



Light-treated silica-coated gold nanorods having highly enhanced catalytic performances and reusability



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ABSTRACT

A simple post-treatment method of irradiation with a Xe lamp for 2 h has been observed to enhance the catalytic performances of a nanocatalyst on a large scale. The light treatment of mesoporous silica-coated gold nanorods having an average diameter of 17.5 nm and a typical aspect ratio of 4 with a uniform shell thickness of 20 nm improves the catalytic activity of the nanocatalyst for the reduction of 4-nitrophenol in the presence of NaBH_4 extensively without deteriorating the encapsulation effect of mesoporous silica that enhances the stability and reusability of the nanocatalyst by preventing the aggregation and dissolution of gold nanorods. Irradiation increases the catalytic rate constant largely with reducing the activation energy and the induction time of the catalytic reaction substantially; surface atom restructuring induced by photothermal annealing during irradiation has rendered the metallic surface to adsorb reactants easily and to facilitate rapid electron relays from BH_4^- to 4-nitrophenol, lowering the kinetic barrier of the catalytic reaction considerably.

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1. Introduction

Nanostructured materials with functional properties have been widely explored as they can be employed potentially in a diverse range of technologies [1,2]. In particular, the control of the sizes, shapes, and compositions of noble-metal nanostructures has been broadly studied for applications such as catalysts, optoelectronics, and biomedicines [3,4]. Unique properties of noble-metal nanoparticles compared with bulk metals, due to their quantum effects and extremely high surface-to-volume ratios, facilitate catalytic performances in synthesis reactions [5]. Among the nanostructures of noble metals, gold nanoparticles have attracted widespread interest in the field of nanocatalysis as gold exhibits unique catalytic activity for important chemical reactions such as selective reduction and oxidation reactions [6–8].

The reduction of 4-nitrophenol (4NP) by NaBH_4 to form 4-aminophenol has been used as a model reaction to estimate the catalytic performances of noble metal nanoparticles [9–11]. The reduction mechanism of 4NP has been demonstrated based on the Langmuir–Hinshelwood model in previous reports [9,12] that the catalytic reaction takes place when both of the electron donor BH_4^- and the electron acceptor 4NP are adsorbed onto a catalyst surface. Zeng et al. [10] have compared the catalytic activities of gold-based nanocages, nanoboxes, and nanoparticles in the

reduction of 4NP, suggesting that a high surface area enhances catalytic efficiency. So far, although a few studies have been reported about the catalytic reactivity of gold nanorods [5,11], their stability and reusability have been hardly reported yet. Bai et al. [11] have studied the dependence of catalytic performances on the aspect ratios of gold nanorods, revealing that short gold nanorods have excellent catalytic efficiency.

For catalytic applications, nanoparticles need to be highly stable against the surrounding medium, heat, and recycling while being catalytically active. The surface of gold nanorods (NRs) is often surrounded by the surfactant of cetyltrimethylammonium bromide (CTAB). Positively charged gold NRs surrounded by a CTAB bilayer are prevented from their aggregation in an aqueous solution via electrostatic repulsion [13]. However, in the case of an organic solution, the desorption of CTAB into the surrounding medium can induce the aggregation of CTAB-stabilized gold nanorods (Au@CTAB NRs), losing their catalytic properties. Also, due to higher surface-to-volume ratios, Au@CTAB NRs are thermodynamically unstable and tend to reduce their surface energy, transforming into spherical nanostructures [14]. To overcome the aforesaid disadvantages, it is necessary to design stable and reactive nanocatalysts by coating an additional material on the surface of gold NRs to lower the overall price of the noble-metal nanocatalysts. In principle, the shell-coating method should be straightforward to form a deposit on the surface of a catalyst and to give chemical and thermal stability to the catalyst, ensuring the reuse of the catalyst after a reaction. The shell structure should not hinder reactants from access to the catalyst surface in order to preserve catalytic reactivity. For

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example, nonporous shells generally result in separation between the core surface and its solvent environment [15,16], making it difficult for outside reactants to diffuse in and out [17]. However, a porous shell, especially mesoporous silica, does not cover the entire active surface of a nanocatalyst, enabling reactants to penetrate through pores [15–21]. A mesoporous silica shell has many advantages. First, the silica shell provides high stability in tough conditions such as heat, solvent exchange, and centrifugation. Moreover, it does not deteriorate the optical properties of the core noble-metal nanoparticle because silica is transparent in the visible. Last, mesoporous silica shells have large pore volumes so that reactant molecules can diffuse through pores into the surface of catalysts [22,23]. For the first time, Gorelikov et al. [16] have reported a method to coat mesoporous silica on Au@CTAB NRs directly without having any intermediary coating step. Gold nanorods with a mesoporous silica shell have attracted numerous interests in diverse fields such as bioimaging and photothermal therapy [13,23,24]. However, the catalytic performances of mesoporous silica-coated gold nanorods (Au@mSiO₂ NRs) have not been studied so far.

In this paper, we have demonstrated a facile and effective post-treatment strategy to enhance the catalytic performances of Au@mSiO₂ NRs highly by simply irradiating light to the colloidal solution. First of all, we have synthesized gold nanorods and coated them with mesoporous SiO₂ to provide stability for the metallic nanocatalysts. Then, Au@mSiO₂ NRs have been irradiated by a Xe lamp for 2 h. Finally, we have chosen the reduction of 4-nitrophenol with NaBH₄ to produce 4-aminophenol as a model reaction to investigate the catalytic efficiencies of Au@CTAB NRs, Au@mSiO₂ NRs, and irradiated Au@mSiO₂ NRs. It is found that the nanocatalyst of irradiated Au@mSiO₂ NRs exhibits highly enhanced catalytic performances as well as excellent catalytic reusability.

2. Experimental

2.1. Chemicals

CTAB (s, 96%), HAuCl₄·3H₂O (s, 99.9%), 37% HCl(aq), methanol(l), 4-nitrophenol (s, ≥99%), AgNO₃ (s, ≥99%), NaBH₄ (s, 96%), NaOH (s, ≥98%), and tetraethyl orthosilane (TEOS, l, ≥99%) were used as purchased from Sigma–Aldrich. Ultrapure deionized water (>17 MΩ cm) was obtained using a Millipore Milli-Q system.

2.2. Preparation of gold nanorods

Au@CTAB NRs were synthesized using a seed-mediated and CTAB-assisted method [25]. 0.25 mL of 10 mM HAuCl₄(aq) was added to 9.75 mL of 0.10 M CTAB(aq) with gentle shaking for 10 s. Then, 0.60 mL of freshly prepared ice-cold 10 mM NaBH₄(aq) was added quickly to the mixture solution under vigorous stirring for 2 min. This seed solution was kept in a 27 °C water bath for at least 2 h before further use. 3.0 mL of 10 mM HAuCl₄(aq) and 0.40 mL of 10 mM AgNO₃(aq) were first mixed with 40 mL of 0.10 M CTAB(aq). 0.80 mL of 1.0 M HCl(aq) was added to adjust the pH of the growth solution, and 0.32 mL of 0.10 M ascorbic acid(aq) was then added to the mixture. After the growth solution was shaken gently, 96 μL of the gold seed solution was added. The mixed solution was gently mixed and then left undisturbed overnight at 27 °C. The aqueous colloidal solution of as-synthesized gold nanorods was centrifuged at 8500 rpm for 8 min, the supernatant was discarded carefully, and the precipitates were dispersed in 16 mL of water. The centrifugation and dispersion processes were repeated. The concentration of CTAB in the finally purified gold colloidal solution was estimated to be 0.12 mM. During centrifugation, temperature was maintained

at 26–30 °C to prevent the crystallization of CTAB in the solution.

2.3. Preparation of mesoporous silica-coated gold nanorods

Mesoporous silica coating was performed according to the previously published procedures [16,24] with some modifications. 30 μL of 0.10 M CTAB(aq) was added to 3.0 mL of the gold colloidal solution described above and stirred for 30 min at 27 °C. Then, 30 μL of 0.10 M NaOH(aq) was added with vigorous stirring and then 30 μL of 20% TEOS in methanol was injected under gentle stirring three times at a 30 min interval. The mixture was allowed to react under gentle stirring for 24 h. The resultant solution was centrifuged and washed with ethanol repeatedly, and then the precipitate of Au@mSiO₂ NRs was dispersed in 3.0 mL of water.

2.4. Irradiation of a Xe lamp to mesoporous silica-coated gold nanorods

The colloidal solution of as-prepared Au@mSiO₂ NRs contained in a cuvette having a path length of 2 mm were irradiated with a 300 W Xe lamp for 2 h at room temperature to produce irradiated Au@mSiO₂ NRs. The cuvette was 10 cm away from the light source and the entire face of the sample facing the light source (1 cm × 3 cm) was uniformly irradiated by the Xe lamp. To prevent the sample from evaporation, the top of the cuvette was sealed with paraffin film.

2.5. Catalysis experiment

The catalytic properties of gold NRs were measured by monitoring the reduction reaction of 4-nitrophenol in the presence of NaBH₄ [26]. 0.12 mL of 2.0 mM 4-nitrophenol(aq) was diluted with 1.6 mL of water in a polyphenyl cell having a path length of 10 mm, and then 0.30 mL of a colloidal diluted solution containing Au@CTAB NRs, Au@mSiO₂ NRs, or irradiated Au@mSiO₂ NRs was added, making the final concentration of a nanocatalyst as 13 pM (2.6 ng L⁻¹). The resulting solution was shaken gently and 2.0 mL of ice-cold 60 mM NaBH₄(aq) was added at once. Then, the absorption spectral changes of 4-nitrophenol were measured at scheduled intervals using a temperature-controllable spectrophotometer. The concentration of gold nanorods was estimated using the wavelengths at the surface-plasmon maximum and the associated extinction coefficient of gold NRs obtained from an optical spectrum [27]. We have assumed that the concentration of gold nanorods remains invariant during the silica coating process. So, the concentration of gold nanorods in each as-prepared colloidal solution of Au@CTAB NRs or Au@mSiO₂ NRs was found to be 0.63 nM. 1.0 mL of each as-prepared colloidal solution was diluted by adding 2.5 mL of water to be used as a nanocatalyst. To study the reusability of nanocatalysts, used gold NRs were separated from the reaction mixture by centrifugation (13,000 rpm, 3 min) at the end of each run and then re-dispersed in water.

2.6. Characterization

Transmission electron microscopic (TEM) images were obtained by a Hitachi H-7600 microscope. High-resolution TEM (HRTEM) and scanning TEM (STEM) images and energy-dispersive X-ray (EDX) line-scanned elemental intensity profiles were measured by a JEOL JEM-2100F microscope. UV–vis absorption spectra were measured using a temperature-controllable Scinco S-3000 spectrophotometer.

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