



Synthesis and catalytic performance of multiple gold nanodots core–mesoporous silica shell nanoparticles



Joonsung Pak, Hyojong Yoo*

Department of Chemistry, Hallym University, Chuncheon, Gangwon-do 200-702, Republic of Korea

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ABSTRACT

Multiple gold (Au) nanodots core–mesoporous silica shell nanoparticles (multi-Au@mesoporous-SiO₂ NPs) were successfully synthesized in solution through a soft-etching methodology. Thermal treatment of the multi-Au@SiO₂ NPs in water without adding any other additives lead to generation of mesopores over the silica shell without any change in the size and number of the Au nanodots. The multi-Au@mesoporous-SiO₂ NPs showed much higher catalytic activity in the reduction of 4-aminophenol than multi-Au@SiO₂ NPs and other single Au nanodot core–silica shell nanoparticles with york-shell morphologies, which were also effectively fabricated (single-Au@SiO₂ NPs and single-Au@mesoporous-SiO₂ NPs). The enhanced catalytic activity is mainly due to the efficient diffusion of reactants onto the multiple Au nanodots through mesopores within the silica shell as well as the higher surface area of multiple Au nanodots.

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1. Introduction

Catalytic applications of colloidal gold (Au) nanoparticles have attracted great attention because they often show high activity and selectivity in a variety of heterogeneous green catalytic processes [1–4]. In general, specific supports such as metal oxides [4–6] or activated carbon [7,8] have been used to improve the activity in the adsorption of reactants, stability of Au nanoparticles, and reusability of catalysts. The adsorption reactivity of molecules on the surface of Au nanocatalysts can be a result of the quantum effects of Au nanoparticles, which interact with oxide supports [9,10]. Significant effort has been made to develop Au nanocatalytic systems that mainly include discovering adequate oxide supports and efficient deposition methodologies [11], fabricating core–shell type morphologies [12], integrating active nanoparticles [13], and so on. In particular, controlled assemblies of colloidal nanoparticles are expected to exhibit collective properties that are distinctly different from those of the corresponding individual particles [14–17]. Therefore, assembling Au nanoparticles by surrounding them with silica (SiO₂) shells as an oxide support could be a potentially useful method for the preparation of highly active nanocatalyst assemblies.

Recently, a useful technique for assembling Au nanoparticles within a silica shell was reported by our research group [18]. Highly spherical nanoparticles with a core comprising multiple Au nanodots and a silica shell (multi-Au@SiO₂ NPs) were synthe-

sized via a reverse (water-in-oil) microemulsion-based method. The silica-encapsulated Au nanodots with diameters of 2–5 nm were arranged such that the interparticle gaps were in the sub-nanometer range. However, the Au nanodots within multi-Au@SiO₂ NPs were surrounded by a thick and dense silica shell, which might restrict the potential availability of multiple Au nanodots and the interparticle gaps. To use the physical and structural properties of the Au nanodot assembly of multi-Au@SiO₂ NPs in a variety of applications, further modifications of the silica shell such as imparting porosity were required [19,20]. In an endeavor to develop multi-Au@SiO₂ NPs, we employed a “soft-etching” methodology through a thermal treatment without any surface-protective agents. This synthetic method is based on the fact that amorphous silica nanoparticles can be dissolved in the form of monomeric Si(OH)₄ in water, and the solubility increases with temperature [21–23]. Although single Au nanoparticle core–mesoporous silica shell nanoparticles have been fabricated through similar strategies [24,25], there has been no example of silica etching in types of multi-Au@SiO₂ NPs. We found that thermal treatment of the multi-Au@SiO₂ NPs in water without adding any other additives lead to generation of mesopores over the silica shell without any change in the size and number of the Au nanodots. Herein, we report multiple Au nanodots core–mesoporous silica shell nanoparticles (multi-Au@mesoporous-SiO₂ NPs), which were successfully synthesized by heating multi-Au@SiO₂ NPs in an aqueous media. The multi-Au@mesoporous-SiO₂ NPs showed significantly higher catalytic activity in the reduction of 4-aminophenol compared to other Au core–silica shell nanoparticles.

* Corresponding author. Tel.: +82 33 248 2072; fax: +82 33 256 3421.

E-mail address: hyojong@hallym.ac.kr (H. Yoo).

2. Experimental

2.1. Reagents

Polyoxyethylene glycol dodecyl ether ((C₂H₄O)₂₃C₁₂H₂₅OH, Brij35, Acros Organics), tetraethylorthosilicate (TEOS, 99%, Sigma–Aldrich), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99.9%, Sigma–Aldrich), polyvinylpyrrolidone ((C₆H₉NO)_n, PVP10, average mol wt 10,000, Sigma–Aldrich), 4-nitrophenol (O₂NC₆H₄OH, 99%, Sigma–Aldrich), sodium borohydride (NaBH₄, 98%, Sigma–Aldrich), ammonium hydroxide (NH₄OH, 28–30 wt% ammonia, Sigma–Aldrich), cyclohexane (C₆H₁₂, 99%, Sigma–Aldrich), 1-hexanol (C₆H₁₃OH, 98%, Sigma–Aldrich), HCl, HNO₃, acetone, and ethyl alcohol were used as received. All stock solutions were freshly prepared before each reaction. Prior to use, all glassware was washed with aqua regia (3:1 ratio by volume of HCl and HNO₃; Caution: Aqua Regia is highly toxic and corrosive and must be handled in a fume hood with proper personal protection equipment) and rinsed thoroughly with nanopure water.

2.2. Synthesis of multi-Au@SiO₂ NPs

Multiple Au nanodots core–silica shell nanoparticles (Multi-Au@SiO₂ NPs) were synthesized through the reduction of Au³⁺ ions (HAuCl₄) during the formation of silica nanoparticles in the reverse microemulsion, which was generated using polyoxyethylene glycol dodecyl ether ((C₂H₄O)₂₃C₁₂H₂₅OH, Brij35) as the surfactant. The microemulsion was prepared by mixing Brij35 (2 g), a co-surfactant (n-hexanol, 1.6 mL), and an organic solvent (cyclohexane, 7.7 mL) and completely redissolving them via sonication. 0.03 mL of 0.1 M HAuCl₄ (aq.) (0.003 mmol) was added to the reverse microemulsion and the mixture was sonicated for 30 min at room temperature. Next, tetraethylorthosilicate (TEOS, 0.05 mL) and ammonium hydroxide (0.5 mL of 14.8 M NH₄OH (aq.)) were sequentially added to the reverse microemulsion while stirring it for 30 min, and the reaction mixture was further stirred at room temperature for 12 h. After the completion of the reaction, the microemulsion system was destabilized by adding acetone (20 mL), followed by centrifugation at 2000 rpm for 5 min. The generated multi-Au@SiO₂ NPs were purified by repeated washing in ethanol and centrifugation.

2.3. Synthesis of multi-Au@mesoporous-SiO₂ NPs

The multi-Au@mesoporous-SiO₂ NPs were prepared by thermal treatment of the multi-Au@SiO₂ NPs. The purified multi-Au@SiO₂ NPs were redispersed in nanopure water (1 mL), and then heated at 90 °C for 12–36 h. After the heating, the reaction mixture was slowly cooled down to room temperature, and centrifuged (13,500 rpm, 5 min). The prepared nanoparticles were kept in ethanol for the further use.

2.4. Synthesis of single-Au@SiO₂ NPs and single-Au@mesoporous-SiO₂ NPs

A polyvinylpyrrolidone (PVP10) aqueous solution (mixture of 0.1 g of PVP10 and 1 mL of nanopure water) was added to the purified multi-Au@SiO₂ NPs and stirred at room temperature. Initially, a yellowish gray reaction mixture was formed that turned pale-red after 6 h of stirring. The reaction was terminated after 12 h, and the resulting nanoparticles (single-Au@SiO₂ NPs) were purified by repeatedly washing in ethanol and centrifugation. For the synthesis of single-Au@mesoporous-SiO₂ NPs, the purified single-Au@SiO₂ NPs were redispersed in nanopure water (1 mL), and then heated at 90 °C for 12 h. After heating, the reaction mixture was slowly

cooled down to room temperature and centrifuged (13,500 rpm, 5 min).

2.5. Catalytic reduction of 4-nitrophenol

The reduction of 4-nitrophenol (4-NP) by nanoparticles in the presence of NaBH₄ was carried out to examine the catalytic activity. 2 mL of deionized water, 1.7 mL of 0.2 mM 4-nitrophenol, and 1 mL of 15 mM NaBH₄ solutions were mixed in a quartz cuvette followed by the addition of 1 mL of the Au@SiO₂ NPs solution. The solution changed gradually from a yellow color to clear as the reaction proceeded. UV–Vis spectrometry was used to record the change in absorbance at a time interval of 5 min.

2.6. Characterization

The resulting nanoparticles were imaged using a Hitachi S-4800 scanning electron microscope (SEM), a LEO-912AB OMEGA, Carl Zeiss, Germany transmission electron microscope (TEM). High-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX) analysis, and selected-area electron diffraction (SAED) were measured using JEOL JEM-2100F microscope. Samples for analysis using the TEM were prepared by concentrating the nanoparticle mixture by centrifuging it twice for 5 min at 13,500 rpm. Following this, the particles were resuspended in 100 μL of nanopure water and immobilized from 10 μL portions of the solution on Formvar-coated Cu grids. UV–Vis spectra were recorded with a UV Spectrophotometer (UV-1800 Shimadzu).

3. Results and discussion

The multi-Au@mesoporous-SiO₂ NPs were prepared by thermal treatment of the multi-Au@SiO₂ NPs, which were synthesized according to procedures in literature [18,26]. Briefly, Au³⁺ ions were reduced during the formation of silica nanoparticles from tetraethylorthosilicate (TEOS) and NH₄OH in a reverse microemulsion, which was generated using polyoxyethylene glycol dodecyl ether ((C₂H₄O)₂₃C₁₂H₂₅OH, Brij35), n-hexanol, and cyclohexane. The generated multi-Au@SiO₂ NPs were purified, redispersed in water, and then heated at 90 °C for 12–36 h. The formation of multi-Au@mesoporous-SiO₂ NPs was clearly observed in transmission electron microscopy (TEM) images. Fig. 1a is the TEM image of multi-Au@SiO₂ NPs that was acquired before heating, and Fig. 1b and Fig. S1 are the images of nanoparticles after heating at 90 °C for 12 h. Although both nanoparticles show spherical geometries, the nanoparticles in Fig. 1b show much more and larger holes over the silica shells than those in Fig. 1a. These empty spaces are attributed to mesopores, which were generated by the etching of silica shells in water at high temperature [24,25]. The average diameter of individual multi-Au@mesoporous-SiO₂ NPs was 41.1 ± 2.90 nm, which was similar to that of multi-Au@SiO₂ NPs (40.79 ± 2.76 nm). Importantly, the multiple Au nanodots core was not affected by the thermal treatment; the average size and number of Au nanodots in multi-Au@mesoporous-SiO₂ NPs were 2.96 ± 0.66 and 4.53 ± 1.99 nm, respectively, and these values were not critically different from those of multi-Au@SiO₂ NPs (3.60 ± 0.91 and 3.38 ± 1.49 nm [18], more than 100 silica NPs were evaluated in every measurements). Therefore, we can conclude that thermal etching in water without adding any other additives is a facile and valuable synthetic strategy to prepare multiple nanoparticles core–mesoporous silica shell nanoparticles, without disturbing the structural motifs of Au nanodot assemblies.

Fig. 1c shows the UV–Vis spectral changes of multi-Au@SiO₂ NPs as a function of heating time at 90 °C in water. As described in the previous report, almost no surface plasmon resonances

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