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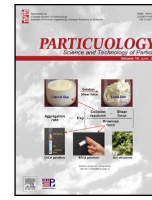

A microemulsion method for preparation of thiol-functionalized gold nanoparticles

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ABSTRACT

A new microemulsion method using tetraoctylammonium bromide as a cationic surfactant has been formulated to fabricate thiol-functionalized gold nanoparticles. The nanoparticles were compared with those synthesized by the multistep Brust two-phase method. The nanoparticle sizes and size distributions fabricated by the two methods were characterized by UV–vis absorbance spectroscopy and transmittance electron microscopy. The simple microemulsion method produced the same results as those obtained by the Brust method.

Introduction

Metallic and functionalized metallic nanoparticles are becoming increasing widespread owing to broad applications in electronics, medicine, food industry, environmental applications, and cosmetics (Boisselier & Astruc, 2009; Khan, Rashid, Murtaza, & Zahra, 2014; Luo, Du, Wang, Lu, & Xu, 2011; Thanh & Green, 2010). Because they are relatively less cytotoxic, gold nanoparticles (AuNPs) have abundant applications in biotechnology and biomedicine, including gene and drug delivery (Connor, Mwamuka, Gole, Murphy, & Wyatt, 2005; Ghosh, Han, De, Kim, & Rotello, 2008; Khademi-Azandehi & Moghaddam, 2015; Mata, Bhaskaran, & Sadras, 2016; Pissuwan, Niidome, & Cortie, 2011). Therapeutic AuNPs enable hypothermia treatments by binding to specific target cells or proteins before being irradiated with laser light. The AuNPs convert the light to highly localized heat, which damages only the tagged cells, thus enabling the destruction of specific cells with high selectivity and efficiency. Many diseases are considered treatable by this technique, including cancer, which is one of the leading causes of mortality (Tedesco, Doyle, Blasco, Redmond, & Sheehan, 2010).

In order to synthesis AuNPs that are monodispersed with controllable sizes and applicability, functionalization and surface modification must be performed. Because of good stability and chemical versatility in both polar and nonpolar solvents, thiol-stabilized AuNPs have become model systems in nanomaterials research (Ionescu et al., 2017; Porcaro et al., 2016). Alkane thiols are usually used for stabilization and they behave like soft Lewis bases, which complements the soft acid properties of AuNPs (Daniel & Astruc, 2004). Some thiols used in the preparation of thiol-caped AuNPs are modified as $HS(CH_2)_nX$, where X is a specific terminal functionality that enables broad applicability, especially in medicine.

Several methods for preparation of thiol-caped AuNPs have been utilized. Brust, Walker, Bethell, Schiffrin, and Whyman (1994) and Brust, Fink, Bethell, Schiffrin, and Kiely (1995) discussed a two-phase liquid–liquid system, also called two-phase transfer, where the thiol group strongly binds to the AuNP. The Brust method is shown schematically in Fig. 1(a). Briefly, a gold salt is transferred from an aqueous to an organic phase using tetraoctylammonium bromide (TOAB) as the phase transfer agent. The gold ions are then reduced by sodium borohydride in the presence of an alkane thiol to clusters of gold atoms surrounded by thiolates. Shalom et al. (2007) proposed a method for controlled synthesis of thiolated AuNPs by using a microfluidic device, followed by the Brust method. Sugie et al. (2012) also proposed a flow method by using $C_{12}H_{25}SH$. Xu et al. (2005) reported a three-step strategy for synthesizing uniformly sized thiolated AuNPs that prepares Au colloids in an aqueous phase, transfers the particles into an organic solvent, and refluxes the solution. Ionescu et al. (2017) suggested a novel two-step process that uses a physical vapor deposition technique

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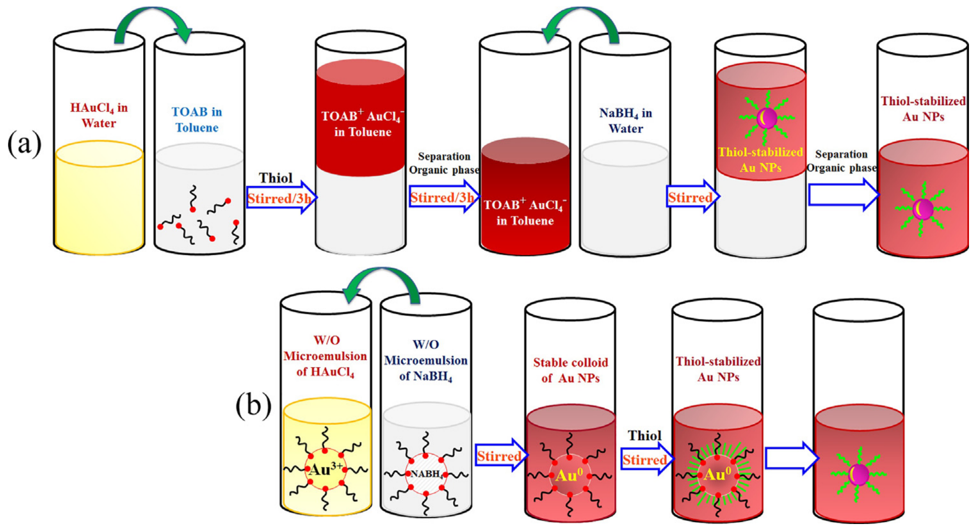

Fig 1. Schematic illustration of thiolated AuNP preparation via (a) the two-phase Brust method, and (b) the microemulsion technique.

to make dispersed, ultra-pure, size-controlled AuNPs, followed by a coating with dodecanethiol.

Based on previous microemulsion procedures for fabrication of special nanoparticles (Salabat, Nabiyouni, & Far, 2011; Salabat & Soleimani, 2014; Soleimani, Salabat, & Tabor, 2014), a new, simple route for synthesis of thiolated AuNPs is presented here. It is compared with the prevalent Brust method.

Microemulsions are isotropic, macroscopically homogeneous, and thermodynamically stable solutions that have three components: a polar phase, a non-polar phase, a surfactant, and, sometimes, a co-surfactant (Eastoe, Hollamby, & Hudson, 2006). The preparation of AuNPs commonly consists of mixing two microemulsions containing a gold ion precursor and a reducing agent, as shown in Fig. 1(b). After mixing the microemulsions, an exchange of reactants between micelles takes place during Brownian collisions with water. There are attractive van der Waals forces and repulsive osmotic and elastic forces between the reverse micelles. The reactant exchange reduces the metal ions by the reducing agent and creates stabilized gold colloids. Here, the biphasic Brust method that uses TOAB for the phase transfer is compared with the microemulsion system, where the TOAB acts as a cationic surfactant to form reverse micelles as soft templates. The usage of TOAB as a surfactant for microemulsions is new. Thiolated AuNPs prepared by these two methods were characterized with UV–vis spectroscopy and transmission electron microscopy (TEM).

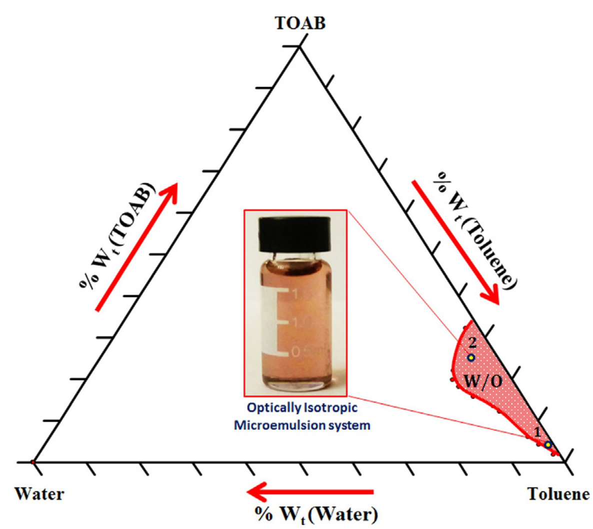

Fig. 2. Partial ternary phase diagram of toluene/TOAB/water at 25 °C.

Experimental section

Materials

Hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4$), as the source of gold nanoparticles, TOAB ($N(C_8H_{17})_4Br$) as a phase transfer agent and also a cationic surfactant in the two-phase and microemulsion methods, respectively, and sodium borohydride ($NaBH_4$) as reducing agent were purchased from Sigma-Aldrich Corp., St. Louis, Mo., U.S.A. Toluene, as an organic and continuous phase, dodecanethiol, as alkane thiol ligand, and ethanol were purchased from Merck (Frankfurt, Germany). All aqueous solutions were prepared with deionized water (0.055 μS/cm) produced with a PKA (Smart two pure) instrument (PKA Company, Sowerby Wood Industrial Estate, Cumbria, UK).

Preparation of thiol-functionalized gold nanoparticles by the two-phase method

Thiolated AuNPs were prepared via the two-phase process as follows (Daniel & Astruc, 2004). In brief, a solution of TOAB in toluene (8 mL, 0.05 M) was mixed with a yellow aqueous solution of $HAuCl_4$ (3 mL, 0.03 M). The two-phase mixture was vigorously stirred for 3 h until all the $AuCl_4^-$ was quantitatively transferred to the organic phase from the aqueous phase by complexation with the cationic part of TOAB. Stirring was continued until the orange-tinted aqueous phase turned colorless, confirming successful transfer of Au^{3+} into the organic layer on top. Dodecanethiol (17 mg) was then added to the organic phase. A freshly prepared aqueous solution of $NaBH_4$ (2.5 mL, 0.4 M) was then slowly added with vigorous stirring. An instant color change occurred in the organic phase from orange to black/brown and, ultimately, to dark purple. After further stirring for 3 h, the organic phase was separated and mixed with ethanol to remove excess thiol. The mixture was cooled for 4 h at −18 °C, and the dark brown precipitate was filtered off and washed with ethanol. The crude product was dissolved in 5 mL of toluene and again precipitated with excess ethanol.

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