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Synthesis; characterization; and growth mechanism of Au/CdS heterostructured nanoflowers constructed with nanorods

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ABSTRACT

Gold/sulfide cadmium (Au/CdS) heterostructured nanocrystals with a flower-like shape were for the first time synthesized through an Au-nanorod-induced hydrothermal method. The Au/CdS nanoflowers possessed the average size of about 350 nm while the nanorods constructing the nanoflowers had the average diameter, length, and aspect ratio of approximately 50 nm, 100 nm, and 2, respectively. Our method suggested that Au-nanorods played a decisive role in the formation of Au/CdS heterostructured nanoflowers, demonstrated by high-resolution transmission electron microscopy (HRTEM), electron diffraction (ED), energy-dispersive X-ray spectroscopy (EDS), and UV–visible absorption spectroscopy measurements. A preliminary experiment model to reveal the Au/CdS growth mechanism was also put forward. The route devised here should be perhaps extendable to fabricate other Au/semiconductor heterostructured nanomaterials, and the Au/CdS nanoflowers may have potential applications in nanodevices, biolabels, and clinical detection and diagnosis.

1. Introduction

Metal/semiconductor heterostructured nanomaterials, combining two or more metal and/or semiconductor nanometer-scale building blocks, have attracted extensive attention because of their novel structures, unique optical, electrical, and catalytic properties, and potential applications in future optoelectronic nanodevices [1–3]. It is well known that the intrinsic properties of a nanoparticle depend largely on its component, structure, size, and shape [4–8]. At present, these parameters of metal or semiconductor nanomaterials have been easily tailored for obtaining their optimum properties and wide applications [9,10]. To further broaden applications of metal or semiconductor nanomaterials, it is often necessary to create new properties through coupling semiconductor or metal components [11,12].

Sulfide cadmium (CdS) is one of the most important IIB-VIA semiconductors, with a large band gap corresponding well with the spectrum of sunlight. Now, numerous methods have been successfully used to fabricate CdS nanomaterials with different shapes [13–16]. To obtain CdS nanomaterials with better properties and wider applications, it is usually feasible to form composite CdS nanomaterials by coupling other components. For example, CdS/Cr nanowires have been prepared by thermal evaporation method [17]. Sathyamoorthy et al. synthesized $Cd_{1-x}Co_xS$ nanocluster alloys through a surfactant-assisted strategy [18]. However, to the best of our knowledge, there are only a few reports on Au/CdS nanoheterostructures. Banin and his co-workers have successfully prepared Au/CdS nanorods by photoinduced and thermal growth methods [19,20]. The Au nanoparticles were grown on the tips or surfaces of CdS nanorods. Recently, Zhang's group also prepared CdS–Au_2S–Au dendritic nanocrystals in toluene solution at 70 °C [21]. But, aforementioned methods were relatively complex and difficult to prepare high-quality Au/CdS heterostructured nanomaterials. In the present work, we reported a straightforward and effective method, i.e., Au-nanorod-induced hydrothermal growth, for the synthesis of rod-constructed Au/CdS heterostructured nanoflowers. In the Au-nanorod-induced hydrothermal growth, Au-nanorods played a vital role in the formation of Au/CdS heterostructured nanoflowers. Without introducing Au-nanorods, the substituted product would be amorphous CdS nanostructures.

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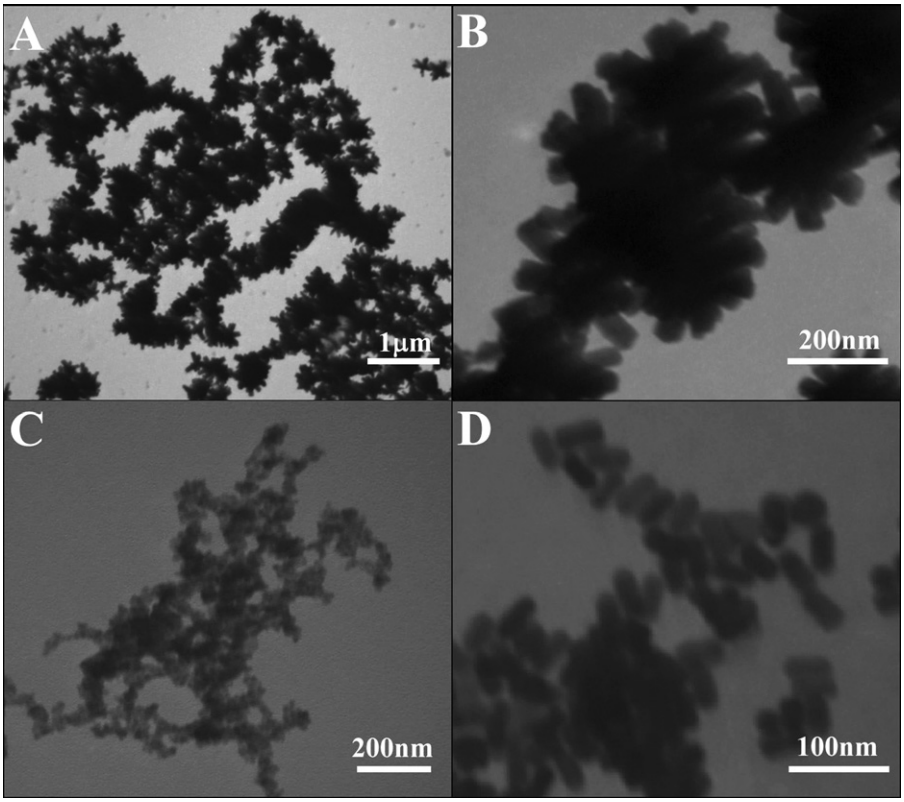

Fig. 1. TEM images of (A, B) Au/CdS heterostructured nanoflowers, (C) amporous CdS nanomateriales, and (D) Au-nanorods. Scale bar: (A) 1 μm, (B, C) 200 nm, and (D) 100 nm.

2. Experimental

2.1. Materials and methods

Hydrochloroauric acid (99%), silver nitrate (99%), cetyltrimethylammonium bromide (CTAB), and sodium borohydride (99%) were purchased from Aldrich. The following analytical reagent-grade reagents were purchased from Guangdong Guanghua Chemical Reagent Co.: cadmium chloride, mercaptoethanol, L-ascorbic acid, and ethylenediamine. All above reagents were used without further purification. Milli-Q water (>18 MΩ cm^{-1}) was used to prepare all aqueous solutions. All glassware used was washed with aqua regia and rinsed with >18 MΩ cm^{-1} water prior to use.

2.2. The preparation of Au/CdS heterostructured nanoflowers

The typical procedure for preparing Au/CdS heterostructured nanoflowerlikes was as follows. First, Au-nanorods were prepared according to the seed-mediated growth method [22]. Then, 2 mL of the as-prepared Au-nanorod colloid was added into the Telfon-lined stainless steel autoclave containing 48 μL of 0.1 M mercaptoethanol, 48 μL of 0.1 M cadmium chloride, and 18 mL of ethylenediamine. Finally, the mixture was kept stirring for 2 h and heated at 180 °C for 24 h. The final product was obtained by centrifuging with ultrapure water and absolute ethanol, respectively. For comparison, CdS nanoparticles were also prepared using the same procedure except that the Au-nanorod colloid was replaced with an equal volume of ethylenediamine.

2.3. Instruments

Transmission electron microscopy (TEM) was performed with a JEM-100 CXII microscope operated at 100 kV. High-resolution TEM (HRTEM), electron diffraction (ED), and energy-dispersive X-ray spectroscopy (EDS) were carried out with JEOL JEM-3000 operated at 300 kV. UV–visible spectra were recorded using a Hitachi U-3010 spectrophotometer.

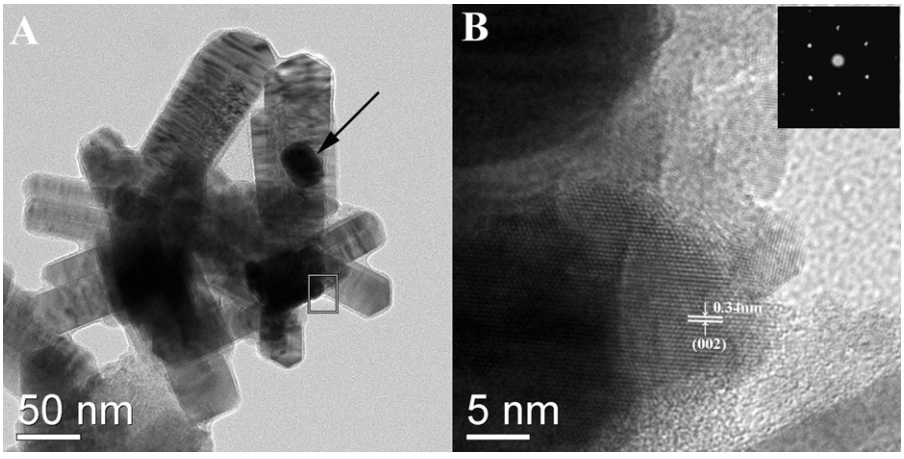

Fig. 2. (A, B) HRTEM images of Au/CdS heterostructured nanoflowers prepared using the Au-nanorod-induced hydrothermal method. The inset: the ED pattern of (B).

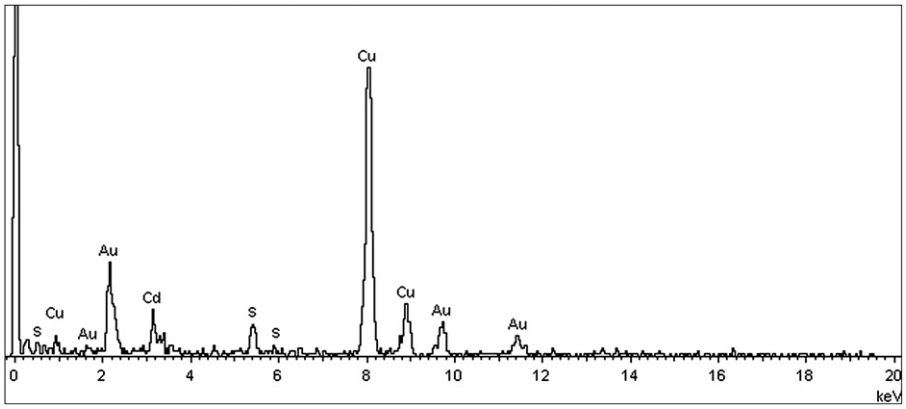

Fig. 3. EDS spectrum of Au/CdS heterostructured nanoflowers prepared using the Au-nanorod-induced hydrothermal method.

3. Results and discussion

3.1. TEM analysis of Au/CdS heterostructured nanoflowers

Au/CdS heterostructure nanocrystals prepared by the Au-nanorod-induced hydrothermal method were first characterized by TEM. From the TEM image of Fig. 1A, the Au/CdS heterostructure nanocrystals possessed a flower-like shape. When Fig. 1A was magnified, it can be clearly seen that the nanoflowers were constructed with nanorods (Fig. 1B). The Au/CdS nanoflowers were estimated with the average size of about 350 nm while the nanorods constructing the nanoflowers had the average diameter, length, and aspect ratio of approximately 50 nm, 100 nm, and 2, respectively. Without introducing Au-nanorods having the average diameter and length of about 22 and 50 nm, respectively (Fig. 1D), the substituted product would be amorphous CdS nanomaterials whose size and shape were difficult to be discerned (Fig. 1C). This result suggested that Au-nanorods played a crucial role in the synthesis of Au/CdS heterostructured nanoflowers. The growth of Au/CdS heterostructured nanoflowers could be perhaps ascribed to the following speculations: (1) Au–S^{2-} was firstly formed on the surface of the Au-nanorods when mercaptoethanol solution was added into Au-nanorods; (2) Then, Au–S^{2-} reacted with Cd^{2+} under hydrothermal atmosphere and grew out of CdS nanorods on the surface of Au-nanorods. The simple route will be perhaps available to fabricate other Au/semiconductor heterostructured nanomaterials through selecting other semiconductor components.

3.2. HRTEM, EDS, and ED analysis of Au/CdS heterostructured nanoflowers

Fig. 2A shows HRTEM image of the Au/CdS heterostructured nanoflowers. It can be clearly seen from Fig. 2A that the majority of CdS nanorods grew out from the surface of Au-nanorods and a minority of Au and CdS nanorods formed core/shell structure (marked with an arrow). The formation of Au/CdS core/shell nanorods may be due to the relative overplus of Au-nanorods in the formation of the Au/CdS heterostructured nanoflowers. Further magnified HRTEM image (the square in Fig. 2A) is shown in Fig. 2B. The lattice stripes of the Au/CdS heterostructured nanoflowers can be clearly observed from Fig. 2B. The distance between the adjacent lattice fringes was estimated to be about 0.34 nm, which was consistent with the lattice spacing of the (0 0 2) planes of the wurtzite CdS [23]. This indicated that the thorns of the Au/CdS nanoflowers mainly consisted of CdS. The inset plot of Fig. 2B gives ED pattern of the Au/CdS heterostructured nanoflowers. These symmetrical diffraction dots demonstrated that the Au/CdS heterostructured nanoflowers were single crystalline. To further verify the component of the nanoflowers, EDS measurement was preformed through detecting the component of single nanoflower in the HRTEM image. The Cu and C elements observed in Fig. 3 were from the copper grid that was used to prepare TEM sample of the Au/CdS heterostructured nanoflowers. The appearance of the Au, Cd, and S elements in the TEM copper grid revealed that the product was Au/CdS heterostructured nanocrystals.

3.3. UV–visible absorption spectroscopy analysis of Au/CdS heterostructured nanoflowers

Plasmon absorption spectroscopy is usually used to examine component-, size-, and shape-controlled nanoparticles because their optical properties in aqueous suspension are related to these properties [6,24,25]. Fig. 4 displays UV–visible absorption spectra of the Au-nanorods and Au/CdS heterostructured nanoflowers. Two obvious UV–visible absorption peaks at around 513 and 658 nm can be clearly discerned in Fig. 4a. The two absorption peaks could be attributed to characteristic transverse and longitude peaks of Au-nanorods [26]. However, when Au-nanorods reacted with mercaptoethanol and formed Au/CdS heterostructured nanoflowers, the transversal and longitudal absorption peaks of Au-nanorods disappeared. Instead of this, a new absorption peak of about 530 nm was observed, which should belong to the UV–visible peak of CdS nanomaterials [23]. These UV–visible spectra suggested that the Au-nanorods served as the cores of the Au/CdS heterostructured nanoflowers are completely coated with CdS nanorods. This was

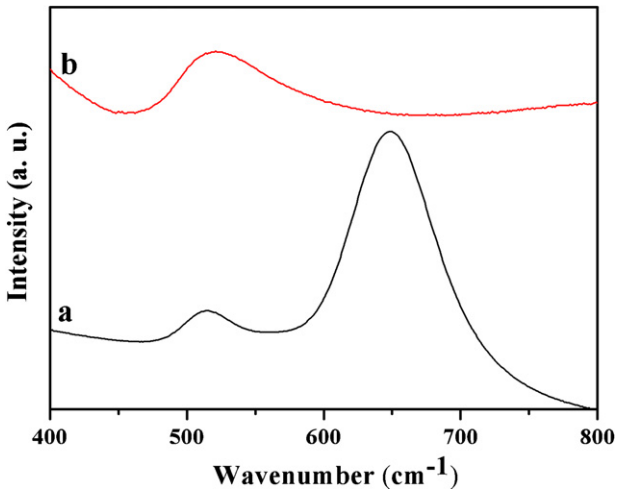

Fig. 4. UV–visible absorption spectra of (a) Au-nanorods and (b) Au/CdS heterostructured nanoflowers.

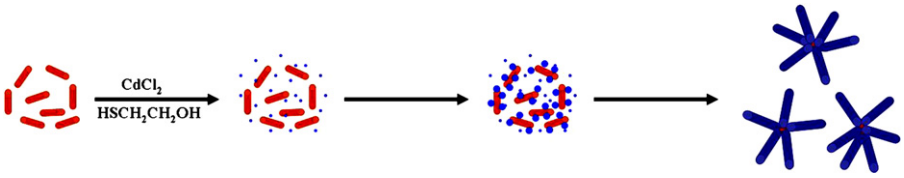

Fig. 5. Schematic illustration of the formation mechanism of Au/CdS heterostructured nanoflowers.

consistent with above TEM and HRTEM measurement results, further indicating the formation of the Au/CdS heterostructures.

3.4. Mechanism analysis of Au/CdS heterostructured nanoflowers

A proposed schematic illustration for the growth process of Au/CdS nanoflowers is shown in Fig. 5. Our results clearly demonstrated that Au-nanorods played a crucial role in the formation of Au/CdS heterostructured nanoflowers. When mercaptoethanol ($HSCH_2CH_2OH$) and cadmium chloride ($CdCl_2$) were introduced into Au-nanorod colloid, CdS monomers instantaneously generated in the hydrothermal atmosphere [6]. Due to the strong covalent interaction of Au-nanorods and S^{2-} ions, the resulting CdS monomers easily formed covalent bond with Au-nanorods. Therefore, CdS nanocrystals preferentially grew on the whole surface of Au-nanorods. Previous studies have proved that high monomer concentrations favored anisotropic growth of nanocrystals and thus resulted in the formation of nanorods or nanowires [27,28]. In our system, the hydrothermal atmosphere (180 °C) and high CdS monomer concentration of the reaction solution led to different growth rates for different faces [29]. Among these facets, there existed a unique facet which chemical potential was higher than other facets. The high chemical potential on the unique facet made the growth rate on the unique facet much faster than those on any other facets. As a result, the CdS monomers easily aggregated and grew on the unique facet and made the unique axis the long axis of CdS nanorods in the presence of Au-nanorods and CTAB. Finally, the Au/CdS heterostructured nanoflowers were obtained.

4. Conclusions

In summary, we have demonstrated that flower-shaped Au/CdS heterostructured nanocrystals can be synthesized in large quantity and high-quality through the simple and effective Au-nanorod-induced hydrothermal method. In the synthesis, Au-nanorods played an important role in the formation of Au/CdS heterostructured nanoflowers. Without introducing the Au-nanorods, the substituted product was amorphous CdS nanostructures. Since the route devised here was very simple, the only requirement seemed to be the selection of a proper semiconductor precursor; this method should therefore also be extendable to fabricate other Au/semiconductor heterostructure nanomaterials, and the Au/CdS nanoflowers may have potential applications in nanodevices, biolabels, and clinical detection and diagnosis. We also suggested an experimental model to explain the formation of the Au/CdS heterostructured nanoflowers. This may be helpful to understand the growth mechanism of other Au/semiconductor heterostructured nanocrystals.

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