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Fabrication of hierarchical core–shell Au@ZnO heteroarchitectures initiated by heteroseed assembly for photocatalytic applications

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ABSTRACT

Three dimensional dandelion-like hierarchical core–shell Au@ZnO heteroarchitectures with ZnO nanorods grown radially on Au nanoparticle (NP) cores have been successfully prepared with a high yield via a simple solution method involving heteroseed-induced nucleation and subsequent heteroepitaxial growth processes. Briefly, mercaptopropionic acid (MA) modified Au NPs were synthesized beforehand and served as nucleation centers for primary ZnO seed generation and Au@ZnO heteroseed formation. Then an epitaxial growth of ZnO nanorods (ZnO NRs) on the Au@ZnO heteroseeds resulted in the formation of Au@ZnO dandelions. The photocatalytic properties of as-prepared Au@ZnO dandelions were evaluated through rhodamine B (RhB) photodegradation under UV irradiation. The result showed that the Au@ZnO dandelions had improved photocatalytic performance compared with pure ZnO NRs and hybrids of ZnO NRs/Au NPs, due likely to the synergistic effect of the metal–semiconductor heterojunction and the unique dandelion-like hierarchical core–shell structure.

1. Introduction

Semiconductor–metal heterostructured nanomaterials have attracted great interest in recent years because they can not only combine the unique properties of metals and semiconductors, but also generate novel electrical, optical, and catalytic properties due to the synergetic interaction between the metal and the semiconductor components [1–6]. As a representative class of semiconductor–metal nanostructured materials, Au–ZnO nanocomposites have received special attention due to their promising applications in solar energy conversion [7], biological detection [8,9], sensing fields [10–12] as well as photocatalysis [13–16]. Moreover, from the perspective of fundamental science, it is of great significance to explore novel photoelectric mechanisms tied to the morphologies and structures of Au–ZnO heterojunction materials, and their relevant catalytic, optical and electric properties [2,17–22]. Therefore, great efforts have been devoted to fabricating Au–ZnO nanocomposites with different shapes and structures recently. For example, a variety of ZnO–Au heterostructures including ZnO NRs/Au NPs [17,18,22–24], flower-like ZnO/Au NPs [7,10,13–14,25–26], ZnO nanocones/Au NPs [15,27], and ZnO NPs/Au NPs [9,28–32] have been synthesized. However, in most of these work, gold NPs were merely dispersed or deposited on the surface of presynthesized ZnO nanostructures. In contrast, inverse structure form of the two components such as Au@ZnO core–shell structures where ZnO nanostructures grown on Au NPs prepared via reverse synthetic approaches was seldom reported [33–35], due probably to the synthesis difficulty of growing ZnO nanostructures on gold nuclei. Nonetheless, as reported by Xu's group, core–shell structured M@TiO_2 (M = Au, Pd, Pt) nanocomposites encapsulating metal NPs within the semiconductor shell in fact exhibited much higher stabilities against aggregation and undesirable metal corrosion in the practical photocatalysis applications than their oxide supported counterparts [36–37]. Thus, more subtle structure design for Au–ZnO core–shell nanocomposites is highly desired to fully explore their potential advantages as promising heterostructured photocatalysts. It is generally recognized that effective separation and transportation of photogenerated charges as well as high light harvesting of photocatalysts play decisive roles in determining their photocatalytic performance [14,19,38]. Therefore, for Au@ZnO heterostructures to acquire high photocatalytic activity, particular structure designs are required: First, complete separation of Au cores and ZnO shells with defined interfaces. This is beneficial for not only effective electron–hole separation and transfer at the interfaces of the cores and shells, but also the subsequent

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reduction and oxidation half reactions proceeded separately in the core and shell regions [39]. Second, highly epitaxial ZnO nanostructure with high carrier mobility. It can facilitate charge transportation and thus reduce charge recombination. Third, open hierarchical architectures of the Au@ZnO nanocomposites with large specific surface area (SSA). These features will guarantee high light trapping capacity and provide abundant accessible sites for effective molecule adsorption/desorption [38].

Through a rational design, here we demonstrate the fabrication of 3D hierarchical core–shell Au@ZnO dandelions through a simple solution approach involving heteroseed induced nucleation and epitaxial growth of ZnO nanorods. The synthesized product is composed of Au NP cores and ZnO shells of nanorod arrays grown radially on Au cores. The as-prepared Au@ZnO dandelions are attractive for photocatalysis according to the structure advantages discussed above: separate Au and ZnO components confined in respective core and shell regions with good interfacial contact for effective charge separation and transfer at the interface of Au cores and ZnO shells, 1D ZnO nanorods with high carrier mobility for fast and direct electron transportation over all shells, dandelion-like hierarchical architectures with relatively high SSA for efficient light trapping and molecule adsorption/desorption. Besides, radial ZnO nanorod arrays anchored tightly on Au NP cores can avoid serious aggregation relative to common catalysts in the form of dispersed nanoparticles, guaranteeing high catalytic stability and long lifetime of the catalyst. To the best of our knowledge, the novel Au@ZnO dandelions are reported here for the first time. As expected, the typical Au@ZnO dandelions display higher photocatalytic activity and stability when evaluated through RhB photodegradation, compared with other pure ZnO nanorods (ZnO NRs), ZnO nanorod-Au NP hybrid (ZnO NRs–Au NPs, prepared by depositing Au NPs on the surface of ZnO nanorods).

2. Materials and methods

2.1. Materials

Chloroauric acid ($HAuCl_4{\cdot}4H_2O$), Rhodamine B (RhB) and mercaptopropionic acid (MA) were purchased from Alfa Aesar. Anhydrous zinc acetate ($Zn(CH_3COO)_2$) and sodium citrate were purchased from Sigma–Aldrich Company. Hexamethylene tetramine(HMT), potassium hydroxide(KOH) and anhydrous ethanol were purchased from Shanghai Chemical Reagent Co., Ltd. All the above reagents are of analytical grade and used as purchased.

2.2. Synthesis of the Au@ZnO dandelions

Briefly, Au nanoparticles with the size of ~20 nm were synthesized by reduction of chloroauric acid ($HAuCl_4$) using citrate according to Ref. [40] and further modified with MA (see S1.1). Then these MA-capped Au nanoparticles were introduced into the solution for growing ZnO seed nanoparticles to fabricate the Au@ZnO heteroseeds (S1.2). Subsequently, the obtained Au@ZnO heteroseeds were casted into 50 mL aqueous solution composed of equimolar zinc nitrate and hexamethylenetetramine (HMT) at 95 °C for preparation of the Au@ZnO dandelions (S1.3).

2.3. Characterization

Morphology was characterized using a scanning electron microscope (SEM, Hitachi S4800, 3 kV) and high-resolution transmission electron microscopy (HR-TEM, JEM 2011, 200 kV). The crystal structure was determined by X-ray diffraction (XRD) using a D/max2550VB3+/PC X-ray diffractometer with Cu Kα radiation with a 1.5418 Å wavelength. A beam voltage of 40 kV and a 100 mA current beam were used. The UV–vis spectra of the samples were recorded on a Cary-50 UV–vis spectrophotometer. The Zeta potential measurements were recorded on a NanoZS90 (Malvern) particle size analyzer.

2.4. Photocatalytic evaluation

A mixture of 30 mL 1.0×10^{-5} M RhB aqueous solution and 6 mg catalyst powder of the Au@ZnO dandelions or pure ZnO NRs or ZnO NRs–Au NPs were stirred for 1 h in a quartz tube in the dark to reach adsorption equilibrium and then irradiated by a 300 W high-pressure mercury lamp under magnetic stirring in air. Samples of the suspension were draw out at regular intervals, centrifuged to completely remove the catalyst, and then measured using a UV–vis spectrophotometer to detect the degree of RhB degradation.

3. Results

The representative SEM images of the product obtained under standard conditions are shown in Fig. 1a and b. According to Fig. 1a, the product consists of high-yield dandelion-like spherical assemblies with about 1–1.5 μm in size. Fig. 1b is an enlarged SEM image of these dandelion-like assemblies, which suggests that each "dandelion" is comprised of radially arrayed nanorods with 50–100 nm in diameter and 500–700 nm in length growing around a core. The typical TEM image in Fig. 1c further reveals that the core is actually made of loosely aggregated nanoparticles with average diameter of ~20 nm, which is in accord with the size of initially introduced Au NPs, suggesting that Au NP clusters are embedded in the cores after the growth process. It is noteworthy that the Au NPs existing in this embedded manner occupy an overwhelming majority and few bare Au NPs are observed on surfaces of the dandelions. After fierce ultrasonic treatment, a piece of nanorod bundle obtained from the shell layer of a dandelion was selected for closer observation (Fig. 1d, inset). The high-magnification TEM image (Fig. 1d), taken from the circled region on a nanorod of the bundle, displays clearly a set of crystal lattices with *d* spacing of 0.26 nm, corresponding to the {002} planes of the hexagonal structured wurtzite ZnO (JCPDS No. 36-1451), which together with the SAED pattern (Fig. S3) indicates the nanorods are single ZnO crystal with the growth direction of [002]. Further composition analysis of the product is confirmed by corresponding XRD data, as shown and indexed in Fig. 1e, where two sets of prominent diffraction peaks correspond to wurtzite ZnO and cubic-phase Au (JCPDS No. 04-0784), respectively. Therefore, the synthesized dandelion-like product actually has a 3D hierarchical core–shell heteroarchitecture, that is, Au NP cores are covered by ZnO shells consisting of radial nanorod arrays.

4. Discussions

To investigate the formation mechanism of the Au@ZnO dandelions, the morphology evolution of Au NPs at different synthesis stages before and after ZnO seed coating was traced (Fig. 2). Fig. 2a presents the typical Au NPs synthesized according to Frens's method [40]. It can be seen that the gold NPs without ZnO seed coating are monodisperse with a uniform diameter of about 20 nm. The HRTEM image (inset in Fig. 1a) shows several discrete lattice fringes with equal lattice distance of 0.23 nm corresponding to the {111} planes of cubic-phase gold, reflecting the multiple twinned crystal nature of Au NPs. However, after ZnO seed coating, Au NPs become obviously aggregated due to the decrease of electrostatic repulsion between the nanoparticles (Zeta potential changed from −32.9 to −7.76 mV, see Table S1). Further HRTEM