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RESEARCH ARTICLE

NOVEL APPROACH FOR ONE-POT SELF-ASSEMBLED MONOLAYER PREPARATION OF GOLD TIPPED CdSe/CdS NANORODS

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ABSTRACT

In this study, CdSe/CdS nanorods (NRs) were synthesized via hot injection method to perform simultaneous self-assembly studies with gold tip formation on the nanorods. In this new approach, we propose and demonstrate reductant chemical and gold organosol-free synthesis of gold-tipped nanocrystals on the subphase. Instead of gold organosol usage, gold precursor was prepared by addition of gold source into subphase, and photocatalytic reduction of gold on the tip of nanorods was achieved by exciting the samples under UV-light excitation. Reduction of gold nanoparticles on the tip of NRs was also tried by heating effect, which results in smaller gold tip formation. The optical properties of these nanorods were determined by spectrophotometric measurements, and gold-tipped nanorods were imaged by TEM analysis. This method enables self-assembly of nanorods and following gold tip formation on the subphase, and it can pave the way to prepare well-defined metal-tipped oriented surfaces that can be used for optical and photocatalysis applications.

Keywords: Gold-tipped nanorod, Self-assembly, CdSe/CdS nanorod

1. INTRODUCTION

Nanocrystals (NCs) with a size regime between 1-10 nm constitute a major class of nanomaterials since they have remarkable properties that can be tuned by controlling their size and shape. Quantum confinement occurs when the size of the material is comparable to exciton Bohr radius and differs in nanocrystal physical properties from bulk materials. Since the size of NCs decreases, the number of atoms also decreases from a few thousand to a few hundred. This results in an increase in the surface/volume ratio. The high surface-to-volume ratio of NCs affects their structural and optical properties significantly. So, the properties of the nanocrystal can be adjusted by changing their sizes [1-4]. New optoelectronic properties can be created by using heteronanocrystals (HNCs) by changing their composition, size, and shape. CdSe/CdS HNC is a significant model since it presents the appealing characteristics of strong, tunable and polarized light emission that can be manipulated by external electric fields [5]. Band alignment of the heteronanocrystals is strongly dependent on the quantum confinement of charge carriers (i.e., electrons and holes) that can be adjusted by changing the size of the CdSe quantum dot (QD) core and the geometry of the CdS shell [6]. In such NRs, CdSe is a spherical core, and CdS is rod shaped shell. This structure presents useful properties for many applications because of the separation of charge carriers. The hole is located in the core while electrons can move through the CdS rod body, as a good example of type $I^{1/2}$ heteronano structures [6]. CdSe/CdS HNRs can be used for emerging applications such as photovoltaics, photodetectors, LEDs, lasers, and single photon sources. They also got great attention for optical labeling, photocatalytic solar fuel production, and photoconductive films because of their high quantum yield and low full width half maximum values of PL.

Diverse combinations of semiconductor/metal hybrid nanostructures have been reported in the literature, such as PbSe/Au, Ag or Pd, CdSe/Au, and CdS/Au or CdSe/CdZnS/Au [7]. Metal tips of such

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multicomponent heterostructures can act both as an electrical contact [8-10] and as an anchor point for self-assembly [11], while the core-shell structure of NRs is responsible for the unique optical properties [10, 12, 13]. Metal-tipped, seeded core-shell semiconductor nanorods exemplify to multifarious functionalized nano structures [14]. An example of metal-tipped heteronanorods is Pt-tipped CdSe/CdS HNRs, which have been used effectively for photocatalytic hydrogen production [15]. The system is composed of a platinum-tipped CdS nanorod with an embedded CdSe seed. In such structures, holes are three-dimensionally confined to the core, whereas the electrons are delocalized through the rod body and can be transferred to the metal tip. Consequently, the separation of the electrons from the holes within a tunable physical length and efficient, long-lasting charge carrier separation can be achieved over three different components. This future makes the metal-tipped heteronanocrystals crucial for solar energy harvesting, photocatalysts, or as building blocks in solar cells.

Understanding and mastering both the synthesis and the self-assembly phenomena has been recently made for various nanocrystals [16, 17]. The self assembly process can be controlled by external fields, by interparticle interactions as well as solvent, subphase or capping ligand choice. Binary solvent/nonsolvent usage also affects the self assembly tendency of the nanocrystals [18]. Ordered assemblies and orientation control of nanorods and their metal tipped counterparts are important for investigation their chemical and physical interactions among nanocrystals. It is also emerging research area for practical applications, as it results in the engineering of new materials and the fabrication of devices [10]. Synthesis of gold-tipped nanocrystals as emerging material for many application reported in the literature [7, 19]. Nevertheless, there is a need for enhancement in the preparation of in-situ self-assembled films of metal tipped nanocrystals.

Herein, a hot injection method with a seeded growth approach was used to synthesize CdSe/CdS nanorods. The optical, morphological and composition characterization of the nanocrystals was performed. This red emissive nanorods were used for self-assembly experiments. The main aim was one-pot formation of gold tipped nanorods without using any reducing, stabilizing agent and simultaneous self assembly of the sample. This new method can be used to prepare all-the same-oriented Au tipped nanorods self assembled monolayer films for furter photocatalysis applications, lasing, and surface enhanced Raman spectroscopy. It also paves the way for conducting the method to other nanocrystals (i.e. nanoplatelets) or other metal precursors (i.e. platinium, silver, and palladium) for improved applications.

2. EXPERIMENTAL

2.1. Materials and Characterization

Cadmium oxide (CdO, Sigma-Aldrich, 99.9%), trioctyl phosphine oxide (TOPO, Alfa Aesar, 98%), trioctyl phosphine (TOP, abcr, 97%), octadecylphosphonic acid (ODPA, abcr, 97%), selenium (Se, Sigma-Aldrich, 99.99%), sulphur (S, Sigma-Aldrich, 90%), ethanol (EtOH, Sigma-Aldrich, 99.8%), methanol (MeOH, Alfa Aesar, 99.9%), tetrahydrofuran (THF, Sigma-Aldrich, 99.9%), hexane (Honeywell), toluene (TOL, Merck, anhydrous), potassium tetrachloroaurate(III) ($KAuCl_4$, CHEMPUR, 99.95%), ethylene glycol (EG, Sigma-Aldrich, 99%) diethylene glycol (DEG, Sigma-Aldrich, 99%) were used.

Transmission electron microscopy (TEM) analysis was conducted using a Hitachi HT7800 T at an accelerating voltage of 100 kV. Spectrophotometric analysis at 25 °C across the wavelength range of 200–700 nm was carried out using UV–VIS spectrophotometry (Perkin Elmer Lambda 35). The Au-NRs sample underwent X-ray diffraction (XRD) measurements using a powder diffractometer (Empyrean, Panalytical) with CuKα irradiation, scanning through 2θ angles ranging from 20 to 90°. Perkin-Elmer LS-55 spectrophotometer was employed to get the photoluminescence (PL) spectra.

2.2. Methods

Preparation of Se precursor

0.058 g of Se powder is weighed and placed in a 2 ml vial, then 1.2 g of TOP is added. A magnetic stirrer is placed to vial and mixed for 1 hour at 80 °C to ensure that all Se powder dissolved. A colorless homogeneous solution formation indicates that interaction between Se powder and TOP has occurred.

Synthesis of CdSe seed

CdSe quantum dots were synthesized by hot injection method, which is performed by injecting a cold chalcogenide precursor into a high-temperature metal precursor. 3 g of TOPO is weighed and placed in a 3-necked flask with a round bottom. While the Vigreux column is attached to it, the other two outlets are closed with a high temperature-resistant rubber septa. The Vigreux column is closed with a t-adapter for nitrogen and vacuum output. In this way, the system is placed in the glove box. 0.06 g CdO and 0.28 g ODPA are added inside the glove box. The taps of the flask and Vigreux column are closed, and the flask is taken out of the box for further attachment to the Schenk line. The mixture is kept in N_2(g) atmosphere until it melts, the oxygen and water in the environment and the chemicals that will disrupt the reaction are removed by stirring for 1 hour under vacuum (4.10^{-2} Torr) at 170 °C. Then, Cd and TOPO-ODPA molecules are allowed to interact at 300 °C. A color change in the solution from brown to colorless indicates that the reaction has occurred. As soon as the solution becomes colorless, the temperature of the environment is increased to 385 °C. The heater is lowered to 380 °C, and when the temperature reach at this value, 1.5 g TOP and then Se-TOP precursor is injected. When the color of the solution in the reaction flask turns brownish red, the heating jacket is quickly removed, the flask is rapidly cooled, and 5 mL of anhydrous toluene is injected. Then, the quantum dot colloidal solution in the flask is transferred to the vial closed with a septum. It is placed in a glove box and the quantum dot is precipitated by adding 2 mL of anhydrous methanol twice. The solution is centrifuged at 3000 rpm for 10 minutes. The remaining supernatant is removed, and 4 mL of TOP is added as a solvent. For nanocrystal characterization, 5 mL QD is taken into a vial, TOP is removed by evaporation at 60 °C, and 3 mL of toluene is added, and absorption and fluorescence spectra are recorded. Using absorption spectroscopy, first the diameter of the synthesized nanocrystal is calculated, and then the concentration of the stock solution.

Preparation of S precursor

0.12 g of S powder was weighed and placed in a 2 ml vial, and 1.5 g of TOP was added and stirred at 80 °C for 1 hour to ensure the interaction of S and TOP ligands. The discoloration of the solution indicated the interaction between S and TOP molecules.

Synthesis of CdSe/CdS NRs

CdSe/CdS NRs synthesized via seeded growth were weighed in a 0.06 g CdO, 3 g TOPO, 0.34 g ODPA glove cabinet and added to a three-necked flask. The water was removed under vacuum for approximately 1 hour at 170 °C. It was heated to 350-380 °C, which is the temperature of the reaction environment. When it reached the injection temperature, 1.5 g of TOP was injected, after which it was heated to the required temperature for the injection of S-TOP and CdSe quantum dot precursors. When it reached 350–380 °C, 200 µL of CdSe core (400 µM) and S-TOP reagent were quickly injected. The temperature drops suddenly but rises again. At this temperature, crystals were allowed to grow for 6 minutes. Rapid cooling of the reaction flask was achieved. When the temperature dropped to 60 °C, 10 mL of toluene was injected and transferred to vials prepared in a nitrogen atmosphere using a syringe. Purification was achieved by centrifugation at 3000 rpm by adding methanol solution [17].

One-pot self assembly and gold tip formation on the NRs

NRs solution (27 mg/mL) in toluene/heptane mixture was prepared. 5 mg of $KAuCl_4$ was dissolved in 20 mL subphase (EG or DEG). The mixture was put into the Petri dish followed by addition of hydrophobic NR solution on top of subphase. The toluene/heptane solvents are allowed to evaporate for the self-assembled layer formation. Then, the self assembled layer was placed under UV-light for 20 minutes for photocatalytic reduction of gold ions into gold tips.

3. RESULTS AND DISCUSSION

Here synthesis of CdSe/CdS core/shell nanorod was performed via hot injection method modified by seeded growth approach using CdSe QD as seed. Narrow size distributions of CdSe/CdS nanorods with strong and tunable light emission from green to red can be performed by this method [17]. Orange-red emissive CdSe/CdS NRs with narrow size distribution were synthesized by using well-defined CdSe QDs as seed. TEM images of the CdSe QDs and NRs are given in Figure 1-a,b, respectively. The mean size of the CdSe seeds was measured as 2.87 nm, while the mean thickness of NRs was 3.52 nm, and the mean length was 71.80 nm.

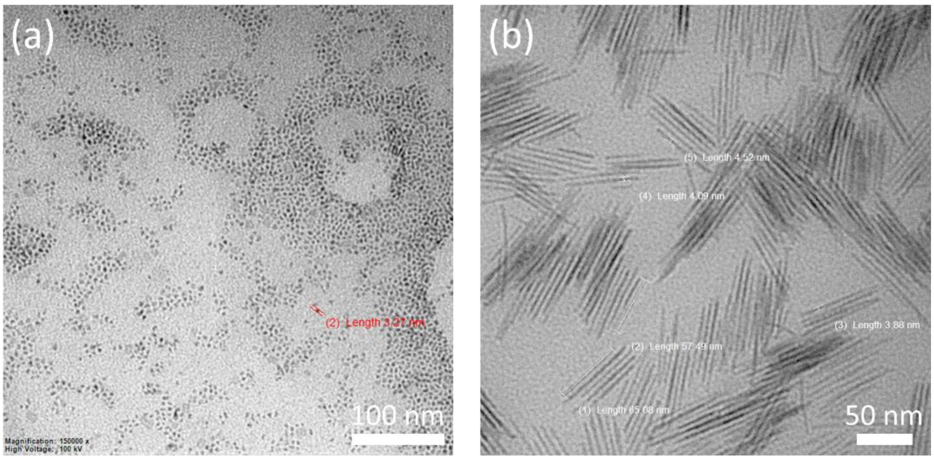

Figure 1. TEM images of CdSe quantum dots (a), and NRs (b).

The absorption from CdS shell as the high-energy peaks and the lowest energy peak originated from electronic transitions from holes confined in the CdSe seed can be seen in the absorption spectrum (Figure 2a). Photoluminescence (PL) peak is at 610 nm as shown in Figure 2b [17, 20]. Digital images of the NRs under daylight and UV-light excitation are given in Figure 2c with an orange-red emission.

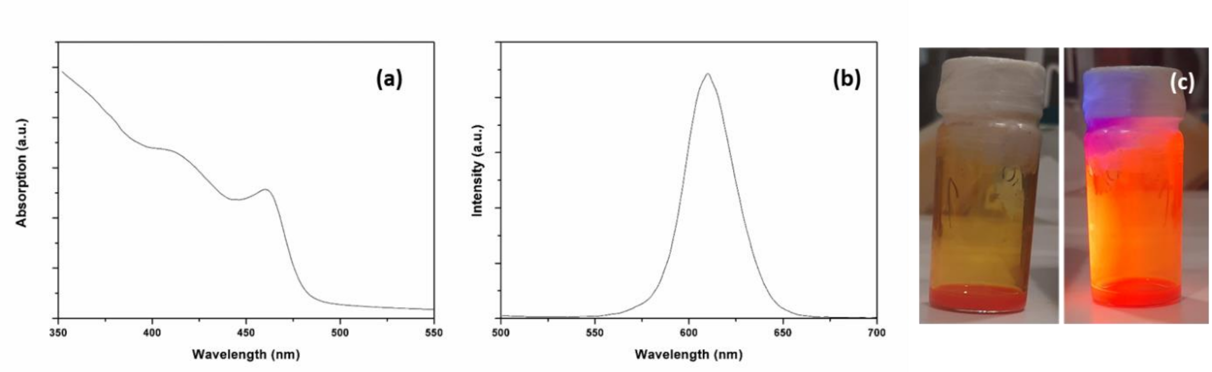

Figure 2. Absorption (a) and photoluminescent (b) spectra of NRs. Digital images of synthesized NRs under daylight (left) and UV-light excitation (right) (c).

The NRs were characterized by X-Ray diffraction pattern as given in Figure 3. The major reflections of hexagonal close-packed cadmium chalcogenide structure are observed at 2θ = 24.86°, 26.45°, 28.21°, 36.61°, 43.78°, and 51.88°, 71.03°, 83.354° which can be assigned to the, (010), (002), (011), (0 12), (1 10), (112), (121), (123) reflections, respectively [21].

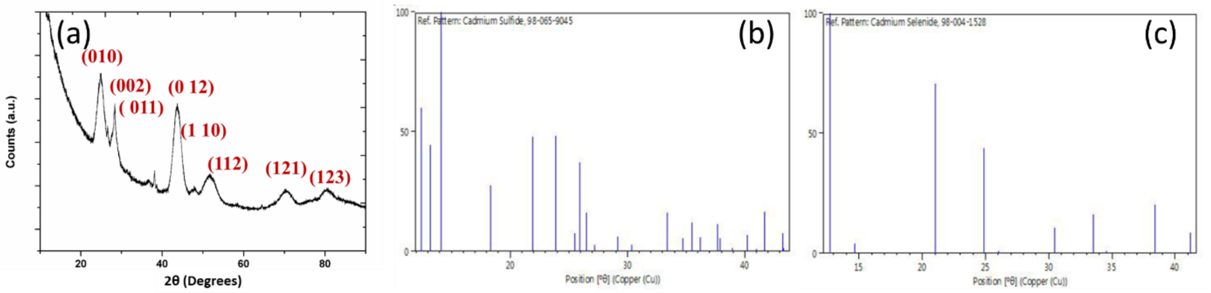

Figure 3. XRD pattern of synthesized NRs (a), reference peak positions of CdS (b), reference peak positions of CdSe (c).

These NRs have a tendency to self-assemble by easily organizing in close-packed ordered arrays on substrates over large areas [16]. Self assembly of NRs were performed on the EG and DEG subphases by dissolving gold source in it. Self-assembly of nanorods is a well-known phenomena for decades however self assembly of metal tipped NRs by orienting the metal tips on the same direction is challenging [17, 22-28]. In our approach, self assembly of NRs is followed by metal tip formation. Thanks to gold precursor containing subphase, gold ions are contacted to one side of NRs and tip formation can be controlled by this approach. The self assembly process on the gold precursor containing subphase is depicted in Figure 4.

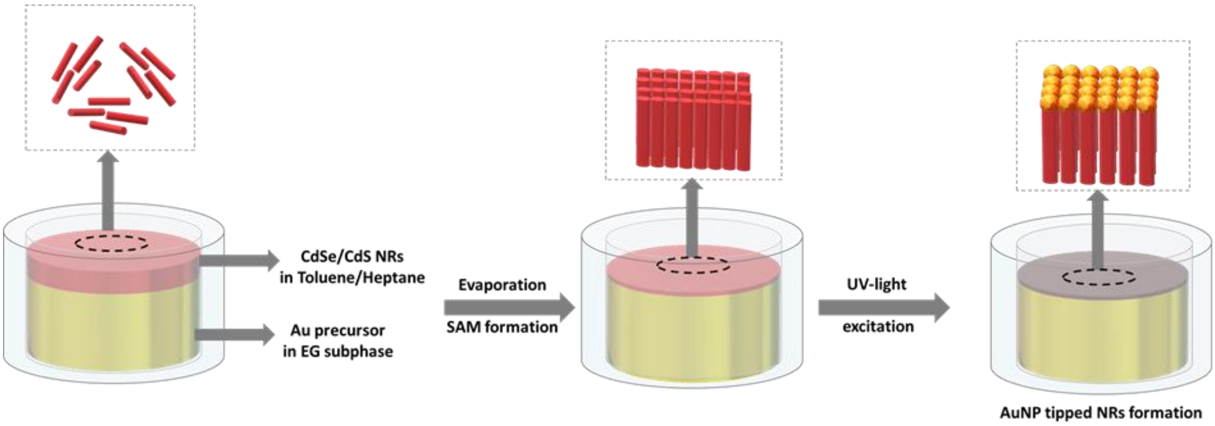

Figure 4. Preparation steps of Au-tipped CdSe/CdS NRs on the subphase

TEM images of self assembled NRs and gold tipped NRs are given in Figure 5a and b-c, respectively. The reduction of gold ions on the NRs was also tried by heat treatment which resulted in smaller gold nanoparticles formation around NRs as given in Figure 5d. If self assembly procedure is carried out in low concentration or on the more hydrophobic subphase (i.e. diethylene glycol), lateral assembly occurs while more hydrophilic (i.e. ethylene glycol) subphase usage or increased concentration results with the vertical orientation of NRs.

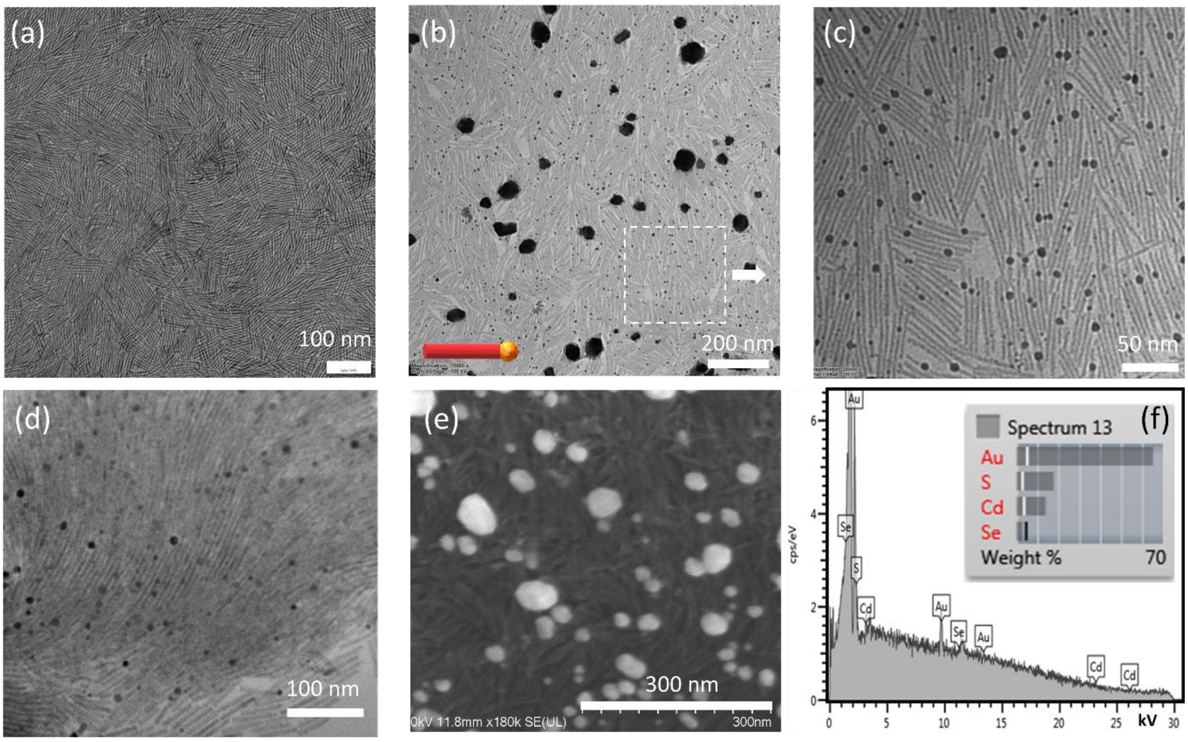

Figure 5. TEM images of self-assembled NRs (a), gold-tipped NRs (b,c) and smaller gold tipped NRs (d). SEM image of gold tipped NRs (e) and EDS analysis of the gold-tipped NRs film on silicon wafer (f).

Thicker film of gold tipped nanorods were prepared for EDS analysis by top picking method onto a silicon wafer as we reported before [18].

Self assembly of such emerging hybrid nanocrystals can be used for efficient charge carrier separation [29] which is crucial for photocatalytic hydrogen production [15] or such surfaces can be used to form cavity for lasing applications [24].

4. CONCLUSION

In conclusion, synthesis of colloidal semiconductor quantum dots and nanorods and characterization of the nanocrystals by electron microscopy, X-ray diffraction pattern and spectrophotometric methods were performed. Such NRs were used for self assembly studies to improve a novel method for metal tipped NR preparation. This new method for one-pot self assembly of metal tipped NRs was demonstrated succesfully. In contrast to reported studies in the literature, gold organosol usage or any reductant, stabilizer chemical was not used to prepare gold tipped NRs. Moreover, orientation control over metal tip formation is possible with this approach. Such self assembled layers of gold tipped NRs can be used as surface enhanced Raman spectroscopy (SERS), catalyst for hydrogen production, solar energy conversion and lasing applications.

CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

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