*, 2014, **136**, 5221–5224.
- 148 M. L. Nguyen, J. A. Murphy, L. C. Hamlet and B. L. T. Lau, *Environ. Sci.: Nano*, 2018, **5**, 1090–1095.
- 149 Y. Zhang, J. Xia, Y. Liu, L. Qiang and L. Zhu, *Environ. Sci. Technol.*, 2016, **50**, 13283–13290.
- 150 J. van Embden, L. Bourgeois, E. Della Gaspera, L. Waddington, Y. Yin, N. V. Medhekar, J. J. Jasieniak and A. S. R. Chesman, *J. Mater. Chem. A*, 2016, **4**, 7060–7070.
- 151 I. du Fossé, S. ten Brinck, I. Infante and A. J. Houtepen, *Chem. Mater.*, 2019, **31**, 4575–4583.
- 152 B. H. R. Suryanto, C. S. M. Kang, D. Wang, C. Xiao, F. Zhou, L. M. Azofra, L. Cavallo, X. Zhang and D. R. MacFarlane, *ACS Energy Lett.*, 2018, **3**, 1219–1224.
- 153 M. Jiang, W. Liu, X. Yang, Z. Jiang, T. Yao, S. Wei and X. Peng, *ACS Nano*, 2015, **9**, 10950–10960.
- 154 B. Wang, S. He, L. Zhang, X. Huang, F. Gao, W. Feng and P. Liu, *Appl. Catal., B*, 2019, **243**, 229–235.
- 155 Z. Wei, F. Yue, Z. Jin, Z. Fengxia, S. Zhenhuan, D. Benlin, D. Y. C. Leung, Z. Lili and X. Jiming, *ACS Appl. Energy Mater.*, 2019, **2**, 694–704.
- 156 T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons and W. E. Buhro, *Science*, 1995, **270**, 1791–1794.
- 157 T. Hanrath and B. A. Korgel, *J. Am. Chem. Soc.*, 2002, **124**, 1424–1429.
- 158 S. Kan, A. Aharoni, T. Mokari and U. Banin, *Faraday Discuss.*, 2004, **125**, 23–38.
- 159 S. Kan, T. Mokari, E. Rothenberg and U. Banin, *Nat. Mater.*, 2003, **2**, 155–158.
- 160 T. J. Trentler, S. C. Goel, K. M. Hickman, A. M. Viano, M. Y. Chiang, A. M. Beatty, P. C. Gibbons and W. E. Buhro, *J. Am. Chem. Soc.*, 1997, **119**, 2172–2181.
- 161 K.-T. Yong, Y. Sahoo, K. R. Choudhury, M. T. Swihart, J. R. Minter and P. N. Prasad, *Chem. Mater.*, 2006, **18**, 5965–5972.





- This journal is © The Royal Society of Chemistry 2020

## Nanoscale Advances

- This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.







## Review

- Nanoscale Adv., 2020, 2, 930–961 | 959

- 356 S. Giménez and J. Bisquert, *Photoelectrochemical Solar Fuel Production*, Springer International Publishing, Cham, 2016.
- 357 K. Khan, X. Tao, Y. Zhao, B. Zeng, M. Shi, N. Ta, J. Li, X. Jin, R. Li and C. Li, *J. Mater. Chem. A*, 2019, **7**, 15607–15614.
- 358 L. Amirav and A. P. Alivisatos, *J. Phys. Chem. Lett.*, 2010, **1**, 1051–1054.
- 359 P. Kalisman, L. Houben, E. Aronovitch, Y. Kauffmann, M. Bar-Sadan and L. Amirav, *J. Mater. Chem. A*, 2015, **3**, 19679–19682.
- 360 E. Aronovitch, P. Kalisman, S. Mangel, L. Houben, L. Amirav and M. Bar-Sadan, *J. Phys. Chem. Lett.*, 2015, **6**, 3760–3764.
- 361 Y. Ben-Shahar, J. P. Philbin, F. Scotognella, L. Ganzer, G. Cerullo, E. Rabani and U. Banin, *Nano Lett.*, 2018, **18**, 5211–5216.
- 362 L. Ma, K. Chen, F. Nan, J.-H. Wang, D.-J. Yang, L. Zhou and Q.-Q. Wang, *Adv. Funct. Mater.*, 2016, **26**, 6076–6083.
- 363 T. Kawawaki, T. Nakagawa, M. Sakamoto and T. Teranishi, *J. Am. Chem. Soc.*, 2019, **141**, 8402–8406.
- 364 X. Li, J. Yu, M. Jaroniec and X. Chen, *Chem. Rev.*, 2019, **119**, 3962–4179.
- 365 S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, *Angew. Chem., Int. Ed.*, 2013, **52**, 7372–7408.
- 366 N. Waiskopf, Y. Ben-Shahar, M. Galchenko, I. Carmel, G. Moshitzky, H. Soreq and U. Banin, *Nano Lett.*, 2016, **16**, 4266–4273.
- 367 S. Wang, Y. Gao, S. Miao, T. Liu, L. Mu, R. Li, F. Fan and C. Li, *J. Am. Chem. Soc.*, 2017, **139**, 11771–11778.
- 368 T. Lan, C. Mundt, M. Tran and S. Padalkar, *J. Mater. Res.*, 2017, **32**, 1656–1664.
- 369 H. Gao, C. Liu, H. E. Jeong and P. Yang, *ACS Nano*, 2012, **6**, 234–240.
- 370 J. F. Miethe, F. Lübckemann, J. Poppe, F. Steinbach, D. Dorfs and N. C. Bigall, *ChemElectroChem*, 2018, **5**, 175–186.
- 371 N. C. Greenham, X. Peng and A. P. Alivisatos, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 17628–17637.
- 372 W. U. Huynh, *Science*, 2002, **295**, 2425–2427.
- 373 C. Cho, J. H. Song, C. Kim, S. Jeong and J.-Y. Lee, *Sci. Rep.*, 2017, **7**, 17393.
- 374 C. Liu, C. Zhao, X. Zhang, W. Guo, K. Liu and S. Ruan, *J. Phys. Chem. C*, 2016, **120**, 6198–6205.
- 375 I. Vangelidis, A. Theodosi, M. J. Beliatas, K. K. Gandhi, A. Laskarakis, P. Patsalas, S. Logothetidis, S. R. P. Silva and E. Lidorikis, *ACS Photonics*, 2018, **5**, 1440–1452.
- 376 H. Wang, Y. Ding, W. Chen, Y. Liu, D. Tang, G. Cui, W. Li, J. Shi and Z. Bo, *ACS Appl. Mater. Interfaces*, 2018, **10**, 30919–30924.
- 377 Q.-D. Ou, Y.-Q. Li and J.-X. Tang, *Adv. Sci.*, 2016, **3**, 1600123.
- 378 Y. H. Jang, Y. J. Jang, S. Kim, L. N. Quan, K. Chung and D. H. Kim, *Chem. Rev.*, 2016, **116**, 14982–15034.
- 379 K. Ueno, T. Oshikiri, Q. Sun, X. Shi and H. Misawa, *Chem. Rev.*, 2018, **118**, 2955–2993.
- 380 W. Wang and L. Qi, *Adv. Funct. Mater.*, 2019, **29**, 1807275.
- 381 G. H. Carey, A. L. Abdelhady, Z. Ning, S. M. Thon, O. M. Bakr and E. H. Sargent, *Chem. Rev.*, 2015, **115**, 12732–12763.
- 382 H. M. Wang, S. Ming, L. Zhang, X. Li, W. Li and Z. Bo, *Nanoscale*, 2018, **10**, 11745–11749.
- 383 J. Fan, M. Liu, C. Li, S. Hong, D. Zheng, X.-H. Liu, S. Chen, H. Cheng and X.-Z. Zhang, *Nanoscale Horiz.*, 2017, **2**, 349–355.
- 384 L. Yan, F. Zhao, J. Wang, Y. Zu, Z. Gu and Y. Zhao, *Adv. Mater.*, 2019, **31**, 1805391.
- 385 G. Jia, Y. Pang, J. Ning, U. Banin and B. Ji, *Adv. Mater.*, 2019, **31**, 1900781.
- 386 Y. Cheng, Y. Chang, Y. Feng, H. Jian, Z. Tang and H. Zhang, *Angew. Chem., Int. Ed.*, 2018, **57**, 246–251.
- 387 R. Bardhan, W. Chen, M. Bartels, C. Perez-Torres, M. F. Botero, R. W. McAninch, A. Contreras, R. Schiffr, R. G. Pautler, N. J. Halas and A. Joshi, *Nano Lett.*, 2010, **10**, 4920–4928.
- 388 K. Ma, Y. Li, Z. Wang, Y. Chen, X. Zhang, C. Chen, H. Yu, J. Huang, Z. Yang, X. Wang and Z. Wang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 29630–29640.
- 389 Y. Liu, C. Wei, L. Huang, W. Liu, J. Lin, L. Chen, Y. Yang, P. Hu, A. Liu and X. Wang, *ACS Biomater. Sci. Eng.*, 2019, **5**, 740–747.
- 390 X. Ding, C. H. Liow, M. Zhang, R. Huang, C. Li, H. Shen, M. Liu, Y. Zou, N. Gao, Z. Zhang, Y. Li, Q. Wang, S. Li and J. Jiang, *J. Am. Chem. Soc.*, 2014, **136**, 15684–15693.
- 391 H. Zhu, Y. Wang, C. Chen, M. Ma, J. Zeng, S. Li, Y. Xia and M. Gao, *ACS Nano*, 2017, **11**, 8273–8281.
- 392 L. Sun, Z. Li, R. Su, Y. Wang, Z. Li, B. Du, Y. Sun, P. Guan, F. Besenbacher and M. Yu, *Angew. Chem., Int. Ed.*, 2018, **57**, 10666–10671.
- 393 Z. Fang, B. Wang, W. Wang, J. Yan and G. Pang, *Eur. J. Inorg. Chem.*, 2019, 245–249.
- 394 J. S. Beveridge, M. R. Buck, J. F. Bondi, R. Misra, P. Schiffer, R. E. Schaak and M. E. Williams, *Angew. Chem., Int. Ed.*, 2011, **50**, 9875–9879.
- 395 A. Hutzler, T. Schmutzler, M. P. M. Jank, R. Branscheid, T. Unruh, E. Spiecker and L. Frey, *Nano Lett.*, 2018, **18**, 7222–7229.
- 396 Y. Cheng, J. Tao, G. Zhu, J. A. Soltis, B. A. Legg, E. Nakouzi, J. J. De Yoreo, M. L. Sushko and J. Liu, *Nanoscale*, 2018, **10**, 11907–11912.
- 397 A. Hutzler, B. Fritsch, M. P. M. Jank, R. Branscheid, R. C. Martens, E. Spiecker and M. März, *Adv. Mater. Interfaces*, 2019, **6**, 1901027.
- 398 L. Luo, Y. Nian, S. Wang, Z. Dong, Y. He, Y. Han and C. Wang, *Angew. Chem., Int. Ed.*, 2020, **59**, 2505–2509.
- 399 S. Lee, J. Im, Y. Yoo, E. Bitzek, D. Kiener, G. Richter, B. Kim and S. H. Oh, *Nat. Commun.*, 2014, **5**, 3033.
- 400 L. Liu, S. Zhang, M. E. Bowden, J. Chaudhuri and J. J. De Yoreo, *Cryst. Growth Des.*, 2018, **18**, 1367–1375.
- 401 C. Hobbs, S. Jaskaniec, E. K. McCarthy, C. Downing, K. Opelt, K. Güth, A. Shmeliov, M. C. D. Mourad, K. Mandel and V. Nicolosi, *npj 2D Mater. Appl.*, 2018, **2**, 4.
- 402 Y.-C. Chou, W.-W. Wu, S.-L. Cheng, B.-Y. Yoo, N. Myung, L. J. Chen and K. N. Tu, *Nano Lett.*, 2008, **8**, 2194–2199.
- 403 X. Peng, A. Abelson, Y. Wang, C. Qian, J. Shangquan, Q. Zhang, L. Yu, Z. W. Yin, W. Zheng, K. C. Bustillo,

## Review

- X. Guo, H. G. Liao, S. G. Sun, M. Law and H. Zheng, *Chem. Mater.*, 2019, **31**, 190–199.
- 404 L. Liu, M. L. Sushko, E. C. Buck, X. Zhang, L. Kovarik, Z. Shen, J. Tao, E. Nakouzi, J. Liu and J. J. De Yoreo, *J. Phys. Chem. Lett.*, 2019, **10**, 6827–6834.
- 405 N. Bhattarai, D. L. Woodall, J. E. Boercker, J. G. Tischler and T. H. Brintlinger, *Nanoscale*, 2019, **11**, 14573–14580.
- 406 T. Woehl, *ACS Nano*, 2019, 12272–12279.
- 407 F.-C. Chen, J.-Y. Chen, Y.-H. Lin, M.-Y. Kuo, Y.-J. Hsu and W.-W. Wu, *Nanoscale*, 2019, **11**, 10486–10492.
- 408 G. Zhou, L. Luo, L. Li, J. Ciston, E. A. Stach, W. A. Saidi and J. C. Yang, *Chem. Commun.*, 2013, **49**, 10862–10864.
- 409 G. Zhu, H. Reiner, H. Cölfen and J. J. De Yoreo, *Micron*, 2019, **118**, 35–42.
- 410 S. Mangel, E. Aronovitch, A. N. Enyashin, L. Houben and M. Bar-Sadan, *J. Am. Chem. Soc.*, 2014, **136**, 12564–12567.
- 411 B. Jin, F. Zhang, G. Wu, T. Yuan, Q. Wang, H. Zhou, Y. Zhao, G. Zhang and X. Hong, *Chem. Commun.*, 2019, **55**, 13176–13178.
- 412 Y.-H. Ting, C.-W. Huang, A. Yasuhara, S.-Y. Chen, J.-Y. Chen, L. Chang, K.-C. Lu and W.-W. Wu, *Nano Lett.*, 2019, DOI: 10.1021/acs.nanolett.9b03510.
- 413 R. R. Zamani and J. Arbiol, *Nanotechnology*, 2019, **30**, 262001.
- 414 H. Gao, Q. Sun, W. Sun, H. H. Tan, C. Jagadish and J. Zou, *Nano Lett.*, 2019, **19**, 8262–8269.
- 415 J. Hong, C. Jin, J. Yuan and Z. Zhang, *Adv. Mater.*, 2017, **29**, 1606434.
- 416 A. Kumamoto, N. Shibata, K. Nayuki, T. Tohei, N. Terasaki, Y. Nagatomo, T. Nagase, K. Akiyama, Y. Kuromitsu and Y. Ikuhara, *Sci. Rep.*, 2016, **6**, 22936.
- 417 E. Aronovitch, P. Kalisman, L. Houben, L. Amirav and M. Bar-Sadan, *Chem. Mater.*, 2016, **28**, 1546–1552.
- 418 J. F. S. Fernando, C. Zhang, K. L. Firestein and D. Golberg, *Small*, 2017, **13**, 1701564.
- 419 M. J. Zachman, J. A. Hachtel, J. C. Idrobo and M. Chi, *Angew. Chem., Int. Ed.*, 2019, 2–15.
- 420 X. Guo, M. K. Chen, X. Gao, C. Xu, M. Sun, G. Liu, X. Guo, Y. Cai, B. Huang, J. Deng, J. Z. Liu, A. Tricoli, N. Wang, C. Dwyer and Y. Zhu, *Chem. Mater.*, 2019, **31**, 5769–5777.
- 421 A. Yamaguchi, M. Haruta, T. Nemoto and H. Kurata, *Appl. Phys. Lett.*, 2018, **113**, 053101.
- 422 D. A. Muller, L. F. Kourkoutis, M. Murfitt, J. H. Song, H. Y. Hwang, J. Silcox, N. Dellby and O. L. Krivanek, *Science*, 2008, **319**, 1073–1076.
- 423 W. Zhan, V. Venkatachalapathy, T. Aarholt, A. Y. Kuznetsov and Ø. Prytz, *Sci. Rep.*, 2018, **8**, 848.
- 424 E. Pomarico, Y. J. Kim, F. J. García De Abajo, O. H. Kwon, F. Carbone and R. M. Van Der Veen, *MRS Bull.*, 2018, **43**, 497–503.
- 425 R. R. Zamani, F. S. Hage, S. Lehmann, Q. M. Ramasse and K. A. Dick, *Nano Lett.*, 2018, **18**, 1557–1563.
- 426 D. Wolf, R. Hübner, T. Niermann, S. Sturm, P. Prete, N. Lovergine, B. Büchner and A. Lubk, *Nano Lett.*, 2018, **18**, 4777–4784.
- 427 M. R. McCartney, R. E. Dunin-Borkowski and D. J. Smith, *Ultramicroscopy*, 2019, **203**, 105–118.
- 428 J. Miao, P. Ercius and S. J. L. Billinge, *Science*, 2016, **353**, aaf2157.
- 429 Y. Yao, C. Patzig, Y. Hu and R. W. J. Scott, *J. Phys. Chem. C*, 2015, **119**, 21209–21218.
- 430 S. Mozaffari, W. Li, M. Dixit, S. Seifert, B. Lee, L. Kovarik, G. Mpourmpakis and A. M. Karim, *Nanoscale Adv.*, 2019, **1**, 4052–4066.
- 431 S. Nilsson, D. Albinsson, T. J. Antosiewicz, J. Fritzsche and C. Langhammer, *Nanoscale*, 2019, **11**, 20725–20733.
- 432 M. D. Susman, Y. Feldman, T. A. Bendikov, A. Vaskevich and I. Rubinstein, *Nanoscale*, 2017, **9**, 12573–12589.
- 433 Y. Bu, C. J. Weststrate, J. W. Niemantsverdriet and H. O. A. Fredriksson, *ACS Catal.*, 2016, **6**, 7994–8003.
- 434 H. Yoshida, R. Kakei, A. Fujiwara, Y. Uchida and M. Machida, *J. Phys. Chem. C*, 2018, **122**, 28173–28181.
- 435 A. Belianinov, A. V. Ievlev, M. Lorenz, N. Borodinov, B. Doughty, S. V. Kalinin, F. M. Fernández and O. S. Ovchinnikova, *ACS Nano*, 2018, **12**, 11798–11818.