



Effects of shell thickness on Ag-Cu₂O core-shell nanoparticles with bumpy structures for enhancing photocatalytic activity and stability

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ABSTRACT

Here we examine Ag-Cu₂O core-shell nanoparticles with bumpy structures for use in plasmonic photocatalysts. We synthesized the nanoparticles using a very simple co-reduction process. The shell thickness of the nanoparticles was controlled in order to investigate the effects of shell thickness on photocatalytic activity and stability. With increasing shell thickness, it was observed that the activity and the stability were simultaneously improved. A thin shell lead to de-wetting of Cu₂O from the Ag core and considerable oxidation of Cu₂O to CuO. The high activity could be due to the unique structure of Ag-Cu₂O, which has a high surface area and plasmonic charge transfer from the Ag core. In addition, we elucidated the stability tendency using conducted density functional theory (DFT) calculation. Strain induced between the Ag core and shell is critical to the stability, leading to de-wetting and oxidation of Cu₂O.

1. Introduction

Photocatalysts are materials that perform catalytic reactions using light as an energy source [1]. They are utilized for an array of applications, including water splitting [2], CO₂ reduction to hydrocarbons [3], and pollutants removal [4]. The most widely used photocatalyst is TiO₂ (titanium dioxide) because it is earth-abundant, non-toxic, and very stable [5]. However, TiO₂ has very wide band gap of 3.0 eV for the rutile structure [6] and 3.2 eV for the anatase structure [7], which is only active under the ultra-violet region of sun-light. Many researchers have tried to develop alternative materials [8,9] or tried to enhance the photocatalytic activity using strategies such as doping [10,11], light absorbers [12], and mixed oxides [13].

Among many alternative materials, Cu₂O (cuprous oxide), as p-type semiconductor with a direct band gap, has been extensively studied due to its relatively narrower bandgap (2.17 eV) compared to TiO₂ [14]. Similar to the benefits of TiO₂, it is earth-abundant and non-toxic. However, a major portion of the reported Cu₂O nanoparticles show a large size and a relatively small surface area [15]. They also have a weak light absorption at longer wavelength regions of light under 450 nm. Additionally, Cu₂O is naturally oxidized into CuO (cupric oxide) under ambient and aqueous conditions, indicating poor stability of Cu₂O [16].

Using plasmonic light absorber has been proposed as a strategy to enhance the photocatalytic activity of Cu₂O [15]. Nano-sized noble metals such as Au, Ag, and Pt show strong absorption of visible light as

a result of their surface plasmon resonance (SPR) property [17]. The absorbed light induces a very strong electric field around the nanoparticles by generating oscillating electrons. The plasmonic light absorber can transfer solar energy into the semiconductor above the conduction band and below the valence band edge, leading to enhanced photocatalytic activity [18]. Ag-Cu₂O core-shell nanoparticles have been reported as excellent plasmonic catalysts among this class of structure and systems [19–21]. It successfully protects the Ag core, which has a respectable price, and has a large active interface between the semiconductor and noble metal. Wu et al. synthesized Ag-Cu₂O core-shell nanoparticles and discussed the mechanism of their enhanced photocatalytic activity [22]. However, the synthesized nanoparticles have the relatively large size (31–100 nm) and the stability of the catalyst has yet to be evaluated. Several reports have studied the stability of Cu₂O nanoparticles under ambient conditions or in water [23–25]. However, the stability of the Ag-Cu₂O core-shell nanoparticles under investigation.

Here in, we have prepared Ag-Cu₂O core-shell nanoparticles with bumpy structures using a very simple co-reduction method. The shell thickness was controlled to find optimum condition. The photocatalytic performance of the nanoparticles was evaluated using the methyl orange (MO) degradation method with changing shell thickness. The optical properties and the surface area of the nanoparticles played a key role in the photocatalytic performance. Furthermore, the stability of the nanoparticles after the photocatalytic reaction was investigated using a combined experimental and theoretical approach.

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2. Experimental methods

2.1. Materials and preparation of Ag-Cu₂O core-shell bumpy nanoparticles

Ag-Cu₂O core-shell bumpy nanoparticles were synthesized using the following facile, one-step co-reduction process. AgNO₃ (Sigma-Aldrich) was used as the silver precursor; copper acetylacetonate (Cu(acac)₂) (Cu(C₅H₇O₂)₂, Sigma-Aldrich) was used as the copper precursor; and oleylamine (C₁₈H₃₇N, Sigma-Aldrich) was used as the solvent, surfactant, and reducing agent. All chemicals were used as received without further purification. In the synthetic procedure, Ag-Cu₂O core-shell bumpy nanoparticles were synthesized with various Cu to Ag molar ratio (2:1, 4:1, and 8:1) using the co-reduction method. In this manner, Cu(acac)₂ (0.514 g, 1.028 g, and 1.542 g), AgNO₃ (0.16 g), and oleylamine (180 ml) were added to a 250-ml three-neck flask. The flask was heated to 230 °C and kept under high purity Ar gas with constant stirring for 3 h. The solution color changed from green to black when the co-reduction process was complete. The solution containing the synthesized nanoparticles was then cooled down to room temperature. The Ag-Cu₂O core-shell bumpy nanoparticles were obtained after centrifuging at 10000 rpm for 30 min and washed three times with hexane (C₆H₁₄ < 96.0%, Junsei Chemical). Lastly, the powdered nanoparticles were obtained by drying under low vacuum at 40 °C for 24 h.

2.2. Characterization of the Ag-Cu₂O core-shell bumpy nanoparticles

The morphology and size distribution of the nanoparticles were investigated using transmission electron microscopy (TEM) (Tecnai G2 F30 S-Twin, FEI) at 300 kV. The core-shell bumpy structure was confirmed using high resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) (JEM-ARM200F, JEOL). The composition of the nanoparticles was also determined using EDS analysis. The crystalline structure was investigated using X-ray diffraction (XRD) (D/MAX-2500, RIGAKU) and the existence of the Cu₂O phase was verified using X-ray photoelectron spectroscopy (XPS) (K-alpha, Thermo VG Scientific). The optical properties of ethanol solutions containing the nanoparticles were investigated using a UV–vis spectrophotometer (Lambda 1050).

2.3. Measurement of photocatalytic activity

The photocatalytic activity was measured by the degradation of a methyl orange aqueous solution under the irradiation of visible-light at ambient condition. The commercial halogen lamp (500 W, Osram) was used as the visible-light source to induce the photocatalytic reaction. The distance between the solution and the light source was 20 cm. The temperature of the 500-ml beaker containing the MO solution was consistently maintained using a water chilling system. A total of 1.0 g powder of the synthesized Ag-Cu₂O core-shell bumpy nanoparticles as well as various Cu to Ag molar ratios were dispersed in 100 ml (10 mg/L methyl orange) aqueous solutions and were ultra-sonicated for 10 min. The solutions were stirred for 2 h in the dark to obtain the adsorption-desorption equilibrium. The solutions were then exposed to visible-light irradiation with constant stirring. At each time interval, 7 ml of the solution was collected using a syringe and centrifuged to remove the nanoparticles. The concentration of MO in the centrifuged solution was analyzed using a UV–vis spectrophotometer (Lambda 1050), and the characteristic absorption of MO at 464 nm was used to calculate its degradation rate. The degradation rate was calculated by (C₀-C)/C₀, where C is the adsorption of the MO solution at each time interval, and C₀ is the adsorption of initial MO immediately after the adsorption-desorption equilibrium.

2.4. Computational procedure

We performed GGA-level spin-polarized density functional theory

(DFT) calculations with plane-wave based on a Vienna ab-initio simulation package (VASP) code [26]. The BEEF-vdw exchange correlation functional [27] was employed to describe interface phenomena and adhesion forces between metal (oxide) and metal oxide due to the consideration of Van der Waals interactions. Cut off energy was set to 500 eV, k-point sampling was chosen with gamma point, and convergence criteria for electronic structure and atomic geometry optimization were set to 10⁻⁵ eV and 0.05 eV/Å, respectively. We made 3 different slab systems Ag (111), Cu₂O (111), CuO (111) as a reference (Fig. S3). Each of systems are expanded to 4 × 4 supercell with 6 layers and bottom 4 layers are fixed in their bulk positions. All the slabs are centered between 10 Å vacuum layer. To describe the stability of copper oxide shell on the Ag core, we calculated adhesion force of CuO and Cu₂O layer when it forms interface with Ag or Cu₂O surfaces. Adhesion force is calculated by below equation.

$$E_{ad} = E_{total} - (E_{core} + E_{shell})$$

where E_{ad} is adhesion force, E_{total} is total energy after interface is formed, E_{core} is bare surface (or core of nanoparticle), and E_{shell} is target layer (or shell of nanoparticle) forms interface with E_{core} . Negative sign of adhesion force represents thermodynamically stable because total energy after interface formation is lower than bare surface.

3. Results and discussion

The Ag-Cu₂O core-shell nanoparticles with bumpy structures were synthesized using a very simple co-reduction method. According to our previous works, Cu²⁺ and Ag⁺ ions have vastly different reduction temperatures when using oleylamine as a reducing agent [28–30]. Cu (acac)₂ can be reduced over 180 °C, whereas AgNO₃ can be reduced at 80 °C. The considerable difference in the reducing temperatures allows for the synthesis of the Ag-Cu₂O nanoparticles with a core-shell structure using the proposed co-reduction method. While increasing the temperature to reach the desired reaction temperature, the Ag core is first reduced at a lower temperature and the Cu₂O shell is reduced at a higher temperature. These sequential reduction processes allow for the formation of the nanoparticles core-shell structure. We gradually increased the Cu to Ag molar ratio (2:1, 4:1, and 8:1) to control the shell thickness. Fig. 1 shows TEM images of the synthesized nanoparticles and their size distributions. The average size for the Ag nanoparticles was 11.0 nm ($\sigma \leq 12.6\%$). As the amount of Cu precursor increased, the average Ag-Cu₂O core-shell nanoparticle sizes were 16.8 nm ($\sigma \leq 6.1\%$), 19.1 nm ($\sigma \leq 6.9\%$) and 22.0 nm ($\sigma \leq 7.9\%$) for the molar ratios (2:1, 4:1, and 8:1) respectively. The sizes of the nanoparticles are much smaller than those of previous reports [19,22,31]. The shell thickness was measured by subtracting the size of the Ag nanoparticles from the size of the Ag-Cu₂O core-shell bumpy nanoparticles. The measured shell thicknesses are 5.8 nm, 8.1 nm and 11.0 nm for each molar ratio. It can be shown that the shell thickness of the nanoparticles is successfully controlled by the facile co-reduction method with different Cu to Ag molar ratio. In this study, we designated the sample names as Ag-Cu₂O(2:1), Ag-Cu₂O(4:1) and Ag-Cu₂O(8:1). Additionally, the HRTEM images indicate that the Ag-Cu₂O core-shell nanoparticles have a multi-seeded structure for the Cu₂O shell, as shown in Fig. 2. It can be clearly seen that the shell thickness gradually grows as the molar ratio is increased. The core-shell structure could be checked from the lattice spacing measured in the HRTEM images. To confirm the core-shell structure of the nanoparticles more distinctly, the EDS line scanning and EDS elemental mapping were conducted. Fig. 3 shows the EDS analysis on Ag-Cu₂O(8:1) nanoparticles, presenting a clear core-shell structure.

Cu₂O has a +1 oxidation state and is a meta-stable state, spontaneously oxidizing to CuO or Cu(OH)₂. Therefore, we have attempted to confirm whether the synthesized nanoparticles consist of Cu₂O or other forms. The binding energy in XPS analysis is changed significantly according to the oxidation state of the species. In case of copper, the Cu⁺

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