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Synthesis of thermostable Au@ZnO core-shell nanorods with efficient visible-light photocatalytic activity

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ABSTRACT

Au@ZnO core-shell nanorods with excellent thermostability and efficient photocatalytic activity were successfully prepared through a facile hydrothermal method. Morphology characterizations proved that the Au@ZnO nanorods exhibit stable core-shell nanostructure and its Au cores still maintained rod-like morphology after being treated at 500 °C. Extinction spectra revealed that thermostable Au@ZnO nanorods have preeminent absorption in ultraviolet, visible, and near-infrared regions. Photocatalytic test indicated that Au@ZnO nanorods possess efficient photocatalytic activity for the degradation of Rhodamine B under visible-light irradiation. The high crystallinity of ZnO nanoshells and strong plasmon resonance of Au were thought to be the reason for the superior photocatalytic activity.

1. Introduction

Semiconductor materials with excellent photocatalytic activity have received wide attention due to their significant applications in environmental protection [1,2]. Coupling of plasmonic metal nanocrystals with semiconductor materials could greatly enhance their photocatalytic performance [3–6]. Au nanorods (NRs) have been widely investigated because of its fantastic characters. The most remarkable properties of Au NRs are its anisotropic morphology, strong transverse surface plasmon resonances (T-SPR) and longitudinal surface plasmon resonances (L-SPR). Au NRs have been accompanied with various semiconductors to construct diverse functional materials [7,8]. As is known to all, the obvious weakness of Au NRs is that the rod-like morphology is unstable, which could dramatically impair its properties. Hence, the Au NRs-based hetero-nanostructures commonly have poor performance after long-term work or being treated at high temperature because the rod-like shape of Au could be easily destroyed. Therefore, the new strategy to protect the Au NR is essential. In other words, to enhance the thermal stability of Au NRs-based hybrids becomes very important.

ZnO nanoparticle with large direct band gap and particular optical properties has been intensively investigated. ZnO also has been coupled with plasmonic metallic nanocrystals for application in photocatalysis [9]. Herein, we synthesized Au@ZnO core-shell NRs with excellent thermal stability through a facile hydrothermal method. The Au@ZnO NRs showed significantly enhanced photocatalytic activity for the degradation of Rhodamine B (RhB) under visible-light irradiation.

2. Materials and method

The thermostable Au@ZnO core-shell NRs was synthesized by hydrothermal method and followed annealing process. Firstly, cetyltrimethylammonium bromide-stabilized Au NRs were prepared by a seed-mediated growth method [10]. Typically, 0.2 mL 0.1 M ascorbic acid and 0.5 mL 0.1 M hexamethylenetetramine were added to 1 mL as-prepared Au NRs solution. After string for 5 min, 0.2 mL 0.1 M $Zn(NO_3)_2$ aqueous solution was added in, then the mixture was kept at 85 °C for 8 h in vacuum oven. To synthesize thermostable Au@ZnO NRs, the as-prepared Au@ZnO were dried at 60 °C. Then, the solid Au@ZnO were transferred to furnace and annealed at 500 °C for 1 h. The final products were washed and dispersed in water for further use.

The photocatalytic testing was described in previous work [11]. The morphologies were investigated by transmission electron microscope (TEM). The extinction spectra were tested by UV–Vis-NIR spectrophotometry. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with a Xe

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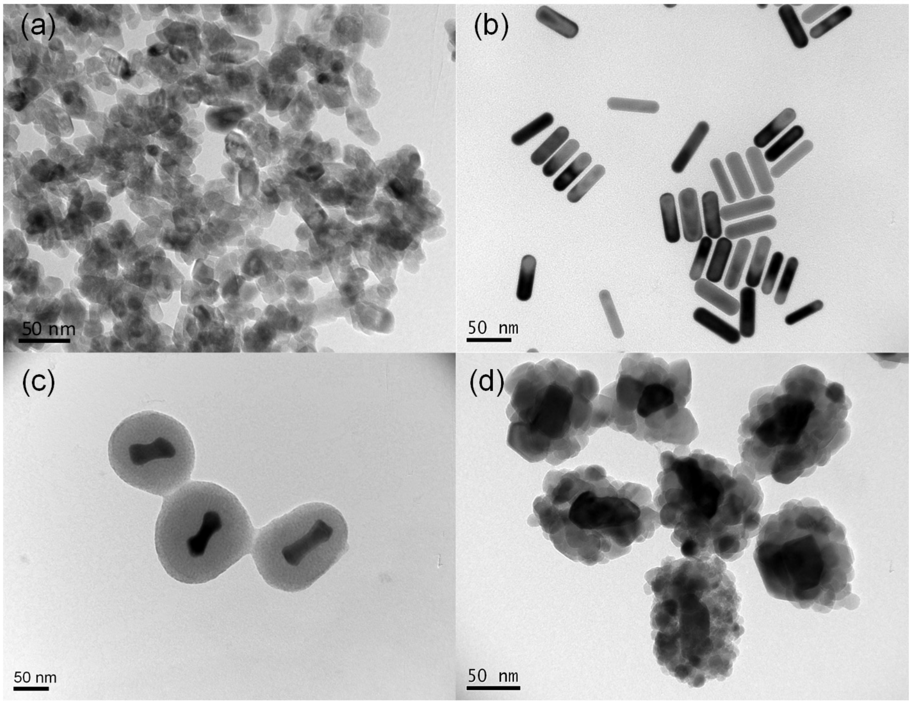

Fig. 1. TEM images of pure ZnO (a), Au NRs (b), untreated Au@ZnO (c) and annealed Au@ZnO (d) hetero-nanostructures.

lamp as the excitation source. X-ray diffraction spectra (XRD) patterns were obtained on a Bruker D8 advance X-ray diffractometer with Cu-Kα irradiation (λ = 0.15418 nm).

3. Results and discussion

The detailed morphology and component characterizations were presented with TEM images and XRD patterns. Fig. 1(a) gives the TEM image of pure ZnO, and Fig. 1(b) exhibits the initial Au NRs with an average length/diameter of 15 ± 3 nm/50 ± 3 nm. Fig. 1(c) shows that the Au@ZnO NRs exhibit a standard core-shell nanostructure. The Au cores with special dumbbell-like morphology is ascribed to the overgrowth of Au NRs, the corresponding growth mechanism had been discussed in our previous work [11]. The ZnO nanoshells have an average thickness of 52 nm and display a loose form. As observed in Fig. 1(d), the annealed Au@ZnO NRs keep uniform core-shell structures, and its Au cores still maintain rod-like morphology. The ZnO nanoshells show dense morphology, suggesting that its crystallinity is highly enhanced.

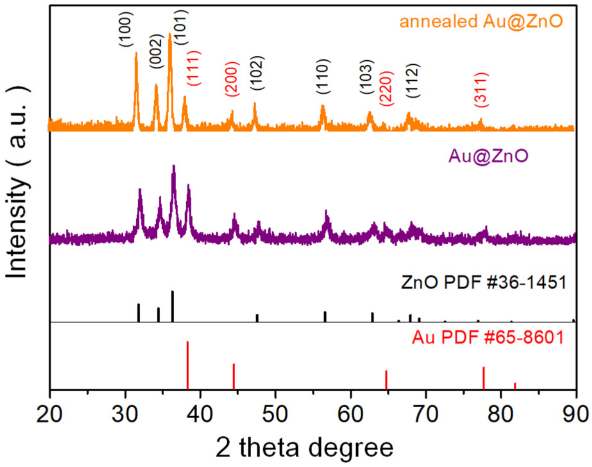

Fig. 2. XRD patterns of untreated and annealed Au@ZnO NRs. The standard patterns of cubic-phase Au (PDF#65-8601) and wurtzite hexagonal-phase ZnO (PDF#36-1451) were displayed.

Fig. 2 reveals the XRD patterns of untreated and annealed Au@ZnO NRs. It can be seen that the two nanostructures almost have the same diffraction peaks. The characteristic peaks at 38.3 °C, 44.4 °C, 64.2 °C, and 77.5 °C are assigned to the (111), (200), (220), and (311) planes of Au with fcc structure. The remaining peaks in the two patterns could be indexed to ZnO with wurtzite hexagonal phase. No more impurity-related peaks were observed, indicating that the two types of Au@ZnO NRs have a high crystalline purity.

The evolution of extinction spectra along with the structural variation is illustrated in Fig. 3(a). It can be obtained that pure ZnO has a sharp ultraviolet (UV) absorption band around 372 nm which belongs to its band-edge excitation. The staring Au NRs clearly exhibit two extinction bands at 515 and 765 nm, corresponding to the T-SPR and L-SPR, respectively. After Au NRs were wrapped with loose ZnO layers, the L-SPR wavelength red-shifts to 709 nm with the T-SPR red-shifting to 535 nm. This redshift is induced by the increased refractive index of the surrounding medium. It's interesting to find that both the intensities of T-SPR and L-SPR are increased, especially for the T-SPR band which is about 3.3 times than that of bare Au NRs. That implies the Au@ZnO NRs have excellent absorption both in visible and near-infrared region. The increased intensity of T-SPR and L-SPR is mainly related to the reshaping and size enlarging of dumbbell-like Au NRs [11]. As for the annealed Au@ZnO NRs, both the T-SPR and L-SPR are successfully maintained and redshift to 746 and 578 nm, respectively. The obvious characteristic extinction peak of ZnO appears, indicating that the annealed Au@ZnO NRs have outstanding absorption in UV, visible, and near-infrared region.

Fig. 3(b) displays the room temperature photoluminescence (PL) spectra of ZnO, untreated and annealed Au@ZnO NRs. The results show that pure ZnO has a narrow UV emission band around 380 nm and a weak blue emission band around 472 nm. The UV