



## Inverse miniemulsion-based preparation of raspberry-like Au/SiO<sub>2</sub> nanocomposite particles with high catalytic activity towards reduction of *p*-nitrophenol



Zhihai Cao<sup>a,\*</sup>, Hangnan Chen<sup>a</sup>, Shudi Zhu<sup>b</sup>, Zhijie Chen<sup>a</sup>, Chang Xu<sup>a</sup>, Dongming Qi<sup>a,\*</sup>, Ulrich Ziener<sup>c</sup>

<sup>a</sup> Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, National & Local United Engineering Laboratory of Textile Fiber Materials and Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China

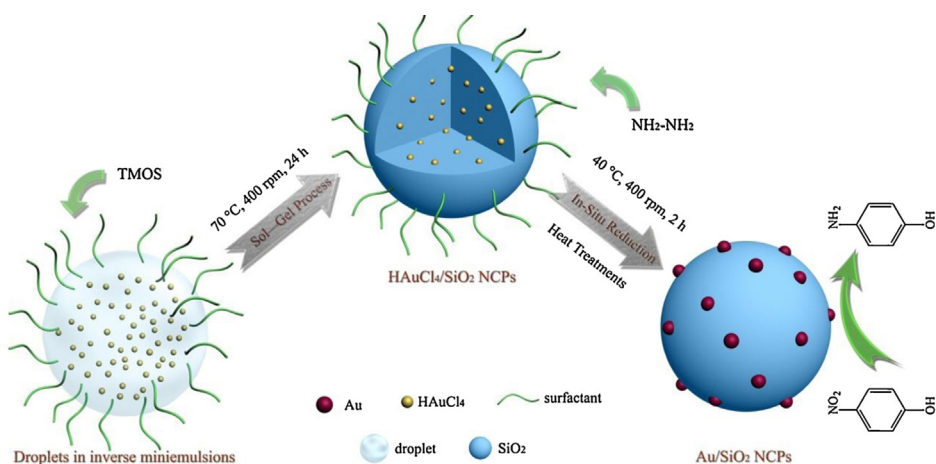
<sup>b</sup> College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Xuelin Street 16, Hangzhou 310036, China

<sup>c</sup> Institute of Organic Chemistry III—Macromolecular Chemistry and Organic Materials, University of Ulm, Albert-Einstein-Allee 11, Ulm 89081, Germany

### HIGHLIGHTS

- A convenient method based on the inverse miniemulsion technique was proposed to prepare raspberry-like Au/SiO<sub>2</sub> nanocomposite particles (NCPs).
- Most of Au nanoparticles were half-embedded in the porous SiO<sub>2</sub> nano-supports, offering a good morphological stability to the Au/SiO<sub>2</sub> NCPs.
- Formation mechanism of raspberry-like Au/SiO<sub>2</sub> NCPs was discussed.
- The Au/SiO<sub>2</sub> NCPs displayed a good catalytic activity and recycling performance towards reduction of *p*-nitrophenol.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A convenient method based on the inverse miniemulsion technique was proposed to prepare raspberry-like Au/SiO<sub>2</sub> nanocomposite particles (NCPs). HAuCl<sub>4</sub> was incorporated into porous SiO<sub>2</sub> nano-supports through a sol-gel process of a silica precursor in inverse miniemulsions. Raspberry-like Au/SiO<sub>2</sub> NCPs were subsequently obtained through in situ reduction of the incorporated HAuCl<sub>4</sub> by hydrazine at the surface of SiO<sub>2</sub> nano-supports. Most of Au nanoparticles (NPs) were half-embedded in the SiO<sub>2</sub> nano-supports and were covered by a thin layer of porous SiO<sub>2</sub>, offering a good morphological stability to the Au/SiO<sub>2</sub> NCPs. The content of Au NPs of the Au/SiO<sub>2</sub> NCPs could be adjusted by the loading of HAuCl<sub>4</sub>. The influences of the HAuCl<sub>4</sub> loading on the particle size and particle morphology of the Au/SiO<sub>2</sub> NCPs, the pore properties of the SiO<sub>2</sub> nano-supports, as well as the properties of the Au NPs were systematically investigated. The formation mechanism of the raspberry-like Au/SiO<sub>2</sub> NCPs was discussed. All the synthesized Au/SiO<sub>2</sub> NCPs displayed a high catalytic activity towards the reduction of *p*-nitrophenol.

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\* Corresponding authors.

E-mail addresses: [zhcao@zstu.edu.cn](mailto:zhcao@zstu.edu.cn) (Z. Cao), [dongmingqi@zstu.edu.cn](mailto:dongmingqi@zstu.edu.cn) (D. Qi).

## 1. Introduction

Noble metal nanoparticles (NPs), such as Au, Ag, Pt, and Pd NPs, have attracted intensive attention because of their excellent optical, electronic, and catalytic properties [1–3]. From the catalytic point of view, it is necessary to reduce the particle size of noble metal NPs to a nano-sized range for increasing their surface area and number of active sites [4]. However, noble metal NPs are inclined to aggregate to minimize their surface area because of the high surface energy [4]. The agglomeration of noble metal NPs may significantly deteriorate their catalytic activity [4]. Stabilizers, for example polymeric stabilizers and organic ligands, are often used to improve the colloidal stability of noble metal NPs [5–8]. However, for catalytic applications, the coating of stabilizer on the surface of noble metal NPs may influence their performance. For instance, the diffusion of reactants to the surface of noble metal NPs may be hindered because of the presence of colloidal stabilizers [9]. Alternatively, to improve dispersion and subsequent catalytic activity, noble metal NPs have been immobilized onto various inorganic supports including silica, [10], zeolite [11], alumina [12], ceria [13], titania [14], and carbon nanotubes [15]. Noble metal NPs could be effectively stabilized by supports and hold their high surface area and catalytic activity [16]. Among these materials, SiO<sub>2</sub> is one of the most widely-used supports because of its good chemical stability, high mechanical strength, porous structure, and high specific surface area [10,17,18]. The catalytic activity of supported noble metal nanocatalysts depends on the type of noble metal, the particle size and morphology of noble metal NPs and SiO<sub>2</sub> support, and the pore structure of SiO<sub>2</sub> support. Therefore, it is a challenging work to synthesize supported noble metal nanocatalysts with a high catalytic activity through optimizing of all these parameters [19].

Au NPs display a high catalytic activity to a series of organic reactions, such as the reduction of *p*-nitrophenol (*p*-NPh), alkyne hydrochlorination, alkene epoxidation, and oxidation of alcohols [20,21]. Attachment of Au NPs to porous SiO<sub>2</sub> nano-supports may increase the dispersibility of Au NPs in various media, completely expose the surface of Au NPs to reactants after calcination, and facilitate the separation and recycling of catalysts from the reaction medium. In comparison to nonporous supports [21], the high specific surface area of porous nano-supports may promote the enrichment of reactants around noble metal NPs. Versatile techniques have been designed to prepare Au/SiO<sub>2</sub> nanocomposite particles (NCPs). For example, Wang et al. prepared Au/SiO<sub>2</sub> NCPs through in situ formation of Au NPs via reduction of HAuCl<sub>4</sub> by aniline-methyl which was pre-attached to the surface of SiO<sub>2</sub> nano-supports [10]. Xiang et al. prepared hollow tubular Au/SiO<sub>2</sub> NCPs with a mesoporous structure by using multi-wall carbon nanotubes (MWCNTs) as templates [22]. The preparation technique includes the sequential deposition of Au and SiO<sub>2</sub> layers onto the surface of MWCNTs via a sol-gel process, and removal of MWCNTs through calcination. Zheng et al. loaded Au NPs onto the surface of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NCPs to obtain Au decorated magnetic particles [23]. However, the attachment of Au NPs to the nano-supports are often weak, sometimes leading to the detachment of Au NPs from the nano-supports in the re-dispersing and catalyzing processes.

In recent years, miniemulsion has been proven to be a promising technique to prepare various NCPs through introducing a second moiety to a polymeric or inorganic matrix [24,25]. Inverse miniemulsions composed of a polar dispersed phase and a low polarity continuous phase can be used to prepare hydrophilic NPs like nanogels, inorganic NPs, or organic-inorganic hybrid NPs [26,27]. For example, Nabih et al. prepared mesoporous CeO<sub>2</sub> NPs in inverse miniemulsions and studied their catalytic properties towards methane oxidation [28]. Schiller et al. obtained Zr-doped anatase TiO<sub>2</sub> with a high phase stability and photocatalytic activity via the inverse miniemulsion technique [29]. Our group has utilized

the sol-gel process of a silica precursor in inverse miniemulsions to prepare mesoporous SiO<sub>2</sub> capsules, magnetic hollow SiO<sub>2</sub> NPs, and nanogel-core silica-shell NCPs [30–33]. In our work, hydrophilic transition metal salts and noble metal salts were used to offer additional functionalities like catalytic activity and magnetism to products through converting the added salts to functional metal oxide or metal NPs. Recently, we combined the sol-gel process and in situ reduction of the incorporated silver salts in inverse miniemulsions to prepare Ag/TiO<sub>2</sub> NCPs with a high visible-light catalytic activity towards photodegradation of Rhodamine B [34].

In the present paper, raspberry-like Au/SiO<sub>2</sub> NCPs were successfully synthesized through combination of the sol-gel process in inverse miniemulsions and in situ reduction of the incorporated gold salts on the surface of the porous SiO<sub>2</sub> nano-supports. Au NPs were half-embedded by the SiO<sub>2</sub> nano-supports, offering a good morphological stability to the Au/SiO<sub>2</sub> NCPs in the re-dispersing and catalyzing processes. The Au content of the Au/SiO<sub>2</sub> NCPs could be conveniently tuned by the HAuCl<sub>4</sub> loading. The influences of the HAuCl<sub>4</sub> loading on the particle properties and catalytic activity of the Au/SiO<sub>2</sub> NCPs were systematically investigated. The raspberry-like Au/SiO<sub>2</sub> NCPs displayed a high catalytic activity to the reduction of *p*-NPh to *p*-aminophenol (*p*-APH) with NaBH<sub>4</sub>.

## 2. Experimental

### 2.1. Materials

Tetrachloroauric acid (HAuCl<sub>4</sub>, 48.0–50.0%), dimethyl sulfoxide (DMSO, 99.0%), hydrazinium hydrate (AR grade, 80.0% solution), *p*-NPh (99.0%), sodium borohydride (NaBH<sub>4</sub>, 98.0%), sodium hydroxide (NaOH, 96.0%), hydrofluoric acid (HF, ≥40.0%), and tetramethoxysilane (TMOS, 98.0%) were purchased from Aladdin Chemistry Co. Ltd. and used as received. Cyclohexane (99.5%) and ethanol (99.7%) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. Tetrahydrofuran (THF, 99.0%) was purchased from Tianjin Yongda Chemical Reagent Co. Ltd. *n*-Hexadecane (HD, 99.0%) was purchased from Acros Organics. Poly(ethylene-co-butylene)-*b*-poly(ethylene oxide) (P(E/B)-PEO) with number-average molecular weight of 7100 g mol<sup>-1</sup> was synthesized according to the literature [35]. The molecular weights of the hydrophobic (E/B) and hydrophilic (EO) blocks are 4000 and 3100 g mol<sup>-1</sup>, respectively. These weights resulted in a P(E/B)-PEO hydrophilic-lipophilic balance of 8.7. Demineralized water (Milli-Q grade; resistivity: 18 MΩ cm) was used.

### 2.2. Preparation of HAuCl<sub>4</sub>/SiO<sub>2</sub> and Au/SiO<sub>2</sub> NCPs

The preparation process of the HAuCl<sub>4</sub>/SiO<sub>2</sub> and Au/SiO<sub>2</sub> NCPs is shown in Fig. 1. A given amount of P(E/B)-PEO was dissolved in HD to form a low polarity solution. HAuCl<sub>4</sub> was dissolved in a mixed solution of DMSO and water to form a polar solution. The two solutions were mixed and pre-emulsified in an oil bath at 40 °C with an agitation of 700 rpm for 15 min. After pre-emulsification, the crude emulsion was sonicated in an ice bath to prepare the inverse miniemulsions. Sonication was performed by applying a pulsed sequence (work 12 s, break 6 s) for 9 min, using a Scientz JY92-II DN sonifier at 400 W. The resulting inverse miniemulsion was introduced to an open glass vessel and placed in an oil bath at 70 °C. A given amount of TMOS was added to the inverse miniemulsion. The sol-gel process of TMOS was run for 24 h with an agitation of 400 rpm to obtain HAuCl<sub>4</sub>/SiO<sub>2</sub> NCPs. The formulations of the prepared HAuCl<sub>4</sub>/SiO<sub>2</sub> NCPs are listed in Table 1.

For the preparation of Au/SiO<sub>2</sub> NCPs, 40 mg of hydrazine were added to 2 g of the dispersion of HAuCl<sub>4</sub>/SiO<sub>2</sub> NCPs to reduce HAuCl<sub>4</sub>. The reduction reaction was run for 2 h

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