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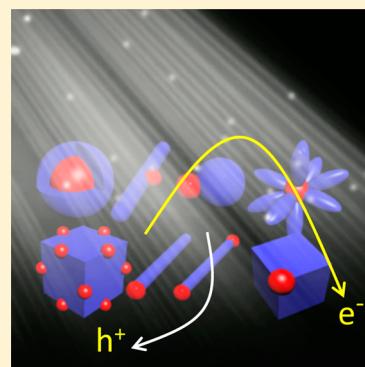
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## Metal Semiconductor Heterostructures for Photocatalytic Conversion of Light Energy

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**ABSTRACT:** For fast separation of the photogenerated charge carriers, metal semiconductor heterostructures have emerged as one of the leading materials in recent years. Among these, metal Au coupled with low bandgap semiconductors remain as ideal materials where both can absorb the solar light in the visible region. It is also established that on excitation, the plasmonic state of gold interacts with excited state of semiconductor and helps for the delocalization of the photogenerated electrons. Focusing these materials where electron transfer preferably occurs from semiconductor to metal Au on excitation, in this Perspective, we report the latest developments in the synthetic chemistry in designing such nano heterostructures and discuss their photocatalytic activities in organic dye degradation/reduction and/or photocatalytic water splitting for generation of hydrogen. Among these, materials such as Au-CZTS, Au-SnS, Au–Bi<sub>2</sub>S<sub>3</sub>, Au-ZnSe, and so forth are emphasized, and their formation chemistry as well as their photocatalytic activities are discussed in this Perspective.



**P**hotocatalysis, where photons are used for catalytically activating chemical reactions on the surface of photosensitized catalysts, remains one of the leading hubs of research for harvesting the solar light.<sup>1–12</sup> Typically, photocatalysts generate the charge carriers on excitation and under suitable conditions, these are transferred from the catalysts to the reaction medium, which in turn initiate the chemical reaction. The efficiency of a typical photocatalytic process mostly depends on (1) the nature of photosensitized catalyst, (2) appropriate photon source for excitation, (3) the substrate which can promptly accept the photogenerated charge carriers, and importantly, (4) the spatial distance between the catalyst and substrate. In recent progress, different size/shape tunable plasmonic noble metals<sup>12–20</sup> and semiconducting nanomaterials<sup>7,21–27</sup> remain the leading inorganic catalytic materials, which can have tunable absorption in solar spectrum and can generate photoelectrons for utilizations in various chemical reactions. In addition, these catalysts have also been used for bacterial detoxifications, organic pollutant removal and generation of hydrogen via catalytic water splitting.<sup>1–5,21,27–34</sup>

However, recent developments suggest that the combination of both plasmonic metal and semiconductor can be an even better catalyst for harvesting the solar energy compared with those individual components.<sup>28,33–46</sup> These combined materials, widely known as heterostructured materials, can retain the properties of the individual entities or generate new properties when placed together within a close proximity. For ideal combination, this can help in quick transfer of the photogenerated charge carriers from one to other; it can delocalize the photoelectrons over the excited states of both metal and semiconductor, which in turn hinders carrier recombination providing a better opportunity for their utilization in activating the chemical reactions.<sup>28,33,38,40,43,47</sup> Further, these materials

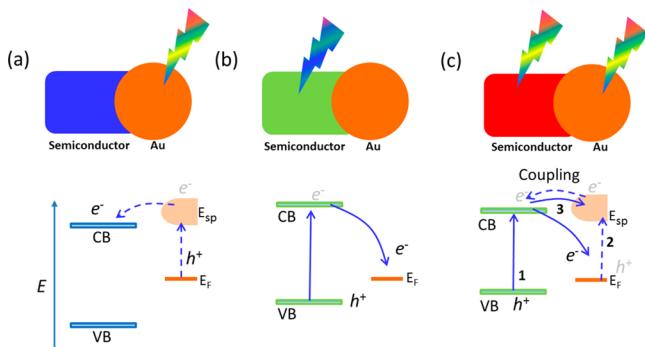
can also provide various combinations of facets on their surfaces, which can give more opportunity for the substrate molecules getting adsorbed.<sup>40,48,49</sup> All these advantages make these metal–semiconductor heterostructures more efficient photocatalysts than only the metal or semiconductor catalysts.

From the literature reports, it is revealed that these metal–semiconductor heterostructured photocatalysts can be broadly classified in two categories. In the first case, either of the materials is photoactive and, on excitation, the excited charge carriers are transferred to other part of the material, which then induces the catalytic process. With plasmonic gold, the combination of high bandgap semiconductors such as TiO<sub>2</sub> falls in this category, where on photoexcitation the plasmon electrons are transferred from Au to the semiconductor for initiating the catalytic reaction.<sup>12,35,37,48,50–53</sup> These are known as plasmonic photocatalysts and these have been widely studied and reported in literature. A possible electron transfer from the surface plasmon state of Au to the high bandgap semiconductor has been schematically shown in Figure 1a.<sup>54,55</sup> The other possibility is that the metal and semiconductor both are photosensitized and absorb the solar light. Materials where the plasmonic gold is coupled with low bandgap semiconductors, such as Au-CdSe, Au-CdS, Au-PbS, and so forth<sup>40,49,56,57</sup> remain in this category. When analyzed, it is observed that there can have possibility of the electron transfer from either Au to semiconductor or vice versa depending on the band alignment as well as the excitation source. For a particular case, with exclusive excitation of the semiconductor can facilitate the electron transfer from the semiconductor conduction band

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**Figure 1.** Schematic presentation of the electron transfer processes in Au-semiconductor heterostructures. For Au-semiconductor heterostructure where (a) only Au is excited, (b) only semiconductor is excited, and (c) there are simultaneous excitations of both Au and semiconductor. The electron transfer path 1 refers for semiconductor excitation followed by electron transfer to Au, path 2 follows just the reverse process, and path 3 shows the coupling of exciton of the semiconductor and plasmon of Au. Here,  $E_{sp}$  refers to the Au surface plasmon state and  $E_F$  refers to the Au Fermi level.

(CB) to Au electronic level and a schematic presentation of such electronic movement has been shown in Figure 1b.<sup>56,58</sup> Similarly, if only Au is excited here, then electron transfer can follow similar to the scheme shown in Figure 1a, provided the surface plasmon state remains above the CB of the semiconductor. But, the case becomes more complicated when both Au and semiconductors are excited together. Even though most of the reports predicted the photoexcited electron transfers from the excited state of semiconductor to Au, but a recent study on Au-CdS showed that, the electron transfer in both ways are possible, though more probable is the transfer from semiconductor to metal Au.<sup>56</sup> There is also a possibility of coupling of the exciton of semiconductor and plasmon of Au. Summarizing all possible processes in this category, we have shown the carrier transfer protocols in Figure 1c.<sup>56,59,60</sup> However, to our understanding, the case where both the metal and semiconductor are photosensitive remains more promising, as both can absorb solar light and generate a greater number of photoexcited charge carriers compared with the other two categories.

However, to our understanding, the case where both the metal and semiconductor are photosensitive remains more promising, as both can absorb solar light and generate a greater number of photoexcited charge carriers.

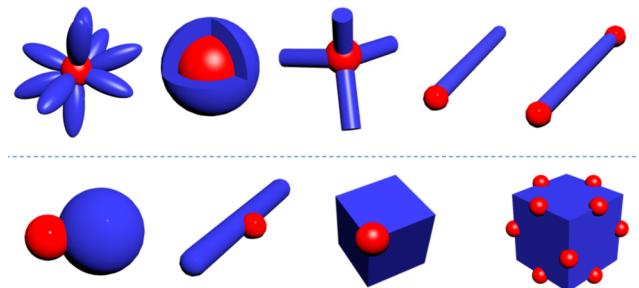
However, while considered for metal–semiconductor heterostructures, apart from Au, other metals are also been coupled with various semiconductors and used in photocatalysis. Metal Pt remains even more efficient in some cases.<sup>28,62</sup> But we focus here mostly the plasmonic metal Au as its surface plasmon resonance (SPR) remains in the intense region of the solar spectrum. Hence, we have confined our discussion mostly to Au-based heterostructures.

Apart from the promising photocatalytic properties, these heterostructured materials also possess interesting chemistry of

their formations, which contributes several new fundamental aspects in the study of crystal growth in solution.<sup>40,43,63</sup> However, in these heterostructures, two different materials having different reactivities cannot just be coupled randomly. The lattice mismatch between these materials typically remains high, and this became the major hurdle in designing such heterostructures in solution. Crystallographic orientations of energetically favorable facets of both materials are essential to minimize the formation energy and to form the stable heterostructure. Although a large number of such materials reported are silent over their epitaxial relations, several recent reports suggest that epitaxial binding is possible even if they have wide lattice mismatches within their approached facets.<sup>64,65</sup> Some of the material properties are even retained, irrespective of the nature of the heterojunction, but epitaxial orientations provide stronger bonds, sustainability at higher temperature and also can facilitate efficient carrier transportation. Several such materials such as Au-CdSe, Au-ZnSe, Au-CZTS, and so forth have recently been reported in colloidal solutions having epitaxial connections.<sup>6,61,64–66</sup> For our best understanding, the chemistry of formation of these heterostructures having proper crystallographic orientation provides importance in architecting the robust nano heterostructures, and this needs to be explored more.

Hence, combining the upcoming chemistry of formation of the nano heterostructures with their photocatalytic properties, in this Perspective, we mostly focus on the very recent developments of heterostructures of Au and low bandgap greener semiconductors. Emphasis has been given on the coupled effects of the SPR of Au and exciton of semiconductor in these heterostructures helping in the better transformation of the solar energy to the chemical energy. However, we restrict the discussion to the heterostructured materials developed in the latest half a decade, their interesting and newly stated formation mechanisms, heteroepitaxies, and their light harvesting properties in the implementations of catalysis for organic reactions and light-driven hydrogen evolution from water splitting.

**Nano Heterostructures: Some Recent Developments.** From the literature reports, it is revealed that soon after the development of high quality quantum confined semiconductor nanostructures, Banin et al.<sup>67</sup> developed the fabulous semiconductor nanorods with metal tips (Au-CdSe),<sup>68</sup> and this became the breakthrough in developing such heterostructured materials. For more than a decade, enormous efforts have been put forward in designing different new nano heterostructures and understanding their synthetic chemistry.<sup>28,43,57,62,66,69–74</sup> Among these, core/shell structures,<sup>6,62,68,70</sup> decorated nanorods,<sup>6,62,68,70</sup> twin structures,<sup>61</sup> tetrapods having metals at core as well as on tips,<sup>65,68</sup> flowerlike complex nanostructures,<sup>28,69,71,77,78</sup> and so forth are well studied. Several review articles demonstrating the synthetic procedures, chemistry of formation, and some leading applications are also documented.<sup>40,43,63,79</sup> Limiting our discussion to only last half a decade developments, we summarize the latest reported shapes of some important Au coupled semiconductor structures schematically in Figure 2. Unfortunately, as stated earlier, most of such structures reported either have nonepitaxial growth or remain silent over the formation of epitaxy at their heterojunctions. For the first time in 2010, Manna et al.<sup>64</sup> reported both postsynthesized fusion and in situ growth of Au-CdSe heterostructures with a clear crystallographic orientation relation between (111) facets of fcc Au and (001) facets of

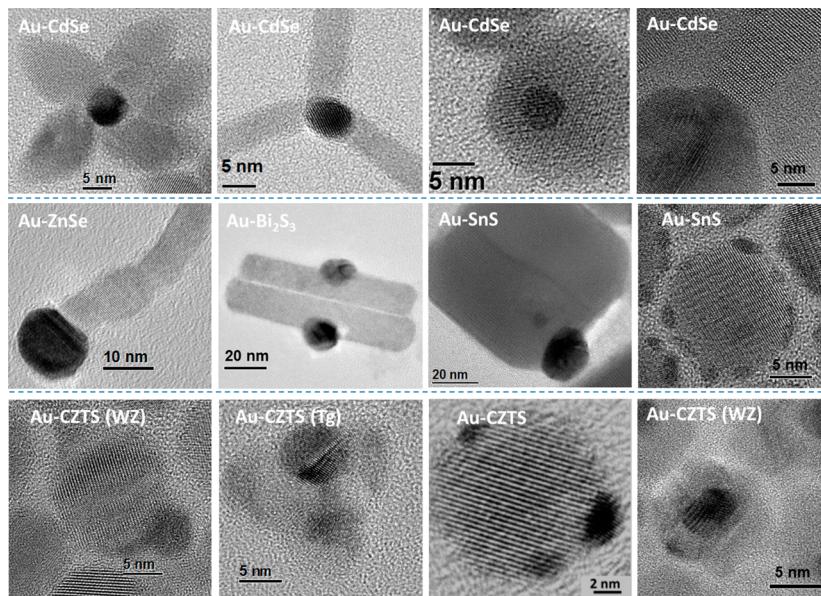


**Figure 2.** Schematic presentations of different shapes of nano-heterostructures reported recently. The red part is for Au, and blue is for semiconductors.

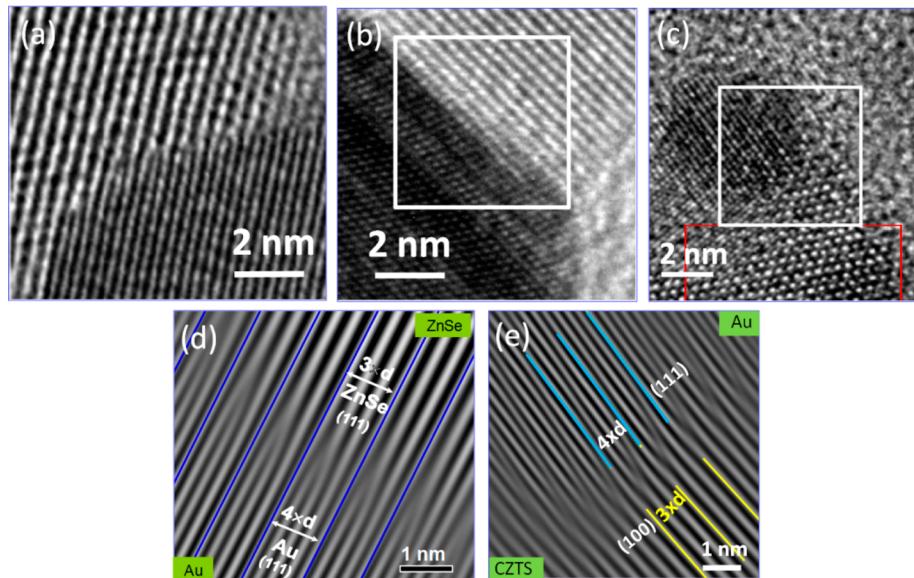
wurtzite (WZ) CdSe. This finding opened up the new possibilities of designing heterostructures via epitaxial growth between a noble metal and semiconductors in colloidal solution. Representative TEM images of some of the heterostructures of Au-CdSe,<sup>64,65</sup> Au-ZnSe,<sup>66</sup> Au-Bi<sub>2</sub>S<sub>3</sub>,<sup>6</sup> Au-SnS,<sup>77</sup> Au-CZTS,<sup>28</sup> and so forth having mostly epitaxial relations at their heterojunctions are depicted in Figure 3. Some of the structures, for example, decorated Au-SnS, Au-CZTS, and so forth, newly reported but not confirmed in their epitaxial orientation, are also presented in same figure.<sup>61,77</sup>

Although a large number of such materials reported are silent over their epitaxial relations, several recent reports suggest that epitaxial binding is possible even if they have wide lattice mismatches within their approached facets.

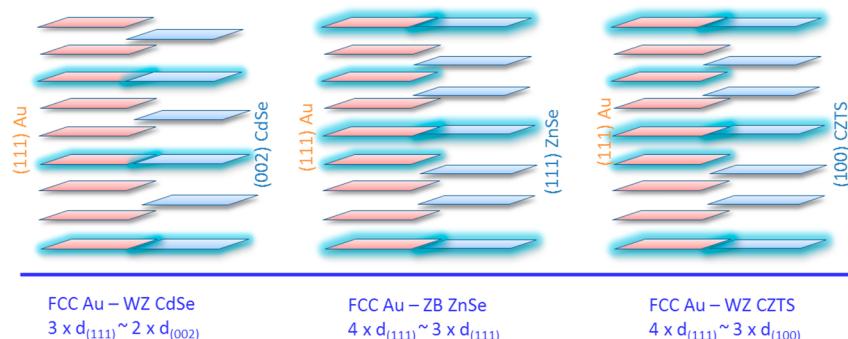
However, for heterostructures either having epitaxial or nonepitaxial crystallographic orientation, understanding the solution chemistry remains important for their fabrication. Several articles based on their growth mechanisms, mostly followed by heterogeneous nucleation, are also reported.<sup>40,43,63</sup> In brief, typically, two types of protocols are adopted for the formation of such structures; one is *in situ* growth of one on the energetically favorable facets of other<sup>64,65</sup> and second is the post synthesis two step growth protocol.<sup>28,77,80</sup> But, the second case is more common and has been adopted in several occasions, where semiconductor nanostructures are synthesized at higher temperature and gold has been grown via an *in situ* reduction mechanism preferably at room temperature. Here, Au(III) ions are reduced on to the surface of semiconductor nanostructures and selectively or randomly deposited on the facets of the seed semiconductors leading to various shapes. Among the different nanostructures depicted in Figure 3, Au-CZTS and Au-SnS nanostructures are very recently reported, which belong to this category,<sup>61,77</sup> though structures of other materials having similar shapes are already present in the literature.<sup>57</sup> In these cases, the deposition of Au has been observed to be random, leading to Au decorated CZTS or SnS nanostructures. However, this synthesis mostly leads to heterostructures having nonepitaxial connection. On the other hand, the heterostructures having epitaxial orientation have been typically synthesized at elevated temperature. For Au-CdSe, Manna et al.<sup>64</sup> discussed that for epitaxy formation the reaction temperature required to be above 250 °C, though it varies from one semiconductor system to other. One ideal example is the formation of three different shapes of nanostructures of Au-CdSe reported by Halder et al., where CdSe is grown on Au seeds at high temperature (~250–300 °C).<sup>65</sup> Varying the reaction conditions, core/shell, tetrapod, and flower shaped structures are fabricated with all having the epitaxial relation along (111) planes of fcc Au with (001) planes of WZ CdSe (Figure 3, upper panels). Core/shell<sup>46</sup> and twin structures of Au-CZTS<sup>61</sup> are also been reported recently,



**Figure 3.** Representative HRTEM images of various nano heterostructures. These shapes are also schematically shown in Figure 2, and each panel in the figure is labeled about the name of the heterostructures. Images of this figure have been obtained from references 6, 28, 64–66, and 77. Reprinted with permission.



**Figure 4.** Typical HRTEM images of (a) Au-CdSe, (b) Au-ZnSe, and (c) Au-CZTS heterojunctions. Simulated HRTEM for (d) Au-ZnSe and (e) Au-CZTS. Images of this figure have been obtained from refs 61, 64, and 66. Reprinted with permission.



**Figure 5.** Schematic presentation of the coincidental site epitaxy of planes in different combinations of Au-semiconductor heterostructures and the periodicity.

where the semiconductor CZTS is allowed to grow on Au under certain reaction condition. Here, the epitaxy has been observed with (111) facets of fcc Au with (100) facets of WZ CZTS nanostructures. Similarly, ZnSe and  $\text{Bi}_2\text{S}_3$  semiconductors are grown on gold seeds at high temperature. Synthesis of such nanostructures needs careful reaction parameter manipulation as presence of excess anions can always leads to dissolution of Au particles and also possess the chance of forming separate nucleation of semiconductor nanostructures. However, the question arises here regarding the driving forces for formation of such epitaxial connection in these heterostructures in spite of their wide lattice mismatches. Chemistry related to this part of heterostructures formation is not yet precisely explored, and in this Perspective, we emphasized on the formation of epitaxy at the heterojunctions considering examples of several nanoheterostructures.

**Epitaxial Heterojunction.** From the literature reports, it has been revealed that when the lattice mismatch remains less than 15%, typically core/shell structures are formed.<sup>81</sup> This statement reflects mostly in case of the semiconductor-semiconductor heterostructures. On the other hand, when the lattice mismatch is above 15%, growth is expected on specific sites of the seed crystal or dislocation of lattice planes may occur at the interface.<sup>66</sup> However, for Au-CdSe, it is reported that

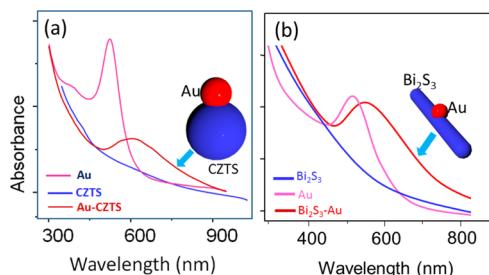
heteroepitaxy can be formed in nanostructures in solution even if the lattice mismatch remains close to 50%. It is established that the coincidental site epitaxy in periodic intervals of the lattice planes enhances the possibility of the epitaxial growth where the resultant misfit of the planes reduces to only few percent.<sup>64,66</sup> From the lattice structures of fcc Au and WZ CdSe, it was explained that three unit cells along [111] of fcc Au can fit with two unit cell along [001] of WZ CdSe.<sup>66</sup> Accordingly, three times the distance of (111) planes of fcc Au closely matches with two times that of (001) planes of WZ CdSe and these planes coincide in periodic intervals along the entire heterojunction forming the epitaxial relation between those two materials. A typical HRTEM image of the Au-CdSe junction has been shown in Figure 4a, which clearly suggests that the coincidental site epitaxy has been observed in periodic intervals.

Very recently, heterostructures of Au-ZnSe nanostructures are reported.<sup>66</sup> Here, epitaxy has been observed along [111] direction of fcc Au with [111] direction of zinc blende ZnSe. The synthetic protocol followed here was also similarly to that in case of Au-CdSe, where ZnSe is allowed to grow on Au under optimized reaction condition. A typical HRTEM image of Au-ZnSe heterostructure is shown in Figure 4b and the simulated HRTEM along [111] direction is represented in

Figure 4d. This clearly indicates that the coincidental site epitaxy is observed in the interval of four (111) planes of Au with three (111) planes of ZnSe. Similar observation has also been made with (100) and (110) planes of both Au and ZnSe. In addition, the fast principle calculation also supports that these combinations of facets possess the minimum energy for formation of heterojunction. It can be speculated that, any arbitrary combination of planes of Au can have the coincidental site epitaxy with the semiconductor at certain combination to form the heterostructures. However, the experimental observation supports only the combination of appropriate planes with minimum energy, which allows the formation of the epitaxy. For example, no observation of epitaxy of (111) of Au with (100) or (110) of ZnSe has been noticed until date and also the calculated energy of formation would be expected to be higher than that in case of with (111) of ZnSe. Similarly, Figure 4c and 4e show the HRTEM image of a twin structure of Au-CZTS and corresponding simulated HRTEM at its heterojunction, respectively. Here, also, the coincidental lattice matching has been observed for (111) planes of fcc Au but with (100) planes of wurtzite CZTS.<sup>61</sup> Similar observations were also observed for Au-CZTS (tetragonal) and Au-SnS nanostructures.<sup>61,77</sup> A schematic presentation of the possible coincidental site epitaxy in Au-CdSe (WZ), Au-ZnSe (ZB), and Au-CZTS (WZ) heterostructures are shown in Figure 5.

When compared further with the numerous reports on nano heterostructures synthesized in colloidal solution, these limited examples might not be sufficient to draw a definite conclusion. Though these findings are still in embryo stage and more nanostructures with different semiconductors are needed to be fabricated and importantly theoretical supports are also required for more vivid understanding, but this gives the message that, heterostructures even with large lattice mismatch can be designed by epitaxially growing one material on other. These materials are expected to be superior in stability, high temperature sustainable and more efficient for designing highly efficient devices or other related applications.

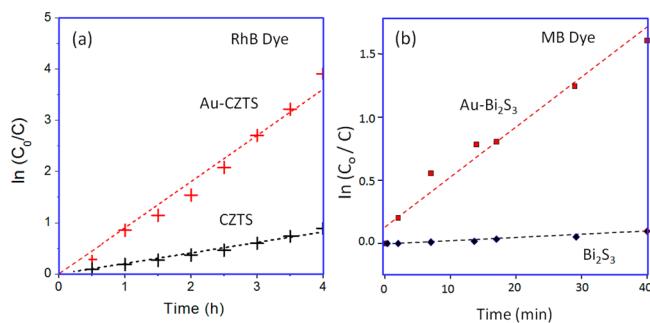
*Plasmon Absorption in Heterostructures.* Apart from the new chemistry of formation of the nano heterostructures, these materials possesses some important and promising material properties; among those, the most contrasting one in the heterostructures with Au is reflected from the change in the nature and position of the plasmon absorption. Here, in case of our main focused materials, that is, low bandgap semiconductors coupled with Au, the plasmon of Au is observed to be red-shifted and broadened. Figure 6 shows the absorption



**Figure 6.** Absorption spectra of (a) Au, CZTS, and coupled Au-CZTS heterostructure and of (b) Au, Bi<sub>2</sub>S<sub>3</sub> and Au-Bi<sub>2</sub>S<sub>3</sub> heterostructure. Panels a and b of this figure have been reproduced following the protocol discussed in ref 61 and 6, respectively. Reprinted with permission.

spectra of Au-CZTS and Au-Bi<sub>2</sub>S<sub>3</sub> nanostructures and in both cases similar changes in the plasmon have been noticed. This change is expected due to the coupling of plasmon of Au with semiconductor exciton. As a result, strong optical field is generated at the interface of Au, which persists into surrounding dielectric for about 10 nm. This field enhancement can exist far from the resonating plasmon excitation energy. This has also been suggested by Talapin et al. for Au-PbS core/shell structure where the coupling tune the plasmon and enhances the excitonic coefficient.<sup>57</sup> Hence, this coupling can be assumed here for the suppression of the exciton, which in turn is expected to help in efficient transfer of the electrons for triggering photocatalytic chemical reactions.

*Heterostructures for Charge-Separation and Photocatalytic Redox Reactions.* Photocatalytic reactions involving heterostructured photocatalysts have already been demonstrated by Banin group for Au tips-CdSe rods.<sup>33</sup> In this case, on excitation, CdSe generates the charge carriers and due to presence of metal Au, the electrons are promptly transferred from CdSe CB to Au as shown in Figure 1b. This has been tested with the organic dye methylene blue (MB). The charge separation and also retention on the heterostructures here was further demonstrated by using preirradiated experiment, which had different observation than the standard in situ experiment. Soon after this report, several other hybrid nanostructures were also reported promoting the dye degradation process. Further, in case of Au-CdS heterostructures the catalytic properties are also studied and depending on the excitation, the electron transfers either from Au to CdS or vice versa has been established. Though under simultaneous excitation, the transfer of electron from semiconductor to metal Au remain predominating.<sup>56,60</sup> Although here the heterostructures used are the CdSe or CdS rods with Au tips at both ends of the rods, a recent report suggests Au even being at the center of Bi<sub>2</sub>S<sub>3</sub> rods also show similar photocatalytic behaviors.<sup>6</sup> The rate of MB reduction using Au-Bi<sub>2</sub>S<sub>3</sub> has been shown in Figure 7b, which follows the similar



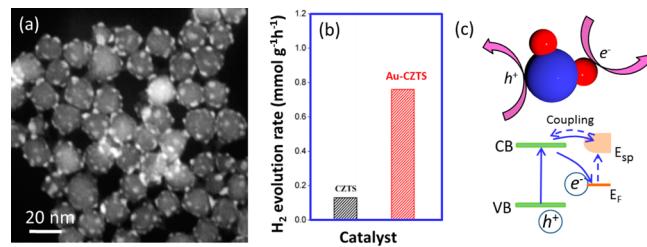
**Figure 7.** Comparison of (a) the rate of degradation of Rhodamine B dye with Au-CZTS and CZTS nanocrystals and (b) rate of degradation of MB with Au-Bi<sub>2</sub>S<sub>3</sub> and Bi<sub>2</sub>S<sub>3</sub> nanorods. In both cases the data on control reaction have also been shown in same panel. Panel a has been obtained from the ref 28 and that of panel b from the ref 6. Reprinted with permission.

electron transfer pathway as in case of Au-CdS and Au-CdSe heterostructures. The dye degradation has also been further tested with Au-CZTS nanostructures, which have emerged as the new metal–multinary–semiconductor heterostructures.<sup>28,47</sup> Figure 7a presents the comparative study of rate of degradation of the dye Rhodamine B (RhB) using CZTS and Au-CZTS nanostructures. This result clearly suggests that the coupled nanostructures with Au acts as more efficient catalyst for the

photocatalytic reactions compared to only CZTS. In addition to the above materials, recent report on plasmonic Au-SnS heterostructures also show enhancement of the rate of catalytic activities in the reduction of the dye MB compared to only SnS nanocrystals.<sup>77</sup> The mechanism in all these cases follow similar path, where the charge carriers recombination is suppressed because of the coupling of the metal plasmon and semiconductor exciton, helping its smooth transfer to the organic dye thus enhancing the catalytic reaction rate. This has been schematically depicted in Figure 1c. For the dye MB, the decolorization is termed either as degradation or reduction in different reports but in either case the electron is transferred to MB, which induces the chemical reaction.

*Nano Heterostructures for Photocatalytic Water Splitting.* Following the similar principle of faster charge carriers separation in these nano heterostructures, these materials also have recently emerged as efficient photo sensitizers for light-driven hydrogen evolution by catalytic water splitting.<sup>28,40,46</sup> In this process, the energy state of the photoexcited electrons of the catalytic materials should be above the redox potential of transformation of  $H^+$  ions to molecular  $H_2$ .<sup>1</sup> Different semiconducting nanostructures having ideal bandgap, have already been used as photocatalysts for promoting this hydrogen generation process. The efficiency of such system has already been shown for different shapes of Au-CZTS nanostructures, an ideal example of metal–multinary-semiconductor heterostructures.<sup>46</sup> The mechanism here is expected to be similar to that of the photocatalysis for the organic reactions, where the photo generated electron is transferred to water for carrying out the redox reaction of transforming  $H^+$  of water to  $H_2$  gas. Even though this catalytic activity has been extensively studied for wide variety of semiconductor nanostructures, but for nano heterostructures, which are also expected to be efficient materials, they are little explored. Again, among these plasmonic Au coupled with high bandgap semiconductors where only the Au is excited; the electron transfer process is somewhat established. On the other hand, for the heterostructures where Au is coupled with low-bandgap, greener semiconductors, where both materials can be simultaneously excited under visible light, the electron transfer process for carrying out the catalytic activities are yet to be explored.

Typically, for an ideal catalyst, when it is dispersed in water and irradiated, the water should generate  $H_2$  and  $O_2$  as shown in the case of CoO nanostructures.<sup>4</sup> But, majority of such process needs an additional set up where the photogenerated holes need a hole scavenger reagent to trap them. In a recent protocol, Cabot et al.<sup>28</sup> have used decorated Au-CZTS (also Pt-CZTS) for splitting of water. They have used  $S^{2-}/SO_3^{2-}$  solution as hole scavenger. Figure 8a shows a typical HAADF-STEM of Au decorated CZTS nanocrystals, and Figure 8b represents the rate of evolution of  $H_2$  gas using both CZTS and Au-CZTS nanocrystals. The result clearly indicates that the heterostructures show higher efficiency than the only semiconductor nanostructures. This high efficiency has been explained again with the fast transfer of the photogenerated electron from the semiconductor to metal gold. Here the surface plasmon resonance of the Au particles has assisted in separating the charge carriers that, again facilitates efficient carrier transportation. The electron here is expected to be transferred from Au and the hole from the semiconductor valence band (VB). A typical mechanism of such charge



**Figure 8.** (a) HAADF-STEM image of Au decorated CZTS nanocrystals, (b) amount of hydrogen evolution using CZTS and decorated Au-CZTS catalysts. These images are obtained from ref 28. Reprinted with permission. (c) Schematic presentation of the separation of electron and hole under excitation.

Here the surface plasmon resonance of the Au particles has assisted in separating the charge carriers that, again facilitates efficient carrier transportation.

separation has been shown in Figure 8c, which follows similar to the path 1 mechanism shown in Figure 1c.

Another example for water splitting for the core/shell heterostructures having Au at the core and CZTS in shell has recently been reported by Wong et al.<sup>46</sup> The size of Au in this case remains larger ( $\sim 15$  nm) and the shell varies within 10 to 15 nm. Authors observed here the red shifting and broadening of the surface plasmon absorption peak, which indicates the extensive perturbation of gold energy states in the near-IR region due to interaction with semiconductor electronic states. It is expected that the Fermi level of gold would reassign its position, which would help for the faster transfer of the photogenerated charge carriers. While studying the catalytic hydrogen evolution by splitting of water using the  $S^{2-}/SO_3^{2-}$  solution as hole scavenger, authors observed that the core/shell structures are more efficient than other shapes of only CZTS nanostructures. The high efficiency in the core/shell structures again is attributed to the similar mechanism, where the SPR of Au couples with the semiconductor exciton and helps in better charge separation. However, as Au remains at the core, in this particular case, both the electron and hole are expected to be transferred through the CB and VB of CZTS only, though both Au and CZTS are excited simultaneously. Hence, either Au is attached on the side or remained at the core, these structures have shown superior and more efficient catalysis than the only the semiconductor for catalytic water splitting.

*Challenges and Outlook.* In summary, we addressed here the latest developments in the synthetic chemistry of nano heterostructures of Au with low bandgap semiconductors and discuss their photocatalytic behaviors. The crystallographic orientation relations of the appropriate facets of metal Au with several semiconductors are correlated, where the coincident site epitaxy is expected as a possible reason for formation of the heterojunction in spite of the large lattice mismatch between the two materials. Further, the exciton–plasmon interaction stabilizing the photoinduced charge separation in these heterostructures, is discussed as a probable reason for enhancing the photocatalytic behavior for generation of hydrogen from water splitting as well as triggering organic reactions.

However, only a few such materials are developed till date, but their promising photocatalytic activities encourage development of a wide variety of such materials, where the appropriate band alignment would support more facile electron transfer. Though analyzed, on the one hand, the chemistry of architecting of these heterostructures needs to be properly understood. The heterogeneous nucleation formation either for the growth of semiconductor on metal or vice versa needs to be optimized without allowing formation of new nucleations. Next, the shape of the nanostructures also plays a crucial role in determining the efficiency of the catalysis. For example, when compared with core/shell Au/TiO<sub>2</sub> nanostructures, Janus-type heterostructures show superior catalytic behavior for the splitting of water and generation of hydrogen.<sup>55</sup> On the contrary, a recent report has shown that for core/shell Au/CZTS, the rate of hydrogen evolution from water is more than the Au-CZTS Janus-type structure.<sup>28</sup> All these results indeed suggest that the shape of the nanostructure and particularly the position of Au are critical in determining the electron transfer process and the rate of the catalytic activities. Hence, wide variety of nanostructures with different shapes needs to be designed and details of the catalytic activities are to be further studied for understanding a clear and concrete mechanism. Next, as the metallic nature of the Au and its plasmon help with the separation of the photogenerated charge carriers, it is important to study the catalytic activities by varying the size of Au particles. It is widely known that when the dimension of Au falls below certain nanometers, the metallic character reduces and it behaves more like semiconductor and the plasmonic behavior of Au reduces. Using both plasmonic and nonplasmonic Au particles, it is observed recently for their heterostructures with SnS that, the catalytic activities drastically reduce with reduction of plasmonic behavior.<sup>77</sup> Although Au is also known for quenching the quantum dot exciton emission, a recent report also suggests that for cluster size nonplasmonic Au, the CdSe still retains the emission to significant extent.<sup>82</sup> These results suggest that the size of Au also plays a crucial role in determining the electron transfer ability and also the catalytic behaviors. Hence, a detailed study in this respect is warranted, and also, more semiconductor heterostructures with different sizes of Au need to be investigated to come out with a conclusion. In addition, the coupling of surface plasmon of Au and the semiconductor exciton, which helps in the delocalization of the electrons in their excited states and enhancing the catalytic activities, can also be tuned more efficiently. Once this plasmon-exciton coupling is properly understood, the catalytic activities can be controlled and these materials can be implemented for catalyzing a wide variety of organic reactions.

Apart from the chemistry of formation and size and shape variation in the semiconductor as well as Au, the most important part is studying the photophysics to understand the involved electron transfer processes. These studies have been limited to CdS, CdSe, and few widely studied materials. However, this needs deep investigation with study of ultrafast spectroscopy in various heterostructure systems for obtaining a generic conclusion. The particular system discussed in this Perspective, where the metal and semiconductor both are excited, the electron transfer processes indeed remains unsolved and complicated. The movement of electrons and holes and their involvement for the catalysis need to be deeply investigated, and hence, a detailed study of the photophysics, including single-particle spectroscopy analysis, is warranted.

Finally, the photocatalysis needs to be further studied with a wide variety of organic systems, including degradation of pollutants and common laboratory organic reactions. This can be extended to biochemical reactions and also as efficient process for detoxifying selective bioorganisms. Importantly, the heterostructures are expected as ideal photoresponse materials for efficient solar light harvesting and also for implementations in photovoltaics.

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