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Influence of Au content on photocatalytic performance of C@ZnO@Au hollow nanospheres

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ABSTRACT

Mesoporous C@ZnO@Au hollow spheres were synthesized through a stepwise method. The photocatalytic activities of the samples to RhB under UV irradiation were investigated. The sample with a 1/1000 mol ratio of Au/ZnO was found to have the best photocatalytic activity, which is far better than P25. The improved performance could come from the larger specific area induced by mesoporous hollow nanostructure, enhanced light absorption, or improved photogenerated electron-hole pair separation. Sample performance is a function of Au content. Too much or too little Au content decreases sample performance. The changes in performance according to Au content are a result of various competing mechanisms. This work serves to help us to better understand the important roles of Au content in the fabricated nano-heterojunction catalysts and also provide us with a feasible route to improve UV photocatalytic activities of ZnO and other metal oxides.

1. Introduction

ZnO, a popular n-type wide bandgap metal-oxide semiconductor, is abundant, widely available, non-toxic in nature, and has a low production cost and promising physical and chemical properties; all properties which make it popular for use in gas sensors [1], transistors [2,3], energy harvesting devices [4], light-emitting diodes [5], biomedicine [6] and photocatalysis [7,8], to name a few.

In the field of photocatalysis, ZnO has been considered as a potential material to improve an increasingly serious energy crisis as well as environmental problems, for several decades [4,9–23]. However, photocatalytic performance of ZnO nanostructures must improve in order to be considered for practical application. What is worse, ZnO nanostructures dispersed into water are not stable and tend to transform into $Zn(OH)_2$ [13]. The physical instability of ZnO nanostructures should also be considered. The nanostructures tend to aggregate in order to minimize their surface energy [24]. Improvements in photocatalytic performance are generally attributed to improved crystallinity [14,15], an exposed crystal plane with high energy [16], heterojunction nanostructures or surface tuning [9,10,12,17–19], ion or atom doping [20,21], or increased specific surface area [14,22,23]. In an effort to design a material, building upon the previous research, which has advantageous chemical stability and photocatalytic performance, several kinds of ZnO-based nanostructures have been examined to look for enhancements in photocatalytic performance. One way to increase photocatalytic performance is by increasing the specific surface area utilizing a hollow morphology and structure. It is believed that a hollow nanostructure belonging to the mesoporous category – a structure with pores in the size range of 2–50 nm – will result in a larger specific surface area than other ZnO nanostructures. Further, the mesoporous hollow sphere nanostructure provides efficient molecular transport pathways to the interior surface. On the other hand, a heterojunction composed of metal-oxide, carbon and noble metal would reduce the recombination efficiency of photogenerated carriers and improve photocatalytic performance [9,10,12,17–19]. Moreover, a carbon and noble metal covering on the surface of the ZnO nanostructures would prevent the direct contact of ZnO and water, most likely suppressing the corrosion rate and improving the chemical stability of ZnO. As a result, the recycling rate of ZnO nanostructures and the photocatalytic activities in cyclic utilization would be increased [13]. To date, little effort has been made to identify and elaborate the relationship between Au content and the photocatalytic performance of C@ZnO@Au hollow spheres.

In this paper, we show that mesoporous C@ZnO@Au hollow spheres of varying Au content are prepared by a stepwise procedure, and that photocatalytic activity could be controlled by the Au content. Furthermore, the influence of Au content on photocatalytic performance of C@ZnO@Au hollow nanospheres were explored. It is hoped

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that this study will provide new insight into the influence of Au content on photocatalytic performance.

2. Experimental section

2.1. Synthesis of C@ZnO hollow spheres

Mesoporous C@ZnO hollow spheres were synthesized by a template technique that was reported in our previous work [25,26]. First, 65 mL, 0.55 mol/L glucose solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, which was then maintained at 180 °C for 9 h. The resulting precipitate of carbon spheres was then collected, washed and desiccated. Next, the suspension composed of 0.30 g carbon spheres, 2.5 g $Zn(AC)_2{\cdot}2H_2O$ and 60 mL ethanol solution was magnetically stirred for 12 h at room temperature, followed by centrifuging repeatedly with ethanol. Finally, the obtained products were desiccated and calcined in air at 550 °C for 4 h to prepare C@ZnO hollow spheres, which were named S0.

2.2. Synthesis of C@ZnO@Au hollow spheres

The mesoporous C@ZnO@Au hollow spheres synthesis begins with the suspension (by sonication for 40 min) containing 0.30 g C@ZnO hollow spheres and 120 mL ethanol magnetically stirred for 0.5 h at 70 °C. Subsequently, 37 mL $HAuCl_4$ aqueous solution were poured into the suspension quickly with a concentration of 10^{-5}, 5×10^{-5}, 10^{-4}, 5×10^{-4} and 10^{-3} mol/L to prepare C@ZnO@Au hollow spheres with varying Au content. The samples were named S1, S2, S3, S4 and S5, respectively. The mole ratio of Au/ZnO (n_{Au}/n_{ZnO}) for the samples was 1/10,000, 5/10,000, 1/1000, 5/1000 and 1/100, respectively. The mixed solution was maintained at 70 °C while irradiated by a high-voltage mercury lamp with a power of 300 W for 40 min. Finally, the obtained products were collected and desiccated.

2.3. Characterization

The crystallinity of the samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2550) with Cu Ka radiation ($\lambda = 0.15406$ nm). Scanning electron microscopy (SEM) (SU 8010) and transmission electron microscopy (TEM, JEM-2010) was used to examine the morphologies of the samples. The inner architectures and specific area of the mesoporous C@ZnO@Au hollow spheres was examined by Brunauer-Emmett-Teller (BET) nitrogen adsorption–desorption (Nova 2000E). Pore-size distribution was determined from the adsorption branch of the isotherms using the Barett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was used to analyze the surface characteristic and chemical composition of the samples. Fluorescence spectrophotometer (PerkinElmer LS55) and UV–Vis spectrophotometer (UV-2550, Shimadzu) were used to obtain the photoluminescence and light-absorption characteristics respectively.

The photocatalytic activities of the samples were evaluated by photocatalytic degradation of RhB in an aqueous solution. 40 mg of the photocatalyst was dispersed in 40 mL of the RhB aqueous solution (10 mg/L). The suspension was magnetic stirred in the dark for 30 min to equilibrate the absorption and desorption between photocatalyst and RhB. The photocatalytic performance was tested under a high-pressure mercury lamp (CHF-XM-300 W) at room temperature. The 5 mL mixed solution was taken out at 5 or 10 min intervals of irradiation and separated by centrifugation to remove the photocatalysts, and then were measured by a UV–visible spectrophotometer.

3. Results and discussion

The samples created for this research are shown in the inset of Fig. 1. Visual inspection indicates that the color of the samples gradually deepens from light purple to deep purple as the Au content is increased. The crystal structures of the samples were determined by XRD analysis. Fig. 1 presents all diffraction data for these samples. It was found that the diffraction peaks were consistent with the wurtzite structure of ZnO (JCPDS No. 36-1451) and face centered cubic (fcc) structure of Au (JCPDS No. 04-0784). However, for S1, S2 and S3, Au diffraction peaks were not observed. This is understandable as those samples contain a very small amount of Au, where the diffraction intensity seems to be below that of background in this XRD data.

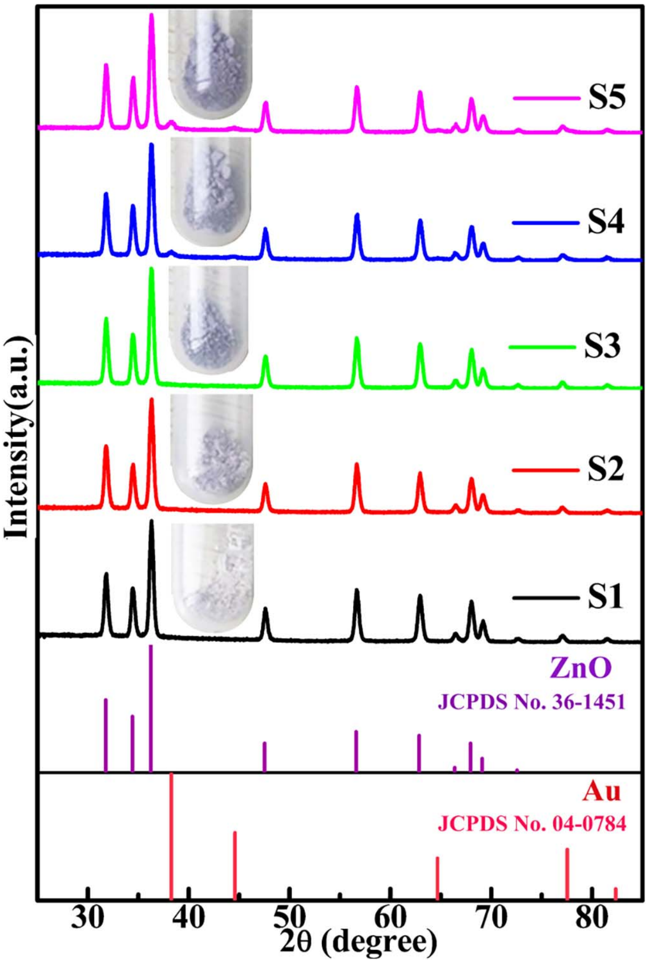

Fig. 1. XRD patterns of the samples, and XRD standard patterns of ZnO with wurtzite structure (JCPDS No. 36-1451) and Au with fcc structure (JCPDS No. 04-0784).

Fig. 2a and h shows the typical SEM images of the as-prepared C@ZnO@Au hollow spheres (S3) with low and high magnification respectively. The sample has a rough surface, as presented in Fig. 2h. This is attributed to a large number of mesopores and the Au nanoparticles (NPs) scattered on the ZnO hollow spheres. From the EDS mapping obtained from an SEM image (Fig. 2b), it is confirmed that the C@ZnO@Au hollow spheres are composed of massive metallic elemental Zn (Fig. 2b) and non-metallic oxygen (Fig. 2c), but few and uniformly distributed metallic Au (Fig. 2d) and non-metallic carbon (Fig. 2f). This suggests that the Au Nps are well loaded on ZnO NPs, and uniformly dispersed on the surface of C@ZnO hollow spheres (metallic elemental Cu shown in Fig. 2e is from the Cu substrate).

TEM and high-resolution TEM (HRTEM) images of C@ZnO@Au hollow spheres (S3) are shown in Fig. 3. The sphere-like morphology was perfectly preserved after Au deposition by heterogeneous nucleation and growth (Fig. 3a) [25,26]. The lattice fringes with spacing of 0.26, 0.19 and 0.20 nm corresponded to (0 0 2), (1 0 2) crystal planes of wurtzite ZnO and (2 0 0) crystal planes of fcc Au (Fig. 3b). These results were in agreement with the XRD analysis, which further confirmed the