Preparation of gold nanoparticles for plasmonic applications

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ARTICLE INFO

ABSTRACT

We present a simple hot injection method for the preparation of colloidal solutions of hydrophobic spherical gold nanoparticles with the diameter around 20 nm and size dispersion below 20%. Various surfactants with different lengths of hydrocarbon chains, such as oleylamine, 1-octadecanethiol, poly (N-vinylpyrrolidone), and $AgNO_3$ in 1,5-pentanediol, were used for sterical stabilization in the colloidal solution. The hydrodynamic nanoparticle size and size dispersion were determined by the dynamic light scattering (DLS) while the small-angle X-ray scattering (SAXS) from the colloidal solution provided information on the size of the metallic nanoparticle core (without surfactant). Plasmon enhanced resonant absorption peaks between 500 nm and 600 nm were detected by the UV–VIS spectrophotometry. The nanoparticle arrays on silicon prepared by solvent evaporation or Langmuir-Schaefer method were inspected by high-resolution scanning electron microscopy and grazing-incidence SAXS (GISAXS). The presence of side maxima in the GISAXS pattern gives evidence of the nanoparticle ordering by self-assembly while very close values of the interparticle distance derived from GISAXS and the nanoparticle size derived from DLS indicate a close-packed order.

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1. Introduction

Nanosized particles of noble metals are a very active field of research because of their potential applications in photovoltaics, spintronics and plasmonics. Plasmonic photovoltaics utilizes plasmonic effects inherent to metallic nanostructures to improve the power conversion efficiency of photovoltaic devices and to decrease their cost. In particular, gold, silver and copper nanoparticles (NPs) strongly absorb light in the visible region as a result of the surface plasmon resonance. The resonance wavelength depends on the nanoparticle size and shape as well as the dielectric constant of the surrounding medium [1–4]. Especially in the colloidal chemistry, gold is known as one of the unique metals to form stable nanoparticles [5]. The preparation of Au NPs generally involves the chemical reduction of gold salts in the aqueous or organic phase or in both of them. However, the high surface energy of Au NPs makes them extremely reactive that results in aggregation unless their surface is protected or passivated. Hence, special precautions have to be taken to avoid their aggregation or precipitation. Typically, Au NPs are prepared by chemical reduction of the corresponding transition metal salts in the presence of a stabilizer bound to their surface that results in high stability, rich linking chemistry and desired charge and solubility properties [6–8]. The size of the nanoparticles prepared by the reduction of the gold salts depends on a number of parameters, such as the type of reducing agent, the type of surfactant, and the molar ratio of

the metal precursor and surfactant [9]. The type of reducing agent determines the rate of the nucleation and nanoparticle growth — slow reduction provides large nanoparticles and vice versa. In addition to the nanoparticle size, the nanoparticle shape plays a crucial role in the optical and electronic properties [10–12].

This paper describes a simple hot injection method for the synthesis of hydrophobic sterically stabilized Au NPs. For the synthesis of nanoparticles, various kinds of stabilizers providing different nanoparticle sizes have been used. This method involves a slow addition of the precursor in the presence of the reducing agent with stabilizer into a hot non-polar solvent. The nanoparticle colloidal solutions were examined by the dynamic light scattering (DLS), UV–VIS spectrophotometry, and small angle X-ray scattering (SAXS) to determine the hydrodynamic diameter, plasmon resonance wavelength, and the metallic core size, respectively. Ordered nanoparticle arrays on silicon substrate were prepared by spontaneous solvent evaporation or modified Langmuir-Schaefer (LS) method was characterized by the scanning electron microscopy (SEM) and grazing incidence small angle X-ray scattering (GISAXS).

2. Experimental part

2.1. Nanoparticle synthesis

As reagents, chloroauric acid ($HAuCl_4.3H_2O$, 52% Au basis), poly (N-vinylpyrrolidone) (PVP mol wt 40,000), 1-octadecanethiol (98%), silver nitrate (99%), 1,5-pentanediol (97%), ethylene glycol (99.8%), toluene for UV spectroscopy (99%) from Sigma Aldrich and ethanol

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for UV spectroscopy (99%) and oleylamine (97%) from Acros Organics were used. Chemical synthesis consisted in chemical reduction of the gold salt in an organic solution in the presence of a stabilizing agent. The chemical reaction was divided in two steps. The gold precursor with a stabilizer was injected into a hot solvent to initiate a temporally separated homogeneous nucleation. In the second step, a controlled growth of the nanoparticles took place. In particular, the mixture of —

A) $HAuCl_4.3H_2O$ (0.05 M) with oleylamine (0.25 M) and toluene (3 ml)
B) $HAuCl_4.3H_2O$ (0.05 M) with PVP (1.7 mM) and toluene (3 ml)
C) $HAuCl_4.3H_2O$ (0.05 M) with 1-octadecanethiol (0.2 mM) and toluene (3 ml)
D) $HAuCl_4.3H_2O$ (0.05 M) with $AgNO_3$ (3 mM) in 1,5-pentanediol (2 ml) and ethylene glycol (3 ml)

was injected very slowly into a flask with a boiling mixture of a small amount of the stabilizer and solvent —

A) oleylamine (0.035 M) and toluene (20 ml) (120 °C)
B) PVP (0.4 mM) and toluene (20 ml) (120 °C)
C) 1-octadecanethiol (0.1 mM) and toluene (20 ml) (120 °C)
D) PVP (0.1 mM) and ethylene glycol (15 ml) (170 °C)

(the corresponding combinations of the reagent and stabilizer/solvent are labelled with the same letter).

The reaction took place in the boiling flask for 120 min at the temperature that depended on the boiling point of the solvent. The mixtures were stirred with a magnetic stirrer. During the refluxing, the color of the reaction mixtures changed — A) from red to purple; B) from brown to purple; C) from red to violet; and D) from brown to orange.

In the next step, the Au NPs were precipitated several times with ethanol, centrifuged to remove the solvent and redispersed in toluene. In Fig. 1, a scheme of the hot injection method to synthesize plasmonic Au NPs is shown.

2.2. Nanoparticle characterization

The size and size distribution of the nanoparticles in the organic solution were measured by the DLS and SAXS techniques. The DLS was measured with a Malvern Zetasizer Nano ZS 90 instrument with a He–Ne laser (633 nm) and 90° collecting optics. The SAXS measurements were performed using a home built apparatus equipped with a microfocus X-ray source with an integrated focusing optics (Incoatec, IμS) working at CuK_α wavelength ($\lambda = 0.154$ nm). The flux of the X-ray photons in vacuum measured with a two-dimensional X-ray detector (Dectris, Pilatus 100 K) was 3.3×10^8 photons/s. The optical properties of the Au NPs colloidal solution were checked by a UV–VIS spectrophotometry (Shimadzu instrument).

Spontaneous evaporation of the solvent and modified horizontal LS method was used to prepare homogeneous nanoparticle ordered
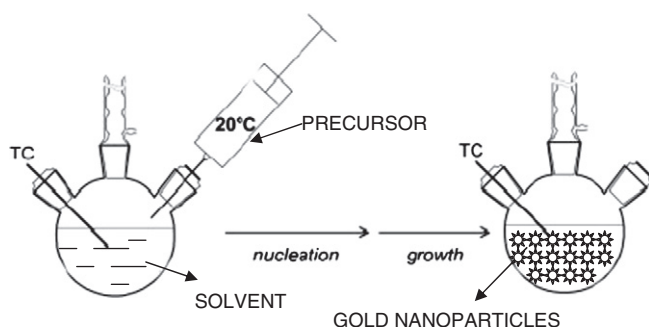
arrays over large area on silicon [13]. In the former method, 5 μl of solution was drop cast onto silicon substrate. In the latter method, Au NPs monolayer was formed on the water surface and transferred onto silicon substrate by a controlled removal of the water subphase at the room temperature. This formation depends on the density of nanoparticles in the solution and volume fraction of the unbound surfactant in the solution. To increase the evaporation rate of the solvent, toluene was substituted by chloroform. In particular, 2 ml of the Au NPs solution (concentration of 20 mg/ml) was dried at room temperature and re-dispersed in chloroform. The nanoparticle solution was applied on the water surface in a computer-controlled Langmuir-Blodgett trough (Nima Technology). On the solvent evaporation, a nanoparticle monolayer was formed at the water/air interface at a surface pressure of 15–20 mN/m depending on the surfactant type. Subsequently, the monolayer was transferred onto a silicon substrate placed horizontally in the trough by a controlled removal of the water subphase.

The nanoparticle morphology and local ordering of the nanoparticle arrays were visualized by SEM (Leo 1550 HR-SEM) while GISAXS measurements provided statistical information on the ordering and regularity of the arrays over large area. The GISAXS measurements were performed at the angle of incidence of 0.3° on the same apparatus as the SAXS ones [14,15].

3. Results and discussion

The DLS technique measures the hydrodynamic nanoparticle diameter, i.e. the diameter of the metallic core and the surfactant, while SAXS measures the metallic core size. The SAXS measurement of Au NPs stabilized with oleylamine (solution A) is shown in Fig. 2. The UV–VIS absorption spectra of the colloidal nanoparticle solutions with different surfactants are shown in Fig. 3, all showing a plasmon resonance peak at around 530 nm (solution A) or 560 nm (solutions B, C, D).

The parameters drawn from the DLS, SAXS and UV–VIS measurements are summarized in Table 1. Different surfactant types result in different hydrodynamic nanoparticle diameters which range from 9 nm (Au NPs stabilized with 1-octadecanethiol, solution C) to 26.8 nm (Au NPs stabilized with PVP, solution B). The Au NPs stabilized with oleylamine (solution A) and PVP (solution B) exhibit the smallest (15%) and largest (20%) size dispersion, respectively. The Au NPs stabilized with 1-octadecanethiol and $AgNO_3$ in 1,5-pentanediol (solutions C, D) have the size dispersion (19%) only slightly smaller than those

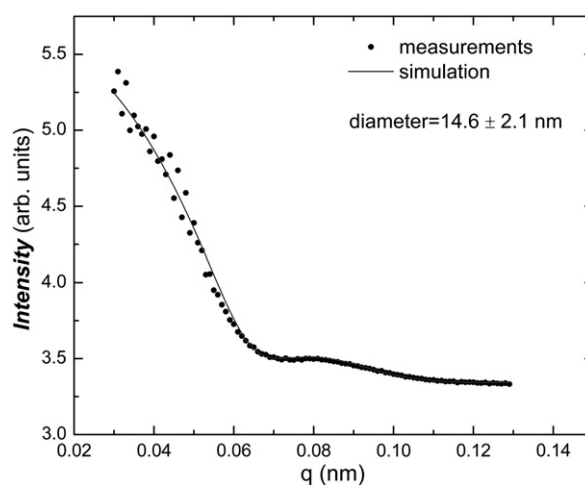**Fig. 1.** Schematic illustration of the hot injection method.

Fig. 2. The radial cut of the SAXS pattern of the solution of Au NPs stabilized with oleylamine. The diameter of the metallic core of the nanoparticles is 14.6 nm; dots — experimental data and line — simulation. The simulation was performed assuming the spherical shape and random distribution of the nanoparticles in the solution.