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ORIGINAL PAPER

Structural and electronic investigation of metal-semiconductor hybrid tetrapod hetero-structures

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Abstract This article highlights the new electronic properties of tetrapod hetero-structures with metal Au core and semiconductor CdSe arms, which is one of the new classes of hybrid metal-semiconductor nanostructures. From the analysis of XRD, HRTEM, HAADF-STEM images, and EDAX line-scan studies, the growth mechanism of all these hetero-structures is proposed. These findings are important from the basic fundamental aspects of understanding the shape control of hetero-structures. Scanning tunneling spectroscopic study confirms the coulomb staircase-like features near Au which is characteristic of Au nanoparticles and the gap increases as we move the tip towards CdSe. Analysis suggests that the resonance tunneling occurs between valance band edge (conduction band edge) of CdSe and coulomb stairs of Au dot. These tetrapod hetero-structures could pave the way for designing new optical-based materials for developing new challenging photonic devices.

Keywords Au/CdSe · Hetero-structures · Nanotetrapod · STM · Coulomb staircase · Resonance tunneling

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Introduction

Metal-semiconductor hybrid nanostructures have recently emerged as a new class of functional materials because of their potential applications in the areas of photonic, optoelectronic, and various leading fields [1–5]. Wide varieties of such nanomaterials are fabricated and reported during the last two decades [6, 7]. These hybrid nanostructures can have various architectures including individual metal conjugated with semiconductor [8, 9], core-shell [10], tetrapods [11, 12], and dumbbell shapes [13].

It is evident that metal-semiconductor (SC) hybrid nanostructures lead to significant change in the electronic structures. Thus, it is important to know the band structure and the interfacial charge transfer process of these hetero-structures for their device applications. Again, nanocontacts of these hybrid nanostructures played an important role for nanoelectronic devices. Sitt et al. [14] have demonstrated the band-gap engineering and optoelectronic applications of colloidal hetero-structured semiconductor nanorods. Steiner et al. [15] have already reported the electronic properties of metal-semiconductor using scanning tunneling spectroscopy in Au/CdSe nanodumbbells. It is also reported that sub-gap structure emerges near the metal-semiconductor nanocontact [16, 17]. However, to best of our knowledge, there is no report on electronic properties of metal-semiconductor tetrapod hetero-structures using scanning tunneling spectroscopy.

Cozzoli et al. [18, 19] have synthesized bimagnetic hybrid nanocrystals using colloidal seeded-growth strategy. Deng et al. [20] have synthesized three-dimensional bimagnetic h-Co/h-CoO nanotetrapods. However, designing of such hetero-

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structures is not straight forward like well-established metal or semiconductor nanostructures; rather, it requires a more selective approach to bring both their counterparts together. This designed decoupled reaction temperature protocols of semiconductor nanostructure formation and metal growths suit for the existence of both metal and semiconductor in the solution. However, the situation remains complicated for the reverse case to nucleate and grow the semiconductor counterparts of the hetero-structures on metal surfaces. This needs a high-temperature reaction system where the metal structures present in the solution might react with semiconductor counter ions (anions) and/or the semiconductor materials could also separately nucleate and grow their own. One such example is tetrapod hetero-structure with metal core and semiconductor arms. It preferably needs the nucleation and growth of semiconductor arms on metal seeds at elevated temperature where the reactivity of metals with the anion present in the solution may also compete with the semiconductor formation. Once this would be achieved, the chemical reactions could be manipulated for the growth of semiconductor arms on metal seeds at elevated temperature to lead different complex hetero-structures.

In the present study, we have synthesized Au/CdSe tetrapod hetero-structures with Au core and CdSe arms and study their electronic properties. Scanning tunneling microscopy and spectroscopy (STM/STS) is being used to investigate the topography and local density of states (LDOS) of the sample with very high resolution. Such knowledge will enable us to construct efficient devices for photonic applications.

Results and discussion

Au nanoparticles were synthesized from reported methods [21–24]. For this particular procedure, Au nanoparticles were about ~6 nm in diameter, with the nearly spherical shape. The synthesis procedure is described in details in the supplementary information. For the formation of hetero-structures of Au/CdSe, the amine-capped Au particles are treated as seeds for CdSe growth at elevated temperature. However, the approach of the Cd and Se precursors to the reaction system played a determining factor for driving the structural transformation. Introducing Cd source first and then Se nucleates and grows separate CdSe nanocrystals leading to the mixture of gold and CdSe particles in the solution. However, switching the approach of these reagents with Se first and Cd next, the system performs differently and Au core with CdSe arm hetero-structures remained the exclusive product. Thus, the addition of precursor chemical plays an important role in making these complex hetero-structured materials. Formation of these different nanostructures with switching the approach of reagent introduction clearly suggests that the structural transformation obtained here is driving by the chemical reactions performed in the reaction system.

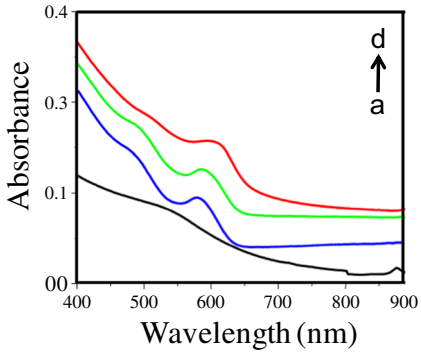

Fig. 1 The time-dependent evaluation of absorption spectra of Au/CdSe hetero-structure (*a–d*)

As both Au and CdSe nanostructures have distinguished optical absorption, the reactions in both approaches have been monitored spectrophotometrically. Figure 1 (b–d) shows the time-dependent evaluation of absorption spectra for reactions with the different sequential approaches of Cd and Se to gold seeds; the plasmonic absorbance centered at 520 nm has been observed due to the gold seed particles (Fig. 1, spectra a). Within 5 min of reaction, a clear absorption band ~578 nm has been observed due to CdSe formation (Fig. 1, spectra b). The gold plasmonic absorption has been expected to be buried within the CdSe absorption spectra. The time-dependent red shift of the band edge absorption reflects the growth of CdSe nanostructures. To understand more about the difference in the spectral tuning and their origin, microscopic picture of different products has been analyzed.

As the initial seeds are spherical and final structures are tetrapod in shape with CdSe arms, it is important to know about the nucleation and growth of CdSe on gold seeds using these XRD, TEM, HRTEM, and HAADF-STEM studies. Figure 2 shows the XRD spectra of gold nanoparticles, CdSe, and Au/CdSe hetero-structure. The initial gold NP shows fcc structure with prominent peak at 38.18° (d = 0.235 nm) (Fig. 2 (b)) and Au/CdSe shows wurtzite CdSe with peaks at 23.9°, 25.5°, 27.07°, 41.9°, and 49.5°, indicating the formation of hetero-structures having wurtzite (WZ) CdSe [22] (Fig. 2 (c)) arms on cubic gold seeds. Peaks at

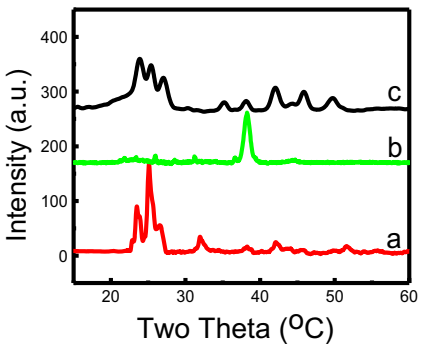

Fig. 2 XRD pattern of *a* wurtzite CdSe, *b* cubic Au, and *c* Au/CdSe nanotetrapod

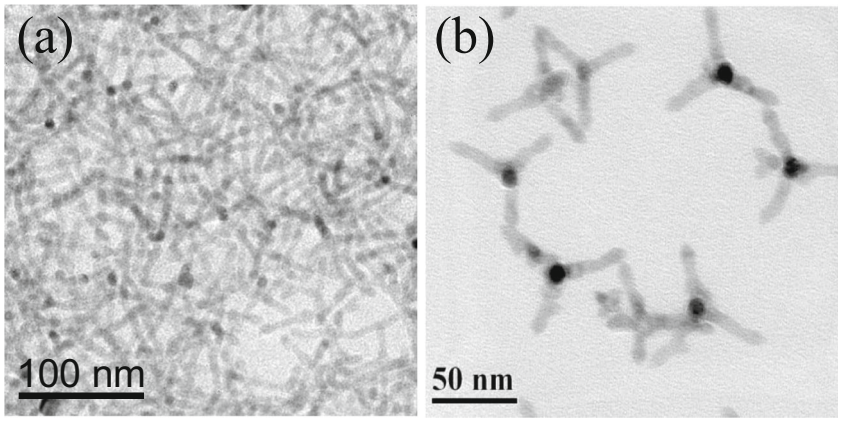

Fig. 3 **a**, **b** The TEM images of Au/CdSe nanotetrapod in a different view

38.14° and 44.3° in the XRD spectra of Au/CdSe also suggest the presence of gold in the hetero-structures. In absence of Au nanoparticles, spherical wurtzite CdSe is formed (Fig. 2 (a)). To support the XRD data, we have seen the TEM image of the as Au/CdSe tetrapod hetero-structure.

The TEM images of Au/CdSe tetrapod hetero-structures are shown in Fig. 3 where Au is in the center and the arms are CdSe. Figure 3b shows a hybrid Au/CdSe tetrapod structure where the dark contrasts Au core has been clearly visible and all the arms are shown in one plane with distinct separation. From the FFT, the arm of each tetrapod supports the hexagonal (WZ) structure which has the d-spacing of 3.71 Å corresponds to (001) planes, i.e., CdSe is grown along [001] direction. Due to the difference in contrast to Au and CdSe and the orientation of the different arms relative to the electron beam, it is always difficult to observe clearly both lattice images of Au and CdSe simultaneously. Figure 4 shows the HRTEM image of Au/CdSe tetrapod hetero-structures where (111) plane of Au attached with (001) plane of CdSe. Figure 4e represents the HRTEM, FFT, inverse FFT, and d-profile of CdSe arms in Au/CdSe tetrapod hetero-structures. From the HRTEM of CdSe arms, the d-spacing of 3.71 Å confirms the (001) plane of CdSe and FFT also supports the hexagonal structure. Mokari et al. [13] have already reported that it is difficult to identify the interface between Au and CdSe and they proposed the formation of Au–Se bonds in the interface upon injection of Se before Cd precursor. Again, de Paiva et al. [25] showed formation of AuSe due to mixing between Au and Se orbitals. Thus, we believe that similar situation may be expected in the present study. The formation of this AuSe layer might help to form the tetrapod hetero-structure formation. ICP and EDAX further confirm the presence of Au elements. Again, the element mapping of the Au/CdSe hetero-structures is done from HAADF-STEM images (Fig. 5). HAADF-STEM images of the tetrapod structures clearly suggest that Au is at the center and confirming the

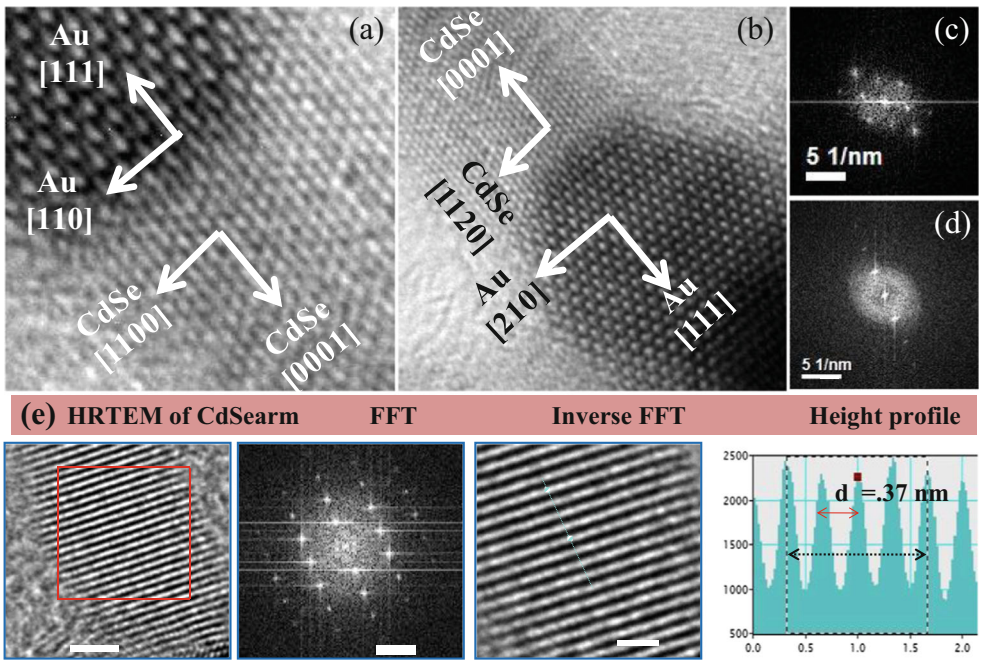

Fig. 4 The HRTEM picture of **a** Au/CdSe tetrapod and **b** the hetero-junction of Au/CdSe tetrapod. **c**, **d** present the FFT patterns of Au and CdSe, respectively. And the selected **e** HRTEM area, FFT, inverse FFT, and the intensity height profile to identify the CdSe planes and the viewing direction

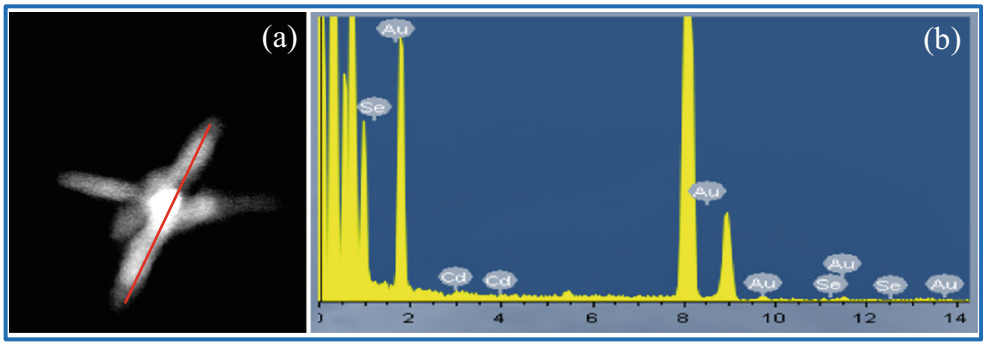

Fig. 5 **a** HAADF image and **b** the EDAX spectra of Au/CdSe nanoparticles (the line-scan electron mapping for the presence of Au, Cd, and Se of Au/CdSe nanotetrapod)

hetero-structures consisting of both metal Au seed and semiconductor CdSe arms (Fig. 5). From the arm patterns, it is clearly observed that tetrapod arms of CdSe are nucleated on the (111) facets of Au and are linearly grown only along the [001] direction.

Analyzing the reaction progress and the XRD, TEM/HAADF-STEM images, we have proposed here the growth mechanism of linear arm formation of Au/CdSe tetrapod hetero-structures. Banin group [13] has designed the growth of Au tips on CdSe nanorods, where the semiconductor CdSe has been synthesized at high temperature and metal Au is deposited at mild reaction condition. Manna group [26, 27] has reported the hetero-epitaxial junction formation between gold and CdSe at higher temperature. Even these methods have the new contribution towards their synthesis, structural shape evolution, and formation mechanism but both methods follow the similar synthetic methodology, i.e., the growth or fusion of metal on pre-synthesized semiconductor nanomaterials leading to similar and/or different shaped hetero-structures. For the case of noble metal growth on wurtzite semiconductor one-dimensional nanostructure at high temperature, the possible mechanism of a preferable axial growth is the electron-rich gold particles and the polar [0001] axis. As the [0001] axis alternatively contains positively charged Cd and negatively charged Se, gold can approach the positively charged Cd and facilitate the growth. However, in the present study, we believe the formation of AuSe interface (Figure S-1) layer which enables the axial semiconductor growth on noble metal surfaces. In this case, the approach of the cation Cd to the Au surface is most probably due to the selenide interface which is the new mechanistic approach here for the directive semiconductor growth. Crystal structure characterization via HRTEM of the AuSe NCs indicated, for the Au, the surface is enriched with Se that was consistent with a cubic AuSe phase. A TEM-EDX performed across a group of AuSe NCs revealed the Au and Se elemental distribution (FigureS-2). The chemical quantification from EDX analysis yielded atomic ratios of Au/Se equal to 3.9:1 for the AuSe. This is also the driving force for restricting the new nucleation of CdSe and forming exclusively the tetrapod hetero-nanostructures as reported in this communication. The reaction temperature is necessary for the high-quality semiconductor nanostructure formation; gold is expected to be highly reactive to react with the anionic counterpart of the semiconductor and lost its identity. Hence, the study of such hetero-crystal growths and gather more information on the formation mechanism of the hetero-junctions remained practically difficult and needs more precisely controlled reaction system for such establishment.

To understand the band structure and electronic properties of metal-semiconductor tetrapod hetero-structures, we used scanning tunneling spectroscopy. Figure 6 shows the topographic image of tetrapods deposited on HOPG. Since the images are taken at constant current, there is not much variation in the intensity as tip moved from the center where the Au nanoparticle is present to the CdSe nanorod. However, one end of the tetrapod looks brighter than the other end due to the presence localized density of state near gold nanoparticles. STS measurements are performed at different locations of the

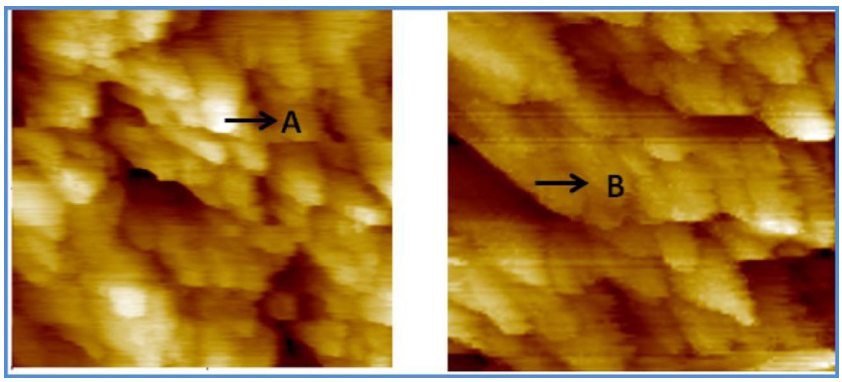

Fig. 6 STM images of tetrapods, 50 nm × 50 nm scan area

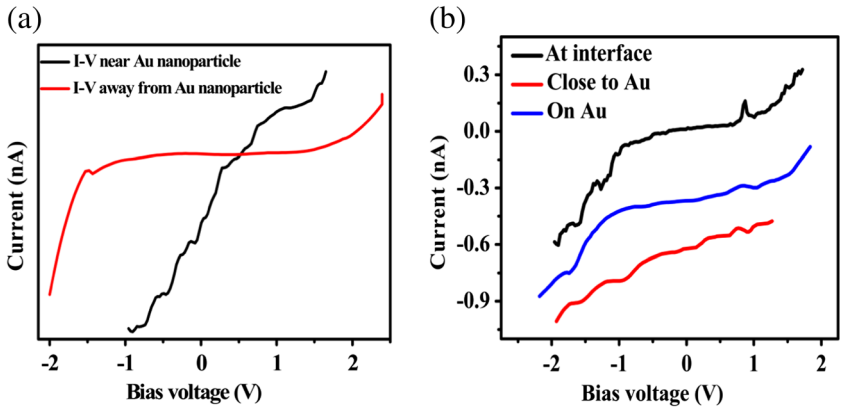

Fig. 7 **a** I-V curves in regions A and B. **b** I-V curves moving from region A to interface showing the presence of room temperature negative differential conductance (NDC)

rod starting from the tip of the rod where it is attached to gold nanoparticle. As shown in Fig. 7a, the I-V characteristics in regions A and B of Fig. 6 are completely different. I-V in region A of the topographic image reveals an enhanced conducting behavior whereas a wide band gap in region B. The different features of I-V in two regions can be explained by an enhanced conduction due to the mid-gap states in region A compared to region B. Figure 7b shows the representative spectra in the region of the interface between the regions A and B. It is clearly seen from I-V curve that the coulomb staircase-like features were observed near Au which is characteristics of Au nanoparticles and the gap increases as we move the tip towards CdSe because the resonant tunneling mechanism occurs between coulomb states of Au particles and CdSe band structure. The figure also shows the emergence of negative differential conductance as a function of distance from the Au particle at −1.7 eV (valence band) and at 0.7 eV (conduction band). These features can be observed more prominently when we take dI/dV as shown in Fig. 8. The spectra (a) in Fig. 8 resemble the spectra of typical metal nanoparticle spectra and as we move from (a) to (f), the curves start resembling a typical curve for CdSe rod. In the curves (b), (c), (d), and (e) though the gap is increasing, there are several sub-gap states which have appeared due to the contribution of Au at the interface. Along with the sub-gap states, there is a presence of sharp peaks and NDC peak in the spectra from (b) to (f). These could be attributed to the resonance tunneling that occurs between valence band edge (conduction band edge) of CdSe and coulomb stairs of Au dot.

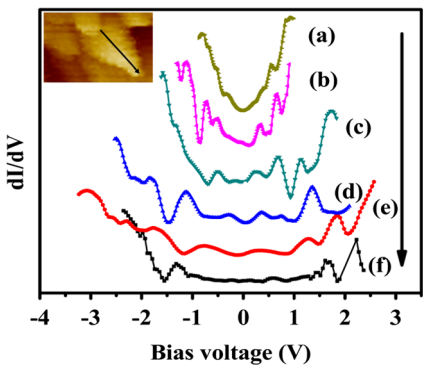

Fig. 8 Evolution of (*a–f*) tunneling spectra from the gold nanoparticle to the CdSe rod shown by the *arrow*

Conclusions

We report here the synthesis of tetrapod-shaped Au/CdSe hetero-nanostructured materials by growing the semiconductor CdSe on the surface of noble metal gold seeds. From the analysis of XRD, HRTEM, HAADF-STEM images, and EDAX line-scan studies, the growth mechanism of all these hetero-structures is proposed. These findings are important from the basic fundamental aspects of understanding the shape control of hetero-structures and these are also important materials for several potential applications. It is evident from scanning tunneling spectroscopic study that the coulomb staircase-like features are observed near Au; the resonant tunneling mechanism occurs between coulomb states of Au particles and CdSe band structure. Au core in these tetrapod structures caused the material to exhibit significant improvement in the photocatalytic activity. The importance of these finding goes beyond the basic science of metal-semiconductor tetrapod hetero-structures and is expected to impact on various applications in photonics.

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