

REVIEW

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

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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.

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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 method¹ 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.² 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,³ through different applications in electronic and optoelectronic devices,⁴ to commercialization in displays and bio-labeling, which are already on the market.⁵

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.*⁶ and Hyeon and co-workers^{7–9} 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,^{10–18} yolk/shell^{19–21} and heterodimers (usually two or more quasi-spherical shapes forming a heterojunction^{22–24} as well as acorn-style structures²⁵). When the QD serves as a seed for an anisotropic structure such as a rod,²⁶ tetrapod^{26,27} or octapod,²⁸ more complex structures result,²⁹ 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)^{6,30,31} or even branched,³² 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,³³ to 'double' QD fixed in a rod with unique optoelectronic properties.³⁴ 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.³⁵

Both shape and size dictate the electronic structure in metals³⁶ and in semiconductors due to different quantum-confinement effects.³⁷ Noteworthy, many electronic and optical properties of nanocrystals result not only from dimensionality and size but also from surface properties.³⁸ 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,

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ranging from inherent physical properties to functional applications such as controlled self-assembly into superlattices without the inherent anisotropy of the HNS.³⁹ The main criterion of distinction between the various possible nanohybrids is the type of the interface present: SC/SC,¹⁶ M/M,⁴⁰ and M/SC.^{41,42} For practical applications such as photocatalysis, multiple interfaces can also be combined.⁴³

In this review, we focus on the tremendous synthetic progress achieved in the formation of hybrid inorganic M/SC nanostructures and their interfaces, mainly in colloidal liquid-phase syntheses. The building blocks of HNSs are commonly referred to as nanocrystals (NCs) and nanoparticles (NPs), with NCs usually referring to a semiconductor and NPs—despite being a general term—usually implies a metallic nano-object. Since the chemical principles of nanoscale synthesis have been reviewed,⁴⁴ we will emphasize the mechanisms of growth and precise control over the formed interfaces between metals and semiconductors (with a special focus on the II–VI family—the metal-chalcogenide (O, S, Se, Te) materials and formation of anisotropy or asymmetry). We refer the reader to excellent reviews by Cozzoli and co-workers,^{45,46} Manna and co-workers,⁴⁷ and Banin and co-workers,⁴⁸ who set the groundwork for the description of hybrid nanostructures, and a recent review from Zhang and co-workers on epitaxial multicomponent HNSs.⁴⁹ These studies give a broad overview of the development of the field and various possible interfaces that can form alongside thermodynamic requirements for the growth of HNSs. Having this knowledge at the reader's disposal allows us to select illustrative HNS examples (including knowledge accumulated in our group) to elaborate the chemical principles of colloidal metal–semiconductor HNS synthesis, and explore new synthetic approaches for the formation of HNSs with increasing complexity (Section 3), which were developed during the last decade such as using a total-synthesis framework for formation of high-order hybrid nanoparticles, developed by Schaak and co-workers.^{50,51}

Furthermore, we mention in Section 2.2 additional non-semiconductor transition metal–nonmetal compounds, which have many synthetic similarities to semiconductors and can form during HNS synthesis. Finally, we demonstrate how the new emergent properties of the various HNSs are beneficial in selected applications, such as (photo)catalysis (Section 4).

2. Formation of binary metal/semiconductor hybrid nanostructures

Discussing M/SC interfaces raises several interesting scientific questions. What is the mechanism behind the possibility of forming an intimate interface between two different (ordered) materials? What keeps the final structure stable? What are the underlying thermodynamic, kinetic and mechanistic principles (and details) that are responsible for the intermediate steps of the reaction? What is the interplay between the chosen precursors and the required external energy source (photons, electrons, thermal energy, electrochemical potential, *etc.*) required to drive the reaction forward? What are the effects of

the size and shape of the domains and the interface on the possible structures? And finally, which new phenomena arise from the successful formation of the hybrid at the nanoscale?

With these scientific questions in mind, a simplified M/SC HNS application-oriented design scheme may be proposed: (i) determine the relevant properties of the individual metal and semiconductor domains; (ii) specify the physical, mechanical, chemical, optical or electronic properties that are expected to change or remain unaltered after the hybrid structure has been synthesized; (iii) verify that the property-combination is suitable for the potential applications. Once decided, the most-suitable synthetic procedure can be designed. Our goal in this review is to give an overview of the most up-to-date answers to the chemistry-of-materials questions, with a focus on the synthetic possibilities.

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,⁵² 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).⁵³

2.1 Colloidal routes to form M/SC interfaces

In the colloidal synthesis realm, nanocrystals either crystallize on predetermined sites or form in a solution due to a nucleation event. Since homogeneous nucleation is less favorable than heterogeneous nucleation on a pre-existing nucleation site, the planned placement of nucleation sites allows the synthesis of complicated nanostructures in a variety of techniques. The same considerations apply during the growth of a material—the free energy barrier is lower for the nucleation of a precursor on an existing crystal than for spontaneous homogeneous nucleation.

This basic thermodynamic principle,⁵⁴ 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



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

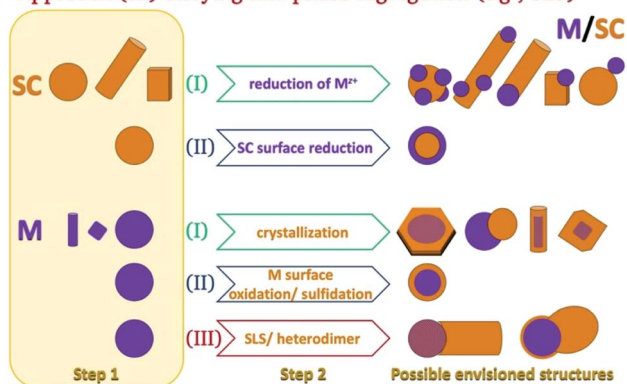


Fig. 1 Schematic options to form nanoscale colloidal-phase heterostructures using a starting semiconductor (SC, orange) or metal (M, purple) structure. Approach (I): nucleation of M over SC or SC over M; approach (II): partial transformation of the first structure (reduction at the surface of a binary 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.*, Cu₂O into Cu₂O/Cu⁰).⁵⁵

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 Au(III) to Au⁰, but alcohols, amines,⁵⁶ *etc.* are also common reducing agents. Noticeable alternatives include the use of metal carbonyl complexes, where the metal's oxidation state is 0.⁵⁷ 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.⁵⁸ Alivisatos and co-workers have shown photodeposition of Pt on CdS and CdSe–CdS core-shell NRs in toluene.⁵⁹ 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.⁶⁰ 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).⁶¹

Carbone *et al.* have used UV light in 9 : 1 v/v CHCl_3 : ethanol (EtOH) to achieve controlled reduction of gold on the tips of CdS and $\text{CdSe}(\text{core})@(\text{shell})\text{CdS}$ NRs.⁶² 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 $\text{CdSe}@ \text{CdS}$ 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.⁶³ 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

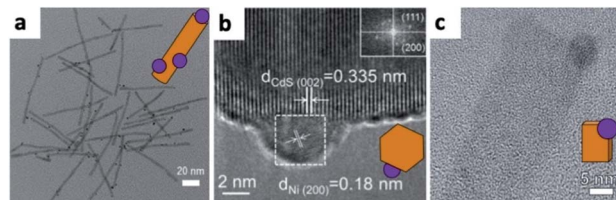
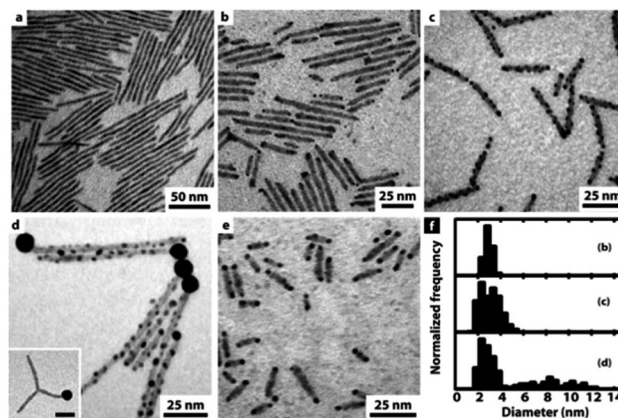


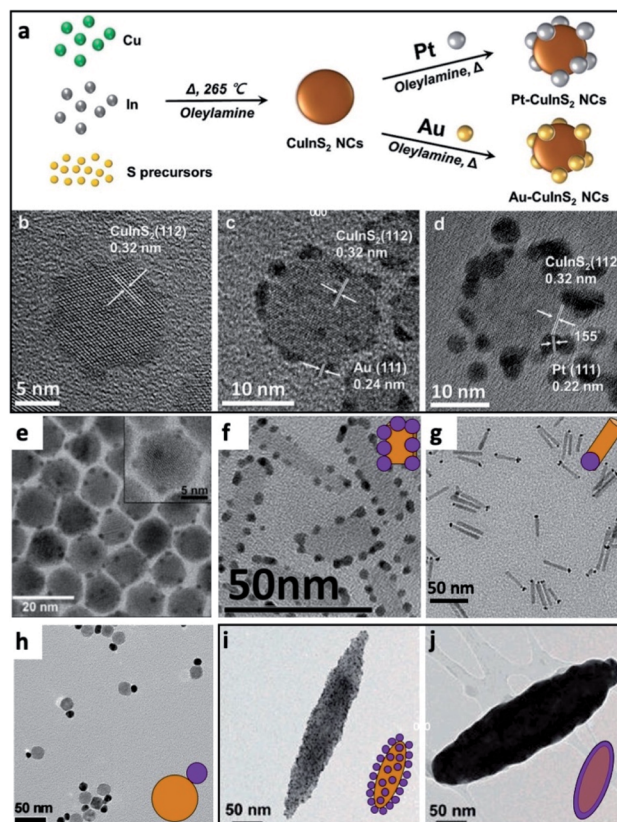
Fig. 2 Examples of metal photodeposition on SCs. (a) Pt/CdSe–CdS NRs *via* a non-selective Pt domain photodeposition reaction carried out in an ionic liquid, adapted from ref. 61, Creative Commons Attribution 4.0 International Public License, published by Beilstein-Institut, copyright 2019. (b) Ni/CdS 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,⁷⁷ 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.^{76,78} 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.⁷⁹ 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.¹⁰¹ 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.*,⁸² 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-CeO₂.¹⁰⁴ An

2.1.3 Metal NPs as seeds for growth of semiconductors.

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of a binary semiconductor to its metal, when the transformation is performed on a metallic ‘reactant’, *e.g.*, formation of Cu(0) particles over Cu₂O films for CO₂ reduction purposes,¹³⁴ and cyclic voltammetry in the presence of Cl[−] anions producing a chloride-stabilized biphasic Cu–Cu₂O electrocatalyst from Cu₂O.¹³⁵

A partial oxidation can take place on various starting morphologies: for example, different spherical NPs,¹³⁶ and nanowires (NWs, such as copper into cuprous oxide forming 1D Cu@Cu₂O NWs).¹³⁷ As discussed by Cozzoli and co-workers,¹³⁸ 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 Cu₂O shell (the thickness of which depends on the elapsed time);¹³⁹ 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 Cu₂O shell due to similarity with the Ag core's crystal structure;¹⁴⁰ Pt-Co core-shell NPs can be oxidized to Pt-CoO by blowing an O₂/Ar 1 : 4 v/v mixture into the solution at 455 K;¹⁴¹ Co is especially prone to oxidation as surface oxidation occurs even when the synthesis is carried out using standard air-free techniques.¹⁴² 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).¹⁴³

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;¹⁴⁴ in this example—by treatment with Na₂S(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) Ag₂S shell HNSs.¹⁴⁵

Schaak and co-workers have designed bimetallic AuCu NPs, which were converted to Au-Cu₂S when heated under bubbling oxygen in the presence of an OY surfactant and sulfur.¹⁴⁶ 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 Cu₂S SC. About 80% chemical yield is achieved, while only 3% of the particles seen in the TEM images are non-hybrid Cu₂S 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–Cu₂S 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 Cu₂S, *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–Cu₂S HNSs were formed but with yield *ca.* 16%—this different low yield suggests that the phase-segregation mechanism is the major reaction path.¹⁴⁶

Silver is especially popular as the metal transformed into Ag₂S.^{147,148} 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 Na₂S the silver was sulfidized, resulting in a M–SC heterodimer.¹⁴⁷ This effect can also happen unintentionally, as in the case of Ag NWs, which are sulfidized under environmental conditions.¹⁴⁹

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 CS₂, and DDT being the solvent) to form either core/shell or heterostructures of Ag/Ag₈GeS₆.¹⁵⁰

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.*, Cd⁰ in a cadmium chalcogenide) has significant influence as it forms a trap.¹⁵¹ On a larger scale, an

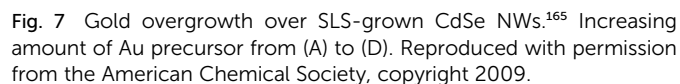
ammonia electrosynthesis catalyst was prepared by reduction of iron oxyhydroxide to form a core-shell α Fe–Fe₃O₄ hybrid by annealing under a reducing H₂(g) environment.¹⁵² Another interesting related example is the formation of a bimetallic thin layer in a HNS: Peng and co-workers have shown that for Pt/Fe₃O₄ core/shell triangular nanoprisms, an interfacial iron-platinum layer is formed.¹⁵³ 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 NaBH₄ 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.¹⁵⁴ Aqueous-phase reduction using NaBH₄ was used to form a complex Ag/AgBr/BiVO₄ photocatalyst.¹⁵⁵ First, AgBr was precipitated over hydrothermally prepared BiVO₄ microspheres from a solution of Ag⁺(aq) and Br[–](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.¹⁵⁵

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.¹⁵⁶ 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.^{157–163} 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.¹⁶⁴ 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).¹⁶⁴ 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 TiO₂ over Ag NW cores, which allows deposition of multiple ZnO NPs as the sheath.¹⁷⁰ 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.¹⁷¹ Since the outcome is attachment based on random physical interactions without controlled interfaces, we will not discuss this synthetic approach further.



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 AuCl₃ reduction procedure.⁸⁰ They have reacted the NCs in the presence of OY and an Au(III) complex resembling Au(III)-DDAB (specifically, AuCl₃ 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

2.1.7 Complementary techniques that allow HNS formation and transformation. An exciting new pathway for control over the metal growth on a SC is the use of various soft templates. Weichelt *et al.* have shown that anchoring DNA functionalization of the surface of CdS NRs allows their placement in DNA origami, which in turn allows pre-determined and controlled deposition of metal.¹⁷⁵ Lin *et al.* have recently shown the formation of hollow hybrids of Au or Pt with TiO₂, ZrO₂ and Ce_xTi_{1-x}O₂ and applied the Pt/ZrO₂ hybrid as a stable catalyst for methane combustion.¹⁷⁶ They have used a sol-gel based synthesis of metal oxides, forming a low-crystallinity oxide. They complete the first step by using urea and formamide polymerization. This step is a polymerization-induced colloid aggregation, which captures both the metal oxide and the metal salt. As a second step they heat the system, which crystallizes and hollows out the metal oxide spheres with metallic nanoparticles trapped within the (now crystalline) metal oxide shell.¹⁷⁶

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TMPs²¹⁷ are common as the metallic cocatalysts in colloidal SC/M systems. Hybrid systems with a light absorbing semiconductor such as CdS include CdS QDs–TMP (CoP, Ni₂P and Cu₂P)²¹⁸ and CdS NRs–TMP (MoP,²¹⁹ Ni₂P and Co₂P²²⁰), which were used for water reduction, while electrostatically assembled Co₃O₄ on CdS NRs were used as water oxidation catalysts.²²¹ It is important to stress that not all phosphides have metal-like properties, and various semiconductors are constantly synthesized and their properties are investigated, for example 1D SnIP.²²²

In the field of electrocatalysis various sulfides, phosphides, nitrides, oxides and (oxy)hydroxides are common catalysts, which are deposited on a substrate that serves as the electrode and they enhance either or both the activity and stability (for example, due to higher stability than the Si substrate in a strong alkaline environment).^{223–227} A common starting high-specific-surface-area metallic substrate is nickel foam (NF), on which gas-phase electrodeposition and a variety of solvothermal reactions are used to deposit the metallic catalyst. Various redox catalysts were deposited on NF such as binary Ni-based materials, *e.g.*, Ni₂P,²²⁸ Mo-doped Ni₂P,²²⁹ ternary amorphous tungsten-doped Ni₂P,²²⁸ or multiphase nickel sulfides,²³⁰ taking advantage of the abundant Ni surface. Electrodeposition allows forming CoPi over NiFe foam as well as Ni and Co oxides over NF.²³¹

3D crystalline Co/amorphous Co₃O₄ core/shell nanosheets were demonstrated by a solution-phase deposition of cobalt oxide on the NF substrate, followed by partial reduction using hydrogen at 200 °C (where the newly formed Co crystals are the core of the amorphous Co₃O₄).²³² More complex systems include NF supported 1D/1D hybrids of Ni₁₂P₅ nanowires over Ni₃S₂ nanorods²³³ and Pt over NF that was transformed into a mixture of nickel phosphides *via* solvothermal phosphorization.²³⁴

Phosphorization is also common in the gas-phase, for example by decomposition of NaH₂PO₂ at elevated temperature under a protective Ar atmosphere to transform a Ni/Cu/polymer into Ni₂P–Cu₂P@NiCuC,²³⁵ or trialkylphosphines over different metal foils, under 5% H₂/Ar flow to eliminate surface oxides.²³⁶ In another recent phosphorization example, In-doped cobalt oxide was transformed into CoO/CoP for OER application in metal–air batteries.²³⁷ Another approach is formation of a hybrid structure which uses low amounts of precious metal (for example, Co₂P/Pt core/shell NRs),²³⁸ and subsequently deposit it on an electrode, possibly in the form of a carbon matrix.

Recently, novel approaches have been utilized for the formation of 3D porous substrates *via* metallization, for the subsequent transformation into metal phosphides *etc.*, for example using virus templates to form Ni₃P or Ni₂P and Ni₅P₄.²³⁹

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.²⁴⁰

2.3 The HNS as a platform for hollow NPs

An interesting synthetic path to achieve hollow nanostructures has been demonstrated by several groups involving types of

core@shell morphologies.²⁴¹ Hollow NP formation is especially easy to detect when the formation is performed *in situ* using the electron beam of an electron microscope.²⁴² Alongside the previously mentioned selective metal etching (using I₂) of an HNS, leaving voids in the SC (Fig. 9a–c),¹³⁰ one of the most common methods to achieve hollow NSs is the nanoscale Kirkendall effect,¹⁴¹ where a void is formed in NPs due to a significant difference in diffusion rates. In their report, Yin *et al.* have first demonstrated a designed experiment that harnesses this effect on the nanoscale with Co NPs. They showed how cobalt is sulfidized upon addition of a sulfur solution into a pre-heated Co NP solution. The hollow Co₉S₈ (at different Co/S ratios, also Co₃S₄ or their mixtures) is formed because the Co core that leaches out through the CoS shell much faster than sulfur is able to diffuse from the exterior, through the formed shell, resulting in hollow CoS as a representative cobalt chalcogenide. Another example is the formation of Ag₂S nanotubes from ZnS NRs while the metallic Au tip is transformed into a bimetallic AuAg tip (Fig. 9d–h).²⁴³

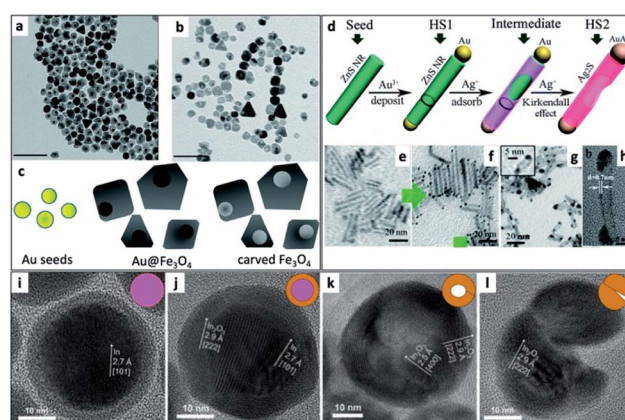


Fig. 9 Hollow nanostructures derived from HNSs. (a–c) Au NPs serve as seeds for the growth of a shell (Au@Fe₃O₄, TEM shown in (a)), subsequently etched with iodine, removing the gold and resulting in carved Fe₃O₄ (b); scale bars are 100 nm; (c) scheme.¹³⁰ (d–h) The nanoscale Kirkendall effect is responsible for the formation of Ag₂S nanotubes with a gold–silver tip: (d) the synthetic scheme, (e) ZnS NRs (*d* ~ 3 nm) serve as seeds for the reduction of gold on its tips (HS1, shown in (f)); following the exposure of HS1 to Ag⁺ ions two phenomena occur—the Au tip is alloyed to form an AuAg tip and the rod is transformed *via* the Kirkendall effect (silver cations diffuse inside, replacing the zinc cations, which diffuse outside) resulting in a hollow silver sulfide nanotube, Ag₂S NT/AuAg (HS2); confirmation of the mechanism is evident from TEM images (g), where *d* ~ 5 nm; a wall thickness of 0.8 ± 0.1 nm is confirmed by (h) HRTEM.²⁴³ (i–l) Hollow indium oxide NPs are formed *via* a non-Kirkendall mechanism in a deaerated atmosphere,²⁴⁹ namely In NPs (i) with a native amorphous InO_x shell are first thermally oxidized to form an In@In₂O₃ core@shell (j), additional heating is responsible for crack formation due to thermal expansion and void-formation, resulting in hollow In₂O₃ (k); some NPs exhibit significant cracking shown in (l); the inset of every TEM image contains a schematic cartoon of the NS. (a–c) Adapted from ref. 130 with permission from the Royal Society of Chemistry, copyright 2018. (d–h) Adapted from ref. 243 with permission from the Royal Society of Chemistry, copyright 2015. (i–l) Adapted with permission from Wiley-VCH Verlag GmbH & Co., copyright 2013.



A 'reversed' nanoscale Kirkendall effect has also been reported, where Au-decorated an InAs HNS was used as the starting material for the formation of a crystalline metallic Au core/amorphous (oxidized) InAs shell with voids due to faster inward diffusion of Au in an InAs matrix compared to the self-diffusion of InAs (outward).²⁴⁴ An additional limiting case of a Kirkendall effect was exploited by Manna and co-workers, who have used the different susceptibility towards oxidation of the ingredients of a copper selenide core/copper sulfide shell nanocrystals.²⁴⁵ They showed how Cu^+ ions diffuse into the solution upon exposure to an oxidizing etchant (CuCl_2). Subsequently, Cu^+ cations diffused outwards from the Cu_{2-x}Se core through the Cu_{2-x}S shell, thus forming various hollow particles, including collapsed NCs. Though not a regular M/SC HNS example, it shows how similar systems can be used to expand the scope of synthesized multicomponent nanostructures (*e.g.*, *via* cation exchange,^{246,247} and confined nano-to-micro particles).^{241,248}

A related anion exchange phenomenon was exploited to form (hollow or void-containing) ZnS@Sn:ZnO nanostructures.²⁵⁰ Furthermore, different diffusion rates can be used to transform hybrid $\text{CdSe/Cu}_3\text{P}$ nanoplatelet systems into Cu_2Se .²⁵¹ Combination of such exchange strategies alongside selective etching was reported by Fenton *et al.* who formed various multi-domain nanostructures with combination of metal-sulfides, metals and voids.²⁵²

Another non-Kirkendall effect has been demonstrated using $\text{In@In}_2\text{O}_3$ core@shell NPs, which fractured upon heating to 250 °C due to the melting of the low-melting-point metal core. As a consequence, hollow indium oxide NPs were obtained (Fig. 9i–l).²⁴⁹

3. Formation of complex nanoparticle systems

3.1 Rational design of nanoparticles with increasing complexity

Multicomponent nanoparticles can be synthesized with multiple materials and domains, thus benefiting from two or more interfaces, at least one containing an M/SC junction. The final morphology can be a variant of a core@(multi-)shell, different multi-domain nanostructures and combinations thereof. Fig. 10a is a schematic representation of various multiple-heterojunction morphologies, which are attained from a single nanoparticle, starting with an 'A' NP, which can react with 'B' and consequently with 'C'.²⁵³ In Fig. 10, some possible heterotrimer morphologies are depicted resulting from deposition of material 'C' on 'A–B' dimers that were formed in a previous step, adapted from Hodges *et al.*²⁵³ The Schaak group has thoroughly investigated the depicted heterostructures,^{253–256} and has even expanded the breadth of these methods, for example, by introduction of a solid-state protective group. Without a protective group (from A–B to C–A–B, marked with a green arrow in Fig. 10a), the third material (the metal) is formed on the metal of the dimer (TEM images in Fig. 10c and d show deposition of Au on $\text{Pt-Fe}_3\text{O}_4$ dimers, forming an Au–Pt–

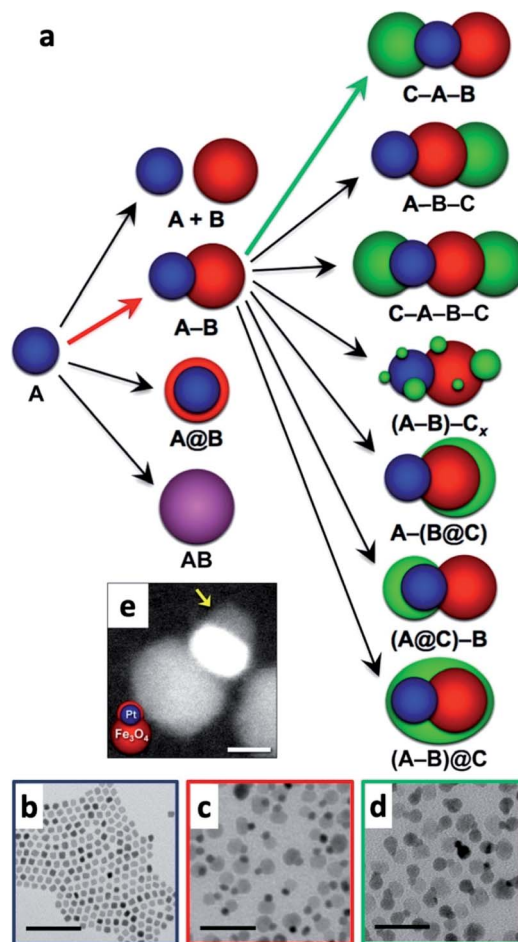


Fig. 10 Sequential seeded-growth allows formation of various higher-order hybrid nanostructures, namely heterodimers and heterotrimers. (a) The first reacting NP is A (blue), which reacts with a second B NP (red), which in turn results in either a mixture of A + B, a heterodimer (A–B), a core@shell morphology (A@B) or an alloy particle (AB implying a solid solution has been formed). The A–B heterodimer serves as the seed for deposition of a subsequent third material C (green).²⁵³ (b–d) TEM examples of the process depicted in (a) using color arrows: (b) Pt cubes serve as the seeds for formation of (c) Pt– Fe_3O_4 heterodimers (through the red arrow) that in the final step (through the green arrow) serve as seeds for selective gold deposition on the metal domain, forming the (d) Au–Pt– Fe_3O_4 heterotrimer.²⁵⁴ (e) Variation of A–B formation, where Fe_3O_4 forms a thin shell over the Pt in this heterodimer example with a protective layer.²⁵⁶ Adapted with permission from the American Chemical Society, (a–d) copyright 2017, (e) copyright 2014.

Fe_3O_4 heterotrimer).²⁵⁴ If, on the other hand, the dimer involves a thin shell, as is the case in the $\text{Pt@Fe}_3\text{O}_4$ example shown in Fig. 10e, where Pt is completely coated with Fe_3O_4 , the subsequent Ag deposition occurs on the iron oxide, opposite to the Pt domain (without the protective group an Ag–Pt– Fe_3O_4 formed).²⁵⁶

An example of a core–multi-shell HNS is Au NRs, which are transformed into Au/AuAg to utilize the option of sulfidation, allowing the synthesis of Au/AuAg/ Ag_2S by reacting with thioacetamide in a basic environment. Finally, an additional shell layer of PbS could also be synthesized.²⁵⁷ A synthesis in the



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,⁵¹ followed by fusion. This is usually achieved by controlled elimination of stabilizing agents, which favors controlled aggregation, for example using iodine to 'weld'

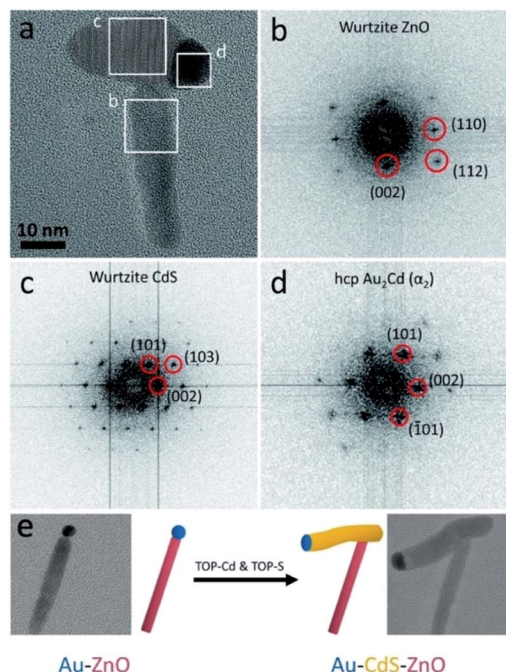


Fig. 11 Ternary hybrid system using an SLS mechanism. (a) High-resolution TEM image of Au–CdS–ZnO with marked areas for fast-Fourier transform (FFT) analysis: (b) from the ZnO, (c) from the CdS, (d) from the Au–Cd. (e) Synthetic scheme and TEM images: Au–ZnO NR formed using the seeded growth approach 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.²⁶⁷

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,²⁶⁸ and also in an all-inorganic system by Chen and co-workers, where a silica is protecting a gold core, *i.e.*, an Au–SiO₂ dumbbell is reacted with another metal, which cannot conformally coat the Au-core due to the existence of the SiO₂ mask.²⁶⁹

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–Fe₃O₄ 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.²⁷⁰ Naya *et al.* have used ZnO, which dissolves under mild conditions to form a ‘nanoegg’ shape, of half-cut Au(core)–CdS(shell).²⁷¹

3.2 Complex (higher-order) systems

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

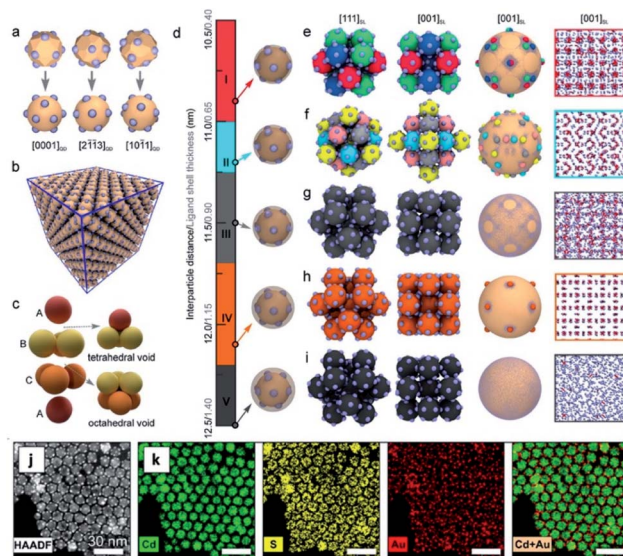


Fig. 12 Self-assembly into superlattices from patchy quantum dot-gold hetero-structural nanocrystals without inherent anisotropy. The top part shows simulation of gold NPs on different facets of wurtzite QD hosts with varying interparticle distance adjusted by the ligand shell (surfactant chain-length) 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 fusion²⁷² and more recently³⁹ 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–Au₂S Janus NPs migrate and coalesce to form CdS–AuS–Au hetero-trimers upon pressure-treatment.²⁷³

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.²⁷⁴

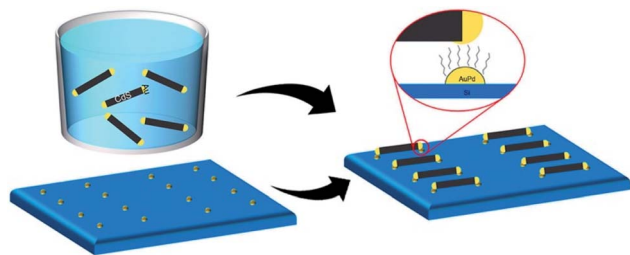


Fig. 13 CdS-Au nano-dumbbells self-assemble on pre-fabricated AuPd NPs on a Si substrate ('nanolithographic docking').²⁷⁴ Reproduced with permission from the American Chemical Society, copyright 2018.

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;²⁷⁵ (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-workers¹⁸⁶ 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.²⁷⁶ Such phenomena can be used for characterization of multicomponent SC nanostructures using variants of probe microscopy²⁷⁷ on the one hand, and for providing a high-chemical yield method to connect metallic domain(s) on various NPs for further integration²⁷⁶ 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.²⁷⁸ 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 measurements²⁷⁶ and CdSe/Au nano-dumbbells, which form linked networks),²⁷⁹ percolation of metallic domains, and different M-SC electronic coupling phenomena (including photoconduction in Pt-CdSe monolayers²⁸⁰) 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.⁷⁰

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 Cu₂O.¹⁴⁰ Control over the oxidation allowed formation of a thin layer (3–6 atomic layers) of Cu₂O, 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 (NaBH₄),¹¹⁷ 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 BH₄[−]).²⁸¹

The oxygen reduction reaction (ORR) is a reaction in the field of batteries (Li-O₂ batteries, for example)²⁸² and fuel cells,²⁸³ where an electrocatalyst (most commonly a precious metal) is responsible for the transformation of O₂ into H₂O (in the case of Pt(100) the ORR is performed *via* the oxygen dissociation mechanism).²⁸⁴ Using the interaction between the metal-oxide support and the metal,^{285–288} the energetics of the catalyst can be improved. Meng *et al.* have epitaxially grown Pt on single-crystal CuO NRs for this purpose.²⁸⁵ 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.²⁸⁹ 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).²⁸⁹ 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.²⁸³



4.2 Photocatalysis

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

The third photocatalytic step is the charge and energy transfer phenomena, usually to the interfaces—the solid heterojunctions and to the surfaces of the HNS, where they meet the molecules relevant to the last catalytic reaction (surface bound ligands, solvent molecules and any other adsorbed molecule, including reactants). At this stage, the quality of the interface, the materials, and their morphology play a significant role (*e.g.*, affecting the kinetics of electron transfer), as will be discussed for the relevant applications. For example, Yu *et al.* have shown a difference between electrons excited to the band edge ('cold electrons') and high-energy electrons ('hot electrons') in CdSe NRs. Comparing CdSe NR/Au and CdSe NR/Pt HNSs showed that hot electron (e^-) injection is faster for the Au-tipped HNS while the cold e^- injection yield is higher in the Pt-tipped one.³⁰⁸

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 one³⁰⁹ (which is relatively low for small colloidal NPs). The metal can thus photo-enhance catalytic reactions,³¹⁰ 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.³¹¹ 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 Ag³¹² or Rh³¹³ nanocubes supported on α -Al₂O₃, different Au NPs supported or coated on TiO₂,^{314,315} SiO₂,^{316,317} or both (*i.e.*, Au@SiO₂@TiO₂),³¹⁸ as well as multi-metal combinations as Al antenna-Ir NPs on an

Al₂O₃ support³¹⁹ for photocatalysis or for studying the interaction arising at the M/SC interface.³²⁰

Of note are the studies of Li, Wei and co-workers, who used plasmon-enhanced Au core(s)@MoS₂ sphere shell HNSs for photocatalytic hydrogen production with stable high rates.^{321,322} In one configuration, the proximity between gold multimers (spacing of 5–10 nm) allowed enhancement of the absorption cross-section and an additional absorption frequency at *ca.* 630 nm appeared due to in-phase coupling in a single-material gold multimer system. A subsequent MoS₂ shell formation results in an HNS with strong absorption both at the characteristic Au response ($\sim$ 640 nm) and at the MoS₂ *E_g* ($\sim$ 510 nm). The multimer hybrid thus exhibits both an improved absorption in the visible range and a higher energy transfer rate relative to single Au@MoS₂, improving photocatalytic H₂ production. The relative high stability of this colloidal system stems from the strength of the Au–S bond in the anchoring of MoS₂ to gold and provides an additional photocatalytic advantage.³²¹ The other system with high stability is the ternary HNS formed by reacting Au@MoS₂ hydrothermally with a zinc source and an amine to form Au@MoS₂–ZnO.³²² The latter system benefits from the mechanical strength of the NRs in the composite (about 6–10 rods per sphere) and higher specific surface area, but more importantly, the introduction of ZnO alters the electronic structure resulting in improved light harvesting in the 350–700 nm range: a new absorbance intensity is measured in the UV (350–400 nm) and the authors ascribe the red shift of the typical MoS₂ absorption at *ca.* 600 nm to 650 nm to the surface plasmon local field effect. Furthermore, ZnO, a known electron conductor, facilitates spatial charge separation, and in part is responsible for the reduced photocorrosion.³²² For further plasmon-enhanced applications we refer the reader to a review from the Wei group regarding various metal–2D hybrids (graphene, MX₂, BN, *etc.*).¹⁹¹

To explain the photocatalytic enhancement of the HNS, the commonly suggested modes of energy transfer are as follows: (i) the metallic NP, which absorbs the radiation performs a direct energy transfer between the LSPR and the coupled electronic state of a damping surface-attached chemical species (*i.e.*, catalysis on the metal's surface), or (ii) indirect energy transfer, where the 'hot' carrier from the plasmonic structure is an intermediate agent that allows the dephasing of the surface plasmon and transfers the excess energy either as an electric charge or as vibrational energy to the interface at the surface.³²³ Fig. 14 further elaborates the possible energy transfer mechanisms from the metal to the SC, based on the work of Cushing *et al.* on a silica-passivated M@SC shell (Au@SiO₂@Cu₂O).¹²⁵ As they point out, there is still no consensus regarding which mechanism is at play for the reported systems, and novel probing techniques are constantly recruited for this task.^{324–327}

One of the consequences of the plasmonic response is local heat generation through electron–phonon scattering,³¹⁸ which has made a distinct contribution to successful photocatalytic CO₂ methanation of Rh/TiO₂, for example.³¹⁸ 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

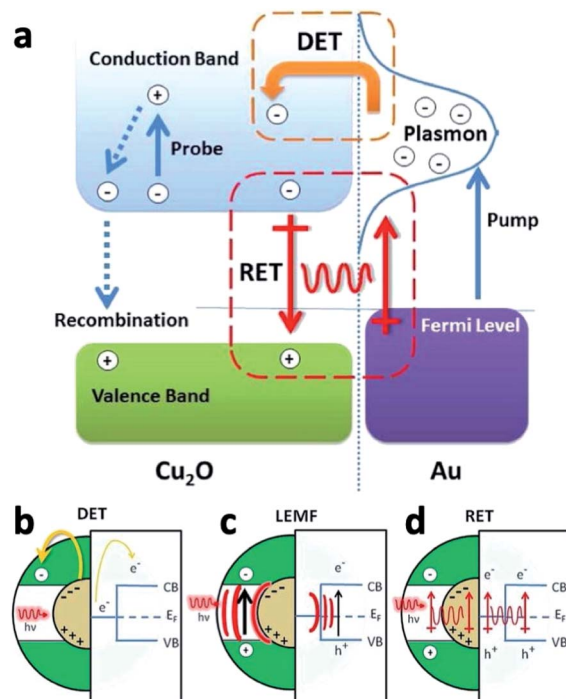


Fig. 14 Various possible energy-transfer and separation processes responsible for plasmon-enhanced photocatalytic activity of Cu₂O/Au-based HNS.¹²⁵ (a) Scheme of energy absorption at the metal (pump) and the subsequent energy-transfer processes: (b–d) illustration of the metal core (Au) and the SC shell (Cu₂O) energy positions (right) and processes (left): (b) direct energy transfer (DET), where LSPR 'hot' electrons are transferred to the SC's CB; (c) local electromagnetic field enhancement (LEMF), where the e^- – h^+ charge-separation in the SC is radiatively aided by the metal excitation; (d) resonant energy transfer (RET), where the LSPR dipole induces e^- – h^+ pair separation in the SC via a non-radiative mechanism that relaxes the localized surface plasmon dipole. Adapted with permission from the American Chemical Society, copyright 2012.

enhancement reported for Cu–Ru NPs³²⁸ and others^{312,315,317}) disregards the local heating effect of the plasmonic structures, and that the measured enhanced photocatalytic effects should be ascribed, *in lieu*, to thermal effects (well-described using a simple Arrhenius model).^{329–332}

This intriguing explanation requires significant improvement of experimental apparatus and procedures both to perform correct control experiments and to allow the measurement of real local temperatures. It paves the way to further improvements by taking into account the resulting thermal gradients³³³ as well as rational design of HNSs that can sustain enhanced heat generation, for example by improving the heat conductance of the supporting oxide.³³⁰

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



oxidation or reduction reactions (possibly with radical intermediates) taking place in aqueous or organic media. Though organic-phase photocatalytic oxidation reactions exist (e.g., 2-mercaptobenzothiazole (MBT) oxidation demonstrated using cesium-lead-halide perovskite QDs in hexane,³³⁴ benzyl alcohol oxidation using titania and titania-iron oxide³³⁵ or using CdS and/or TiO₂ in MeCN (acetonitrile) and or MeCN-trifluorotoluene mixtures³³⁶ and alcohol dehydrogenation in MeCN⁶⁷), they are less common for M/SC hybrids as the metal serves as the electron sink. Therefore, when a SC/M hybrid is used, the electrons from the sink are consumed for the formation of radical species such as $\cdot\text{O}_2$ from dioxygen, which are consumed during the oxidation reaction.³³⁷

A report by Wang *et al.* describes synthesis and use of a hybrid Pd/ZnIn₂S₄ catalyst for alkylation of amines and ketones in alcohols. The organic reaction mechanism involves the dehydrogenation of alcohol to aldehyde, followed by condensation of the aldehyde and a nucleophile (amines and ketones) and then hydrogenation forming the final alkylated product. The semiconductor part photocatalyzes the dehydrogenation (the suitable valence band position slows controllable oxidation), while the Pd catalyzes the hydrogenation of the intermediate at the final step.³³⁸

Probably the most common aqueous-phase photocatalytic reactions are organic pollutant dye degradation and variants of water-splitting (the HER and/or the OER)—both requiring a ligand-exchange procedure, if the HNSs are initially synthesized in an organic phase, to allow their dispersibility. The spatial charge separation pathways and the corresponding energy band diagram are presented in Fig. 15.

Examples of dye decoloration and degradation (mineralization) include methylene blue (MB) using MUA (mercaptoundecanoic acid)-capped Pt/CdS/PbS NRs⁹⁰ and CZTS NRs/Au,⁸⁶ toluidine blue using ZnO of various shapes/Au^{63,167} and ZnO/Au/Pt,⁶⁴ rhodamine B (RhB) using calcined Au/ZnO nanopyramids³³⁹ or Au/Ni/ZnO flower HNSs,¹⁶⁸ rhodamine 6G (Rh6G) using ultrasonicated tip-attached Ag/ZnO nanopyramids,¹⁶⁹ azo-dyes such as methyl orange (MO) using ultrasonicated Au/ZnO nanopyramids⁶⁰ or Au-Cu₂O¹²⁰ and orange G using Ag/ZnO hollow spheres.³⁴⁰ In the last example, the authors verified that the enhanced degradation stems not only from enhanced charge separation but also from the increased concentration of hydroxyl radicals ($\cdot\text{OH}$), formed from surface-attached hydroxyls. 4-NP reduction was demonstrated with triangular- and prism-shaped Au domains/ZnO HNSs, prepared in an aqueous phase.³⁴¹ Epitaxial Au-triangular ZnO NPs (and Pt-Au-ZnO) were used to study the charge accumulation and discharge using degradation of toluidine blue, which allowed monitoring not only degradation (photoreduction) but also measuring on/off characteristics due to its ability to reoxidize.⁶⁴

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-

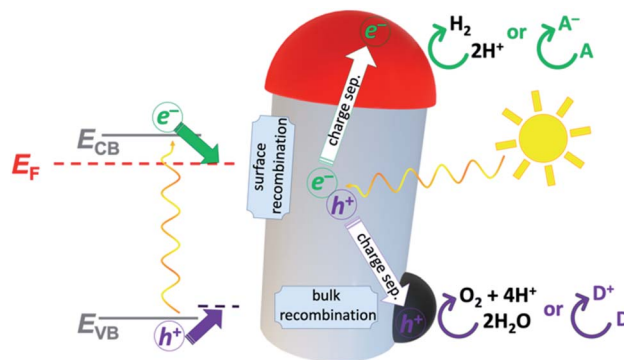


Fig. 15 Schematic charge separation diagram (spatial paths and energy bands) on an HNS, illustrated on a SC nanorod with an M tip (reduction catalyst) and an additional oxidation cocatalyst. First, a semiconductor NR (gray) is excited with sufficient energy to excite an electron from the valence to the conduction band; the desired action is spatial charge separation, where the electron is drawn towards the metal tip (red), which serves as an electron sink at lower energy (the Fermi level, E_F). From the metal, the electron can perform reduction of any adsorbed acceptor ($A \rightarrow A^-$), which in the case of water splitting are protons being reduced to hydrogen (i.e., the HER); in dye degradation experiments the e^- can reduce the dye or form intermediate $\cdot\text{O}_2^-$ species in the presence of oxygen, which in turn form hydrogen peroxide, and finally destructive hydroxyl radicals. While this is occurring, the h^+ oxidizes an adsorbed donor molecule ($D \rightarrow D^+$), which in the case of water splitting is water to oxygen (i.e., the OER) and in the case of dye degradation a possible reaction path is hydroxide (water) oxidation to hydroxyl radicals (and H^+), which in turn mineralize the dye. The competing processes are bulk (volume) and surface recombination, occurring throughout the SC or at its surface (e.g., due to some passivation defect), respectively. To minimize recombination, the charge carrier kinetics is crucial—for example, while no donor accepts the hole, it serves as a coulombic attraction center for electrons. When the h^+ removal is a sluggish process, as is the case in the OER, a possible solution is the addition of a cocatalyst (represented in dark gray), which catalyzes water oxidation, thus removing the h^+ from the HNS and suppresses recombination.

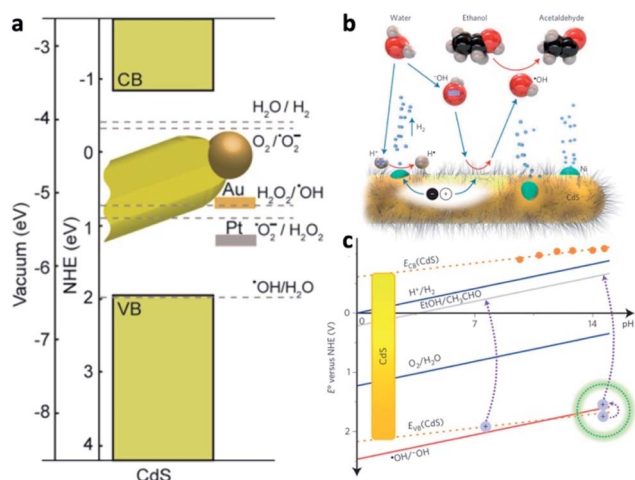
dimethyl-1-pyrroline-*N*-oxide (DMPO).¹⁶⁸ It is important to stress that especially in the case of the common MB dye, decoloration can result from reversible photoreduction to the leucomethylene blue form,^{86,342} which is different from complete degradation (via a photooxidative path).³⁴³ MB can also be degraded from an alcoholic solution, where a catalytic amount can be dispersed even in an organic solvent (e.g., Au-Cu₂S in hexane degrades MB in hexane).¹⁴⁶ 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 H₂O₂. This work demonstrated the ability to distinguish between the charge carriers (h^+ and e^-), 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.³⁴⁴ 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.³⁴⁵



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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 TiO_2/Pd hybrid in water.³³⁷

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,



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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).³⁸³ 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.³⁸⁴ One possible cure is using heavy-metal-free materials, with significant progress achieved, for example, in SC NR-related systems.³⁸⁵

Cheng *et al.* have shown a photothermal effect in a Bi₂S₃ 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. 17.³⁸⁶ Other examples include SiO₂/Au/Fe₃O₄ multi-shell structures for photothermal treatment of breast cancer cells and magnetic stimuli functionality for MRI.³⁸⁷

Related reported systems also include other hybrids with insulators or double hydroxides, such as core-shell Au NRs in Al and Mg hydroxides³⁸⁸ and Au NRs partially embedded in silica (Au-SiO₂ Janus particle with the Au NR partially exposed) that show improved infrared response for photo-triggered drug delivery alongside improved loading.³⁸⁹ 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/Cu₉S₅ HNS, where both the metal and the semiconductor have an LSPR response.³⁹⁰ A related spherical core@shell Au@Cu_{2-x}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.³⁹¹

Huang and co-workers have used the combination of facet-dependent absorption and a plasmonic response to tune photothermal effects of a simple Au-Cu₂O system.⁴¹³ Sun *et al.* have recently shown a very high photothermal anticancer activity with sub-stoichiometric tungsten trioxide (WO_{2.9}) NRs, which exhibit partial metallic character.³⁹²

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.*, NH₄⁺).³⁹³ Biocompatible magnetic domain-containing HNSs are also promising due to their possible magnetic-controllable catch and release, as demonstrated for Au- and FePt-Fe₃O₄ heterodimers,³⁹⁴ and multimodal imaging using M/Fe₃O₄.¹⁰⁸

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^{395–397} and transformation,^{398,399} as well as other inorganic materials.^{400–405} Other related fields such as superlattice self-assembly from NPs are also treated.⁴⁰⁶ Though some studies dealing with HNSs exist,^{407,408} 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)⁴⁰⁹ 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,⁴¹⁰ structural evolution by atom diffusion,⁴¹¹ surface reconstruction,¹⁸⁵ composition and bonding in multilayer or multivalent oxides,⁴¹² crystal structures of growing 1D materials from metallic catalysts (though usually in gas-phase syntheses),^{413,414} defects in 2D materials,⁴¹⁵ liquid metal/metal-nitride interfaces⁴¹⁶ and structural changes on the atomic level of SC NRs/M tips.⁴¹⁷ 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.⁴¹⁸ Advances in electron energy loss spectroscopy (EELS, used in STEM),⁴¹⁹ in particular, could give further insight on the connection between composition (*e.g.*, doping levels, oxidation states)⁴²⁰ and electronic structure

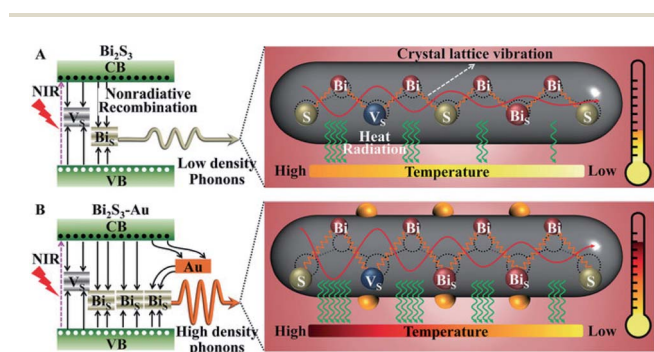


Fig. 17 Schematic photothermal mechanism of (A) Bi₂S₃ NRs and (B) Bi₂S₃/Au HNSs. On the left side an energy diagram shows the SC band edge absorption, vacancy levels and possible gold incorporation are translated into phonons (crystal lattice vibrations, depicted on the right side) that generate the 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 ⁻	Electron
fcc	Face-centered cubic
h ⁺	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

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