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Synthesis and physico-chemical characterization of gold nanoparticles softly coated by AOT

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Abstract

Size-controlled gold nanoparticles/surfactant stable systems were prepared by the combined action of the solvated metal atom dispersion (SMAD) technique and confinement in anhydrous sodium bis(2-ethylhexyl)sulfosuccinate (AOT) micellar solution. From liquid samples, by evaporation of the organic solvent, solid gold nanoparticle–surfactant liquid crystals composites were obtained. Sample characterization was performed by X-ray diffraction (SAXS and WAXS), XPS spectroscopy and UV–vis–NIR spectroscopy. All experimental data consistently revealed the coexistence of two gold nanoparticle size populations: bigger nanoparticles (size 20–50 Å) and smaller ones (size of few Å). The two differently-sized gold nanoparticles can be separated by resuspending the gold/surfactant nanocomposite in *n*-heptane. This operation causes the slow selective precipitation of the bigger nanoparticles softly coated by surfactant leaving, in the surnatant, only the smaller Au nanoparticles. The latter were found to be entrapped in the core of AOT reversed micelles and stabilised by the surfactant adsorption on their surface. Such nanoparticles, as shown by SAXS data, slowly rearrange to a narrower size distribution giving a surnatant containing stable and finely size-controlled gold nanoparticles.

Keywords: Gold nanoparticles; SMAD; AOT; Reversed micelles; Liquid crystals

1. Introduction

Gold nanoparticles stabilized by a monolayer of adsorbed anisotropic molecules have attracted much interest due to their potential applications as building blocks of optical and electronic devices and as specialized catalysts [1]. This because the nanoparticle electronic properties can be tuned not only by changing their size but also the nature of the coating agent and the inter-nanoparticle distance [2]. In this way, effective stability against the thermodynamically spontaneous unlimited growth and peculiar physico-chemical properties can be simultaneously conferred to gold nanoparticles. However, when such nanoparticles are exploited as enhanced catalysts, an easy accessibility of their surface to reacting species is needed. This requirement can be fulfilled by choosing easily displaceable coating agents, i.e. loosely adsorbed on the nanoparticle surface. For this purpose, in contrast with many capping agents which are chemically bonded to the gold nanoparticle surface, of particularly interest are surfactants generally physically and reversibly adsorbed. According to these considerations, a lot of bottom up synthetic protocols for gold nanoparticles have been exploited based on the chemical reduction of gold salts and the subsequent entrapment of their nanoparticles in surfactant-based systems [2–4]. However, the major drawback of such strategy is the presence in the final nanomaterial of side-products coming from the chemical reaction which could affect negatively its physico-chemical properties and, in particular, its catalytic activity. The use of physical methods to produce high-purity metal nanoparticles, followed by their entrapment in surfactant solutions could be an effective solution of the aforementioned problem. In this work, we have exploited the solvated metal atom dispersion (SMAD) technique as a method to produce solvated gold atoms followed by their entrapment in solutions of dry sodium bis(2-ethylhexyl)sulfosuccinate (AOT)

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reversed micelles. In such conditions, competition between gold nanoparticle growth within the micellar core and surfactant adsorption on the nanoparticle surface leads to fast and complete inhibition of gold nanoparticle growth.

2. Experimental

2.1. Materials

Acetone (Aldrich, 97.00%) was further purified by distillation. Sodium (bis-2ethylhexyl)sulfosuccinate (AOT, Sigma 99%) was used after storage in a dessiccator at least 1 week. *n*-Heptane (Aldrich 99%, spectrophotometric grade), carbon tetrachloride (Sigma, 99.97%) and gold foil (Aldrich, 99.99%) were used as received. AOT/*n*-heptane solutions at fixed surfactant concentration (0.1 mol kg^{-1}) were used in all experiments.

2.2. Methods

Solvated metal atom dispersions of gold nanoparticles entrapped in dry AOT reversed micelles were obtained by the following procedure. Acetone was introduced in a closed glass reactor under vacuum at low temperature (liquid N_2), in order to cover the internal vessel walls with a thin layer of frozen organic solvent. Then, by Joule effect (6–9 V, 45 A), gold atoms were thermally evaporated inside the reactor from high purity metal foil. In such conditions, atoms and small clusters of gold are trapped within the frozen acetone. Finally, the acetone solution of solvated metal atoms was warmed up to room temperature, concentrated and mixed with dry AOT/*n*-heptane solution (Au/AOT molar ratio = 0.05). The addition of the reversed micellar solution, has been proved usefull for a fast and complete inhibition of gold nanoparticle growth [5]. Solvent evaporation from gold nanoparticles in AOT/*n*-heptane solution was performed using a desiccator connected to a diaphragm vacuum pump (MZ2C, Vacuubrand). The resulting gold nanoparticle/AOT composites were employed for solid state investigations (SAXS, WAXS and XPS), while full redispersion of these nanocomposites was achieved by adding the appropriate amount of pure *n*-heptane to obtain the initial AOT concentration for liquid phase investigations (UV–vis–NIR and SAXS).

UV–vis–NIR spectra were recorded in the wavelength range 400–1200 nm by a Perkin-Elmer (Lambda-900) spectrometer.

The small-angle X-ray scattering (SAXS) patterns have been recorded by a laboratory instrumentation consisting of a Philips PW 1830 X-ray generator providing Cu Kα, Ni filtered ($\lambda = 1.5418$ Å) radiation with a Kratky small-angle camera in the ‘finite slit’ height geometry, equipped with step scanning motor and scintillation counter. Data were analysed by home made programs using the CERN minimization program called MINUITS. X-ray powder diffraction spectra were collected by a Philips diffractometer (PW1050/39 X Change) equipped with a copper anode (Cu Kα 1.5418 Å).

The surface chemical composition of the samples was studied by XPS in an ultrahigh vacuum (UHV) chamber with a base pressure in the range of 10^{-8} Torr during data collection. Photoemission spectra were collected by a VG Microtech ESCA 3000 Multilab spectrometer, equipped with a standard Al Kα excitation source ($h\nu = 1486.6$ eV) and a nine-channeltrons detection system. The hemispherical analyser operated in the CAE mode, at a constant pass energy of 20 eV. The binding energy (BE) scale was calibrated by measuring C 1s peak (BE = 285.1 eV) from the surface contamination. Photoemission data were collected and processed by using the VGX900 software. The peaks were fitted by a nonlinear least square fitting program using a properly weighted sum of Lorentzian and Gaussian component curves, after background subtraction according to Shirley and Sherwood [6,7]. The relative atomic concentrations were calculated by the instrument provided programme, from fitted peak areas using appropriate sensitivity factors. The binding energy values are quoted with a precision of 0.1 eV. The uncertainty on the atomic concentration is of the order of 10%.

3. Results and discussion

3.1. SAXS

The comparison between SAXS spectra of freshly prepared gold/AOT nanocomposites and that of pure AOT is shown in Fig. 1. It is worth remembering that the pure AOT possess a two-dimensional hexagonal structure with long mutually parallel AOT rods [8]. At a first glance, the SAXS pattern of Au/AOT sample shows two structural contributions. The first one, occurring in the $0.06 < q < 0.2$ Å^{-1} range, is absent in pure AOT and indicates the presence of nanoparticles of approximately 20 Å, the second one at $q \approx 0.3$ Å^{-1}, is also observed in pure AOT and is due to the reflection of the (1 0 0) plane of the two-dimensional hexagonal array of

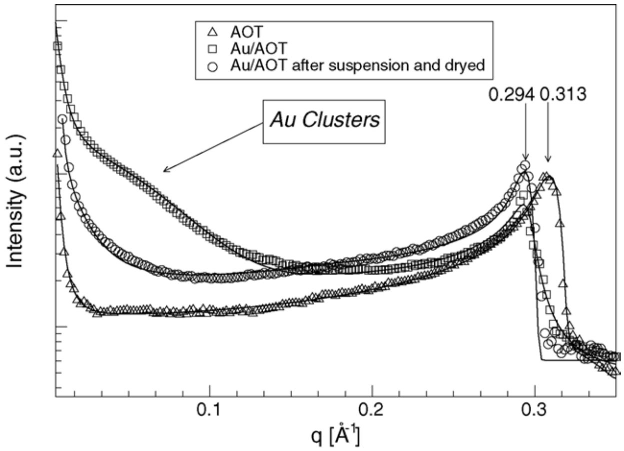

Fig. 1. SAXS spectra of pure AOT, freshly prepared gold/AOT nanocomposites (sample A) before and after resuspension and drying.