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Easily recyclable and highly active rice roll-like Au/SiO₂ nanocatalysts from inverse miniemulsion

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HIGHLIGHTS

- Rice roll-like Au/SiO₂ nanocatalysts were synthesized through one-step inverse miniemulsion-based technique.
- The rice roll-like Au/SiO₂ nanocatalysts embody excellent catalytic activity and good recycling catalytic performance.
- The rice roll-like Au/SiO₂ nanocatalysts display good aqueous dispersibility and pH-dependent, reversible colloidal stability.
- A formation mechanism of rice roll-like Au/SiO₂ nanocatalysts was proposed.

GRAPHICAL ABSTRACT
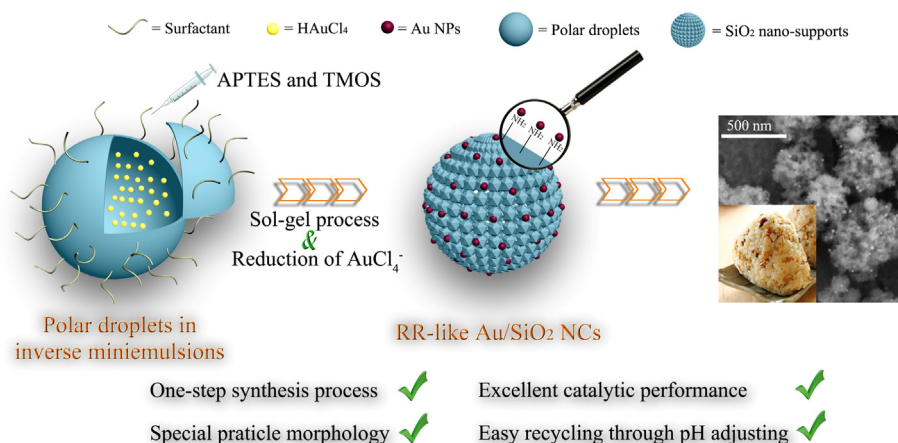
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ABSTRACT

Rice roll-like (RR-like) Au/SiO₂ nanocatalysts (NCs) were synthesized through simultaneous sol–gel process of tetramethoxysilane and 3-aminopropyltriethoxysilane (APTES) and *in situ* reduction of gold salt in inverse miniemulsions. APTES played an important role in formation of RR-like SiO₂ nano-supports, reduction of gold salts to narrowly size-distributed sub–10 nm Au nanoparticles (NPs), and improved attachment of Au NPs to the SiO₂ nano-supports. The prepared RR-like Au/SiO₂ NCs displayed a pH-dependent, reversible colloidal stability in water, which facilitated to recycle them through tuning the pH value of the dispersion. Most importantly, the catalytic activity of the RR-like Au/SiO₂ NCs towards reduction of *p*-nitrophenol was about 7–9 times higher than that of the raspberry-like Au/SiO₂ NCs reported in our previous paper (Colloids Surf. A, 489, 2016, 223–233). The formation mechanism of the RR-like Au/SiO₂ NCs was also discussed.

1. Introduction

In recent years, Au nanoparticles (NPs) have been intensively investigated due to their excellent catalytic activity towards *p*-

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nitrophenol (*p*-NPh) reduction [1], alkyne hydrochlorination [2], alkene epoxidation [3], and alcoholoxidation [4]. A notorious problem in the use of sub–10 nm Au NPs is the agglomeration caused by their high surface energy [5]. Colloidal stabilizers, such as small molecular surfactants, polymer dispersants, and organic ligands, can effectively prevent Au NPs from agglomeration [6,7]. However, the catalytic activity of Au NPs is more or less deteriorated by the cover of colloidal stabilizer on their surface [8].

Alternatively, the dispersibility of Au NPs could be improved through immobilization of them onto porous nano-supports [9,10]. Versatile materials, such as SiO_2 [8,11,12], TiO_2 [13], ZnO [14], and C [15], have been used as nano-supports. Among them, SiO_2 may be one of the most widely used inorganic materials for preparing noble metal/SiO_2 nanocatalysts (NCs) taking advantage of its tunable porous structure, good chemical and thermal stabilities, good biocompatibility, and good mechanical strength. Impregnation of SiO_2 supports with Au NPs has been applied to prepare Au/SiO_2 NCs [16,17]. Normally, this method includes two steps: (1) predispersing of the SiO_2 nano-supports in an aqueous solution of gold salt; (2) reduction of gold salt to Au NPs with reducing agents. However, this technique often gives relatively low immobilization efficiency of Au NPs to the supports. This drawback may be overcome through introducing an interaction between Au NPs and SiO_2 supports. To this objective, modifications of supports or gold salts have been made prior to the reduction of gold salts [18,19]. However, pre-modification definitely increase the complexity of the preparation process. Thus, more efficient and simpler techniques are still highly desirable for preparation of immobilized Au-based NCs.

Inverse miniemulsions consist of a polar dispersed phase and a low polarity continuous phase [20]. Versatile hydrophilic nanomaterials have been prepared in inverse miniemulsions through various reaction mechanisms including polymerization and sol–gel process [20]. Landfester et al. prepared porous inorganic nanomaterials, such as SiO_2 and TiO_2 NPs, through a sol–gel process of hydrophilic inorganic precursors in inverse miniemulsions [21,22]. Recently, we devised an inverse miniemulsion-based technique to prepare noble metal/inorganic support NCs [10,23–25]. Firstly, noble metal salt/inorganic support nanocomposite particles (NCPs) were prepared through a sol–gel process of inorganic precursors; secondly, the incorporated noble metal salts were *in situ* reduced in the NCPs through post-addition of a strong reducing agent. Through this technique, raspberry-like Au/SiO_2 NCs [10], Janus Pd/SiO_2 NCs [23], and raspberry-like Ag/TiO_2 NCs [25] have been successfully prepared. Advantages of this technique are as follows: (1) The immobilization efficiency of noble metal NPs is high due to the *in situ* reduction of noble metal salts inside the NCPs; (2) the type of the NCPs can be easily tuned through varying the type of noble metal salts or inorganic precursors; (3) the content of noble metal NPs can be conveniently tuned in a wide range through adjusting the loading of noble metal salts. However, we found that the particle size and the particle size distribution of noble metal NPs could not be well controlled by this technique [10]. The particle size of Au NPs was much larger than 10 nm, due to the fast reduction rate and agglomeration of Au nuclei in the same NCP [10]. It has been reported that sub–10 nm Au NPs displayed higher catalytic activity [26]. Therefore, the catalytic activity of the Au/SiO_2 NCs may be further improved through reducing the particle size of Au NPs and narrowing their particle size distribution.

Different from the previously reported two-step inverse miniemulsion-based preparation technique [10,23–25], we designed a novel one-step preparation technique for preparation of Au/SiO_2 NCs in this work. Rice roll-like (RR-like) Au/SiO_2 NCs were synthesized through a simultaneous sol–gel process of two silica precursors and *in situ* reduction of $HAuCl_4$ in inverse miniemulsions. Narrowly size-distributed sub–10 nm Au NPs

were obtained, and they mainly attached to the surface of SiO_2 nano-supports. The RR-like Au/SiO_2 NCs showed a good aqueous dispersibility and a pH-dependent, reversible colloidal stability. Most importantly, they embodied a very high catalytic activity and excellent recycling performance towards reduction of *p*-NPh.

2. Experimental section

2.1. Materials

Tetrachloroauric acid ($HAuCl_4$, 48%–50%), tetramethoxysilane (TMOS, 98%), 3-aminopropyltriethoxysilane (APTES, 99%), dimethyl sulfoxide (DMSO, 99%), urea (AR, 99%), *p*-nitrophenol (99%), and sodium borohydride ($NaBH_4$, 98%) were purchased from Aladdin Chemistry Co. Ltd. and used as received. Cyclohexane ($\geq$99.5%) and ethanol ($\geq$99.7%) were purchased from Hangzhou Gaojing Fine Chemical Co. Ltd. *n*-Hexadecane (HD, 98%) was purchased from Macklin. Poly(ethylene-*co*-butylene)-*b*-poly(ethylene oxide) (P(E/B)–PEO) with number average molecular weight of 7100 g mol^{-1} was synthesized according to the literature [27]. The molecular weights of the hydrophobic (E/B) and hydrophilic (EO) blocks are 4000 and 3100 g mol^{-1}, respectively. These weights resulted in a P(E/B)–PEO hydrophilic–lipophilic balance of 8.7. Demineralized water was self-made and used in all experiments.

2.2. Preparation of RR-like Au/SiO_2 NCs

Schematic representation of the synthesis of RR-like Au/SiO_2 NCs is shown in Scheme 1. 0.3 g of aqueous solution of urea (0.04 M) was mixed with 1.0 g of DMSO to form a polar solution. 43 mg of $HAuCl_4$ was dissolved in this polar solution, and the $HAuCl_4$-containing solution was used as the dispersed phase. 4 wt% of P(E/B)–PEO relative to the dispersed phase was dissolved in 12.5 g of HD to form a hydrophobic solution which was used as the continuous phase. Two solutions were mixed with an agitation of 700 rpm at 40 °C for 15 min to form a crude emulsion. The crude emulsion was further sonicated by using a pulse mode (work 12 s, break 6 s for 9 min) at 42% maximum power of the sonifier (JY92-II DN) to form an inverse miniemulsion.

2 g of the prepared inverse miniemulsion was poured into a glass vessel. A mixture of TMOS (0.05 g) and APTES (0.073 g) was dropwisely added to the inverse miniemulsion. The reaction ran at 90 °C with an agitation of 400 rpm for 24 h to form the RR-like Au/SiO_2 NCs.

The obtained Au/SiO_2 NCs were purified through two centrifugation–redispersion cycles in cyclohexane and three centrifugation–redispersion cycles in ethanol. The purified Au/SiO_2 NCs were further dried overnight at 50 °C in a vacuum oven. The dried powders were calcined at 500 °C for 1 h in a muffle furnace to remove organic components.

2.3. Evaluation of aqueous dispersibility and pH-dependent colloidal stability of the RR-like Au/SiO_2 NCs

5 mg of the RR-like Au/SiO_2 NCs was dispersed in 40 mL of water through sonication with a 5% maximum power of the sonifier (JY92-II DN) for 20 min by using a pulse mode (work 12 s, break 6 s). The pH value of the obtained dispersions was tuned by the aqueous solution of HCl or NaOH. The particle sizes and zeta-potential values of the RR-like Au/SiO_2 NCs at various pH values were measured to evaluate their aqueous dispersibility and colloidal stability. In addition, the colloidal stability of the dispersions at various pH values was also visually observed after storing for 12 h.

The protocol for evaluation of the pH-dependent, reversible colloidal stability of the RR-like Au/SiO_2 NCs was as follows: The pH value of the aqueous dispersion of the RR-like Au/SiO_2 NCs was