Colloids and Surfaces B: Biointerfaces 90 (2012) 48–52

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Silver nanoparticles to self-assembled films: Green synthesis and characterization

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ARTICLE INFO

Article history:
Received 25 April 2011
Accepted 23 September 2011
Available online 13 October 2011

Keywords:
Silver nanoparticles
Self-assembled
Oxalic acid
Thin film

ABSTRACT

In the present paper silver nanoparticle was synthesized by chemical reduction of silver nitrate by oxalic acid in aqueous solution. The nanoparticle film (self-assembled; mirror like illumination) on the wall of the clean glass surface was also observed after some days. The synthesized silver particles show an intense surface resonance plasmon band in the visible region at 425 nm. Transmission electron microscopy, selected areas electron diffraction, and UV–visible spectroscopy have been employed to characterize Ag-nanoparticles. The nanoparticle films were also observed using conventional visual and scanning electron microscope (spherical particles and size ranging from 23 to 245 nm). The transmission electron micrograph revealed that the average size of silver nanoparticle were ≤10 nm and 21–60 nm, respectively.

1. Introduction

Advanced nanomaterials of noble metals are currently being studied extensively because of several properties that can be used in science and technology. The right preparation is important for the size, shape, and chemical surrounding are the determinants on the catalytic, electronic, magnetic, and optical properties of nanoparticles [1–4]. Numerous effective approaches have been employed to prepare shape- and size-controlled noble metallic nanoparticles over the past few years by a number of research groups [5–8]. Silver nanoparticle preparation is also being experimented upon and studied to find the most cost-efficient and effective way to synthesize them. It has been shown that the size, morphology, stability, and properties (chemical or physical) of these nanoparticles have a strong dependence on the specificity of the preparation method and the experimental conditions [9,10]. At specific wavelengths of light the surface plasmon are driven into resonance and the silver nanoparticles have a distinct color that is a function of their size, shape, and environment. The plasmon resonance of silver nanoparticles is responsible for their yellow color in solution. Any visible change to the color of the nanoparticles in solution typically indicates that the aggregation state of the nanoparticles has changed. Changes in the optical properties are usually due to aggregation, photo-activity, or Ostwald's ripening, which typically manifest in the UV–vis spectrum as reduced peak height and increased peak width [11,12]. Most of the methods reported in literature are extremely expensive and they also involve the use of toxic, hazardous chemicals as the stabilizers which may pose potential environmental and biological risks. Because of the increasing environmental concerns by chemical synthesis routes, an environmentally sustainable synthesis process has led to bio-mimetic approaches, which refers to applying biological principles in material formation [13–15]. The simplest and the most commonly used bulk-solution synthetic method for metal nanoparticles is the chemical reduction of metal salts. Using chemical reduction methods for synthesis of different morphologies nanoparticles can be advantageous over other biosynthetic processes because it involves reduction of an ionic salt in the presence of surfactant using a reducing agent as well as it is cost effective, easily scaled up for large-scale synthesis and further there is no need to use high pressure, energy and temperature [16,17]. Selection of solvent medium, environmentally benign reducing agent and nontoxic substances for the nanoparticle stability are the main steps based on green chemistry perspectives [18]. To the best of our knowledge, there are no reports about the use of oxalic acid–Ag^+ redox reaction in the growth of surfactant-induced anisotropic silver nanoparticles. Incidentally, this study appears to be the first report on the visual observation of self-assembled film of silver nanoparticles.

2. Experimental

2.1. Materials and preparation of silver nanoparticles

Cetyltrimethylammonium bromide, CTAB (Fluka; Germany) was used as a stabilizing agent. Silver nitrate, $AgNO_3$ (Merck; India)

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doi:10.1016/j.colsurfb.2011.09.037

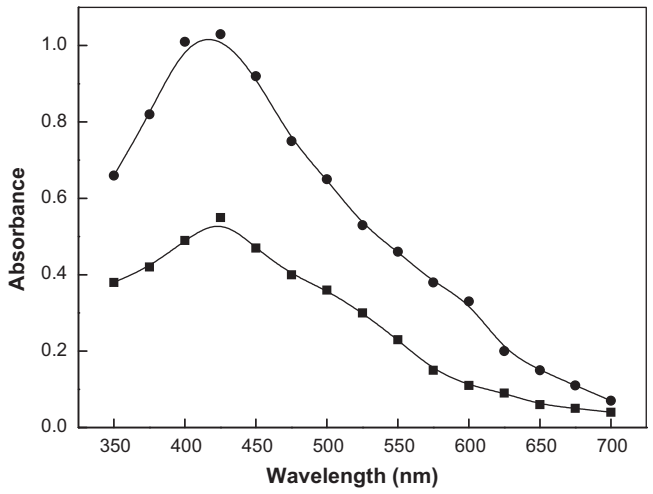

Fig. 1. UV–visible spectra of yellow color silver sol. *Reaction conditions*: $[Ag^+] = 20.0 \times 10^{-4}$ mol dm^{-3}; [oxalic acid] = 4.0×10^{-4} mol dm^{-3}; [CTAB] = 10.0×10^{-4} mol dm^{-3}; temperature = 30 °C.

and oxalic acid, $C_2H_2O_4{\cdot}2H_2O$ (Merck; India) were used as oxidant and reducer, respectively, without any further purification. Doubled distilled (first time from alkaline potassium permanganate), CO_2-free and deionized water was used as solvent to prepare the all working solutions. $AgNO_3$ solutions were stored in a dark glass bottle.

In a typical experiment, an aqueous solution of $AgNO_3$ (2.0 ml, 0.01 mol dm^{-3}) and stabilizer (5.0 ml, 0.01 mol dm^{-3}) was taken in a Erlenmeyer flask, and then 2.0 ml of the oxalic acid (0.01 mol dm^{-3}) and required amount of water were added so that the final concentration of oxidant and reducer in the reaction mixture became 4.0×10^{-4} mol dm^{-3}. The reduction of Ag^+ ions was roughly monitored by visual inspection of the solution. The conversion of the colorless reaction mixture to a dark yellow color clearly indicates the formation of silver nanoparticles [11]. The appearance of color was monitored by measuring the absorbance of the solution at different time intervals on Bausch & Lomb Spectronic 20-D spectrophotometer. The silver nanoparticles were measured in a wavelength ranging from 300 to 800 nm. The appearance of mirror like illumination on the walls of the Erlenmeyer flask after some time also clearly indicated the formation of self-assembled film of silver nanoparticles.

2.2. Determination of morphology of nanoparticles

Morphology, size and the electron diffraction patterns of the silver nanoparticle were investigated with the transmission electron microscopy (TEM) on a Transmission electron microscope (JEOL, JEM-1011; Japan). Samples were prepared by placing a drop of working solution on a carbon-coated standard copper grid (300 mesh) operating at 80 kV. Randomly selected area electron diffraction (SADE) images of the samples were recorded to see the ring patterns of silver nanocrystals. Scanning electron microscope (JSM 35 CF JEOL) was also used for the analysis of self-assembled thin film (mirror-like illumination). The size of the particle can be calculated by using the scale provided in the micrograph.

3. Results and discussion

3.1. UV–visible spectra, TEM and SEM images of nanoparticles

When an aqueous solution of oxalic acid was mixed with the aqueous silver nitrate solution in presence of CTAB, the color changed from light yellow to a yellowish-brown (prefect transparent) as the reaction proceeds. In absence of any surfactant, silver nanoparticles precipitated within 10 min due to unlimited growth of crystals. The UV–vis spectra of the yellowish-color showed a well defined surface plasmon band centered at around 425 nm (Fig. 1), which is the characteristic extinction coefficient of small monodispersed spherical silver particles and clearly indicated the formation of nanoparticles in solution [11,19,20]. There is no significant difference on the surface plasmon absorption peak positions at different times of reaction. It has been established that the exact position of absorbance depends on a number of factors such as the dielectric constant of the medium, size of the particle [2,21]. Fig. 1 exhibits spectral features similar to those reported for silver nanoparticles prepared by chemical reduction method using CTAB as stabilizer [8,22]. The plasmon bands are broad with an absorption tail in the longer wavelengths, which could be in practice due to the size distribution of the particle. Fig. 1 also shows that as reaction proceeds the absorbance tail (at high wavelengths) raises from zero, indicating the transition from separated nanoparticles to bulk silver metal [23].

The sizes and morphology of synthesized silver nanoparticles have been imaged using TEM (Fig. 2). All the nanoparticles appear to be almost spherical. It shows that the particles with an average diameter 19 nm are arranged in good order, but their shapes are irregular. It can be seen from Fig. 2a that, although the size of the nanoparticles are not uniform, they are basically quantum dots or tinier particles; size less than 6 nm and some dispersed spherical nanoparticles (average size is ca. 19 nm). There are two main ranges of particle size; one is approximately $\leq$7 nm, the other $\geq$19 nm measured from photographs of the TEM images. The big nanoparticles are probably assembled from the little one; quantum dots [22]. Interestingly, different kinds of silver nanoparticles morphologies arranged in a clear star-like model are observed in the same sample as shown in Fig. 2b. Morphology of metal nanoparticles strongly depends on the reducing power of the reducing agents as well as presence of stabilizers. Bakshi and his coworkers suggested that a slow reduction by a weak reducing agent like ascorbic acid provides enough time for lipid molecules to adsorb at a freshly synthesized nanometallic surface [24]. Thus, we may safely conclude that, oxalic acid–Ag^+ redox reaction is the most ideal situation to prepare silver nanoparticles, which takes nearly 3 h to complete the reaction. This provides enough time for surfactant molecules (monomers, dimmers and/or micelles) to cap the nanometallic surface and reduce the maximum chances of secondary nucleation. As a result, quantum dots of silver nanoparticles are aggregated in beautiful star-like manor silver under slow growth conditions. Fig. 1 also presents the UV–vis spectrum of the quantum dots silver colloid. The characteristic adsorption peak is at 425 nm quite near the characteristic extinction coefficient of small monodispersed silver particles [25]. The crystalline nature of the resulting silver nanoparticles was revealed by the electron diffraction patterns. Fig. 3 gives an electron micro-diffraction ring pattern of the single crystalline silver nanoparticle with inter-planar spacing. According to their TEM images, the nanoparticles were formed first in the solution and subsequently aggregated into large particles due to the adsorption of Ag^+ onto the surface of metallic Ag^0 through van der Walles forces.

Visual observation shows that, as the reaction proceeds, the color shifts from light yellow to dark brown, and the solvent allow evaporating in open air. After standing for some days, a mirror-like self-assembled film found on the inner glass surfaces of the beaker. Scanning electron microscope (SEM) was used to inspect the self-assembled nanoparticle films forming on the glass. Fig. 4 is the SEM image of the self-assembled film. It can be seen from Fig. 4A that the film is a compact two-dimensional film but not a systematic arrangement of the resulting silver nanoparticles (array