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CONTROLLED SYNTHESIS AND OPTICAL PROPERTIES OF Ag NANOPARTICLES

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Abstract

Nanosized hydrophobic, oleylamine stabilized silver (Ag) organosols were obtained in the reaction between the related metal salt and oleylamine in various organic solvents. The obtained hydrophobic colloids are stable and retain same particles morphology even after solvent evaporation and redispersion of the dried deposit in chloroform. The sizes of the Ag nanoparticles can be controlled from 8 to 25 nm by reaction temperatures. The position and shape of the surface plasmon resonance band depends upon the size and shape of Ag nanoparticles as well as dielectric constant of the medium.

Introduction

One of the main challenges in the preparation of nanosized colloids is developing the means of directing the particles into specific physicochemical environments, such as organic nonpolar liquids, specific regions within ordered surfactant phases and monolayer assemblies [1,2]. The understanding of the physicochemical properties of metal organosols is important due to their optical and catalytic behaviour [1,3]. From previously described synthetic methods in the literature, it can be assessed that colloidal stability, particle size, and optical properties strongly depend on the specific method and experimental parameters affecting in the efficiency of reaction (temperature, time, solvents, etc.). We present here a simple method for the preparation of dispersions of Ag nanoparticles in different organic solvents (toluene and dichlorobenzene). Special attention was paid to correlation between particle size and optical properties of Ag nanoparticles.

Experimental

Silver nanoparticles in toluene and dichlorobenzene were obtained using modified metod developed by Hiramatsu et al. [4]. 0.3 mM of Ag nitrate and 2.5 ml of oleylamine were dissolved in 50 ml of toluene, was refluxed for 24 h at 110 °C (or 1,2-dichlorobenzene for 8 h at 180 °C). The product was purified with centrifugation-dispersion process to wash off the remaining residues. The solution was first concentrated in a rotary evaporator and purified by precipitation with methanol. The suspension was centrifuged at 12000 rpm for 10 min. The precipitate was dried with argon flow and resuspended in chloroform to give a brown-yellow dispersion. The UV-Vis absorption spectra of the silver organosols were recorded using a Thermo Evolution 600 spectrophotometer. The transmission electron microscopy (TEM) images were acquired with Philips EM-400 at 100 kV.

Results and Discussion

Attempts had been made to make nearly monodisperse Ag nanoparticles with variable size in the mixture of oleylamine and toluene/dichlorobenzene. The mechanism involves the formation of stable complexes of silver ions with amines and then an electron transfer from amines to the silver complex at relatively high temperature [5]. The reduction process leads to formation of dispersions consisting of Ag nanoparticles, which are stable for weeks, although they show a certain tendency to stick to glass walls. The reaction temperature played a key role in nanoparticle size control. The higher reaction temperature (180 °C) results in a faster Ag^+ reduction and growth process, producing large size nanoparticles. At lower reaction temperature (110 °C), the reduction is slowed down and the nucleation process overruns the growth process, yielding small particles.

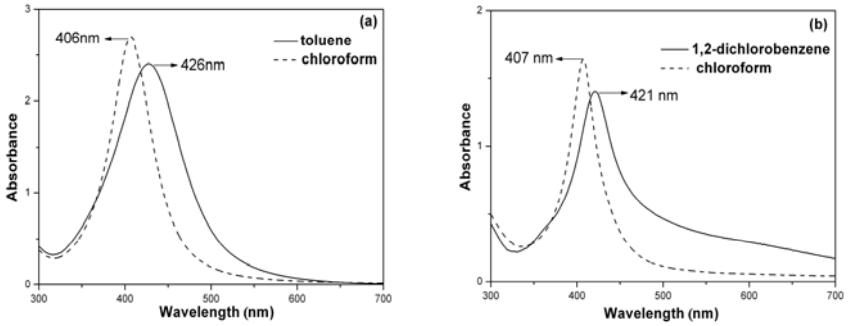

Fig.1 Change in UV-visible spectra of Ag organosols, due to solvent exchange from toluene to chloroform (a), and dichlorobenzene to chloroform (b).

The formation of small particles is kinetically favoured, whereas the formation of large particles is thermodynamically favoured. From a kinetics standpoint, small particles are easier to nucleate but they have a larger surface-area-to-volume ratio and therefore represent a higher energy state compared with larger particles. Hence, small particles are easily formed at lower temperature, but these small particles have a tendency to grow into larger particles to attain a lower energy state when the reaction temperature is higher. The surface modified Ag nanoparticles are characterised by a strong optical surface plasmon resonance band around 400 nm (Fig. 1) [6]. The spectrum of Ag nanoparticles in dichlorobenzene (Fig. 1b) exhibits a considerable tail toward the red, which indicates a size increase of Ag nanoparticles and formations of Ag aggregates. The process of solvent exchange from toluene or dichlorobenzene to chloroform should lead, according to Drude model [3], to a blue shift of the plasmon band, due to the higher refractive index of dichlorobenzene (1.551) and toluene (1.497) with respect to that of chloroform (1.445). Based on TEM measurements (Fig. 2) the diameter of spherical silver nanoparticles was found to be 8.2±3.5 nm when the particles obtained in toluene and 22.1±4.1 nm obtained in dichlorobenzene. The Ag nanoparticles, although closely packed in the case of dichlorobenzene, are well separated due to the presence of the oleylamine layer, adsorbed on the particle surface.

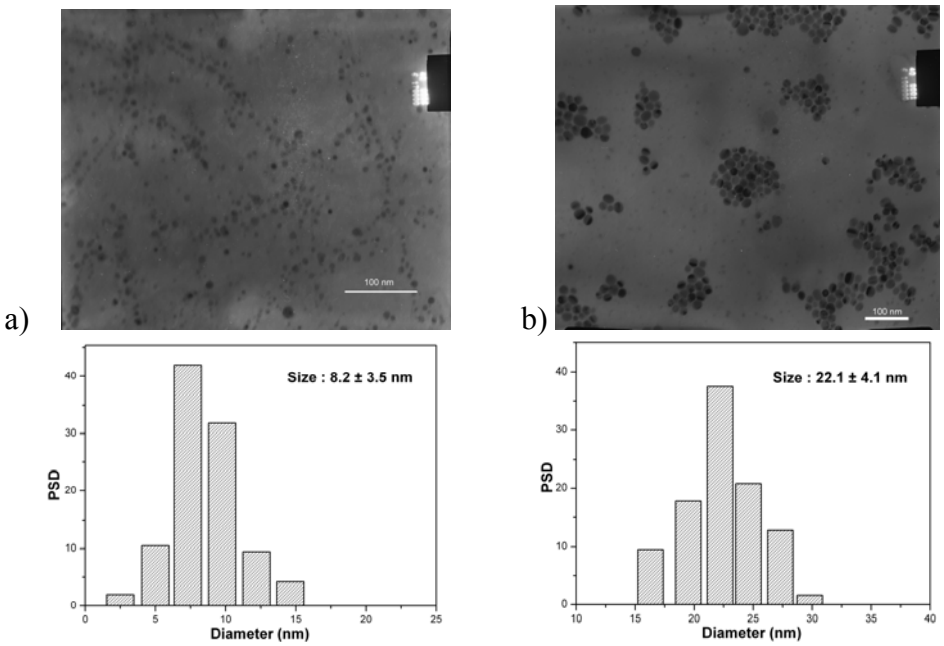

Fig.2 TEM images and the corresponding particle size distributions of the Ag nanoparticles obtained in toluene (a), and dichlorobenzene (b).

Conclusion

From all this work it can be assessed that particle size and its properties depend strongly on the specific method of preparation and the experimental conditions applied. The advantages of such a method can be found in the applications of metal particles as catalysts and has been successfully extended to synthesis of other metallic colloid such as gold and copper.

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