Fluorescent silver nanoparticles via exploding wire technique

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Abstract. Aqueous solution containing spherical silver nanoparticles of 20–80 nm size have been generated using a newly developed novel electro-exploding wire (EEW) technique where thin silver wires have been exploded in double distilled water. Structural properties of the resulted nanoparticles have been studied by means of X-ray diffractometer (XRD) and transmission electron microscopy (TEM). The absorption spectrum of the aqueous solution of silver nanoparticles showed the appearance of a broad surface plasmon resonance (SPR) peak centered at a wavelength of 390 nm. The theoretically generated SPR peak seems to be in good agreement with the experimental one. Strong green fluorescence emission was observed from the water-suspended silver nanoparticles excited with light of wavelengths 340, 360 and 390 nm. The fluorescence of silver nanoparticles could be due to the excitation of the surface plasmon coherent electronic motion with the small size effect and the surface effect considerations.

Keywords. Fluorescence; silver nanoparticles; exploding wire.

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1. Introduction

The control of the optical properties of nanoscale silver particles has led to nanophotonic devices such as nanosensors and wave guides as well as in a wide variety of applications in biotechnology and optical storage. Thus, generation of stable, water-soluble silver nanoclusters will greatly facilitate their use as the elements of the above-mentioned applications. The well-known surface plasmon resonance (SPR) of silver nanoparticles has been studied extensively [1] concluding particle size, shape and surrounding environment dependence. However, only a few researchers were able to observe the fluorescence behavior of silver nanoparticles and hence research is going on in order to understand the physics behind the fluorescence behavior and to model the surface electronic structures of these. In fact, the first observation of optically excited radiative recombination of electrons and holes in metal was reported in 1968 by Mooradian [2] assuming direct interband transitions between the upper d-bands to levels at and above the Fermi level. Recently [3,4], the fluorescence from silver nanodots (Ag_2–Ag_8) was well-established

in silver nanostructures generated photochemically. On the other hand, it is widely accepted that the efficiency of light absorption and emission can be improved by enhancing the local optical fields via localized plasmon resonances [5].

The method, by which nanostructured materials are generated, is considered to play an important role in the tuning of the optical response of these materials. Hence various methods were developed to control the particle size and size distribution. Here the newly developed [6] electro-exploding wire technique is used to generate silver nanoparticle clusters in pure water. These nanoparticles have been examined using X-ray diffractometer and transmission electron microscopy (TEM). The absorption, excitation and emission spectra were recorded and discussed.

2. Experimental details

Pure silver nanoparticles in double distilled water were generated via simple physical method using pure (99.9%) silver wires with 0.2 mm diameter. These wires have been exploded in water by bringing them into sudden contact with pure (99.9%) silver plate when subjected to a potential difference of 36 V DC. High current density was allowed to pass through these thin wires where tensile fracture forces, which are proportional to the square of the current, cause the wires to rupture before becoming unduly softened by the ohmic heating. The clusters of silver particles thus obtained in double distilled water were characterized for their structural and optical properties. The total mass being exploded in water is about 2.0 g/l.

The settled silver nanostructures were allowed to dry on glass substrate for the X-ray diffraction studies that were performed using Cu Kα Rigaku rotaflex diffractometer. Small single drop from the decanted solution was also allowed to dry on carbon-coated grid for the electron microscopy imaging using JEOL JEM 2000EX transmission electron microscopy (TEM). The absorption and the excitation/emission spectra for the decanted solution containing colloidal silver nanoparticles have been recorded using UV-2510PC spectrophotometer and Edinburgh analytical time resolved fluorimeter respectively.

3. Results and discussion

Figure 1 shows the XRD pattern for the silver nanoparticles. The peaks were assigned to the diffractions from the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of FCC silver respectively. The lattice constant calculated from this pattern is in agreement with the literature reports while particle size estimated using Scherrer's formula was 63 nm. TEM images of the silver nanoparticles and their size histogram are shown in figure 2 where well-separated spherical shape particles with sizes ranging from 20 to 80 nm are seen. Figures 2a and 2b show typical TEM images of particles obtained from different portions of the sample. The size histogram in figure 2c was generated from several TEM images. It is seen that most of the particles have mean size of 60 nm. This mean particle size is in good agreement with the size calculated from the XRD patterns above. UV–visible spectrum recorded in the absorbance mode in the range 300–700 nm is shown in figure 3a. The surface
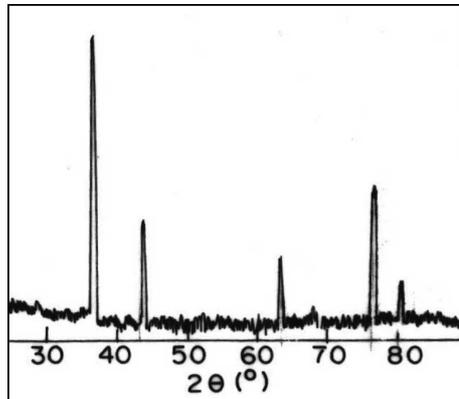
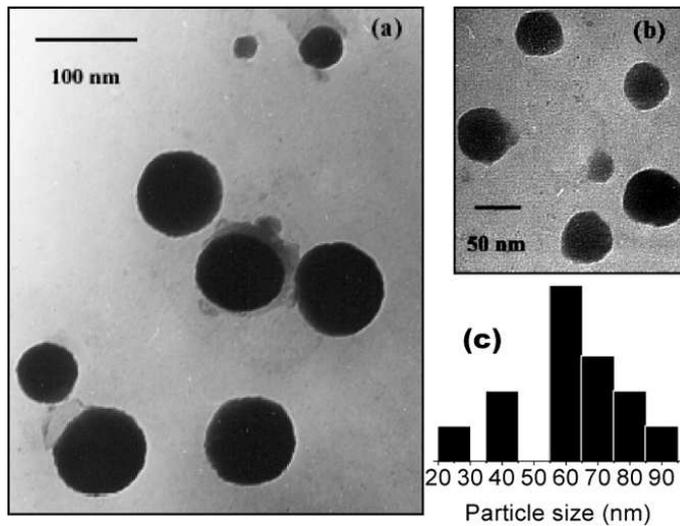**Figure 1.** X-ray diffraction pattern of the silver nanoparticles.

Figure 2. Transmission electron microscopy images of silver nanoparticles taken at magnifications of (**a**) 80 K, (**b**) 120 K and the size histogram (**c**).

plasmon resonance peak appearing at 390 nm shows a broad feature due to the size distribution. This value is in good agreement with the literature reported for spherical silver nanoparticles suspended in water. The theoretical curve shown in figure 3b was generated according to Mie's theory taking into account the size effect damping term in the calculations of the dielectric function of silver nanoparticle [7] as

$$\varepsilon(\omega, R) = \varepsilon_{\text{bulk}}(\omega) + \frac{\omega_{\text{p}}^2}{\omega^2 + i\omega\gamma_0} + \frac{\omega_{\text{p}}^2}{\omega^2 + i\omega(\gamma_0 + A\nu_{\text{F}}/R)},$$

where $\varepsilon_{\text{bulk}}(\omega)$ is the dielectric function of bulk silver as reported by Johnson and Christy [8], ω_{p} is the bulk plasmon frequency of silver, $\gamma_0 = \nu_{\text{F}}/L$ is the bulk
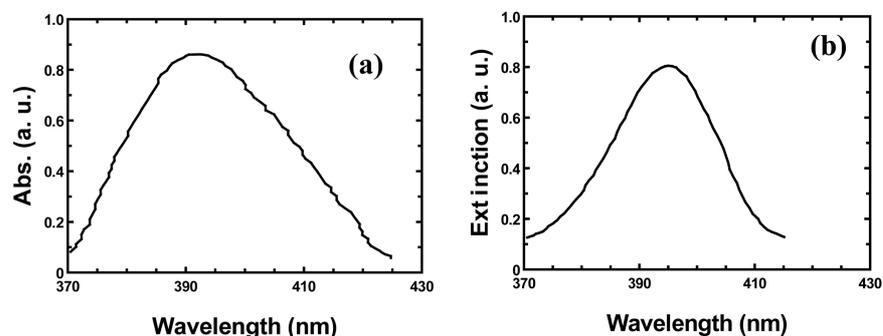
Figure 3. Surface plasmon resonance of silver nanoparticles. (**a**) Experimental UV–visible spectrum and (**b**) Mie's theory for particles with 30 nm radius in water medium.

damping frequency with Fermi velocity (ν_F) and electron mean free path (L). The correction made by inserting a constant A includes the details of the scattering processes, and the particle size R in the expression above gives the size dependence. Particle with 60 nm diameter ($R = 30$ nm) was used throughout the calculations, which is the most probable size as estimated from the XRD and TEM analysis.

The broadening in the peak obtained experimentally is due to the wide size distribution in the solution. The silver nanoparticles suspended in water was then excited at the plasmon peak with light of 390 nm wavelength and the emission spectrum was recorded in the visible range. The fluorescence spectrum is shown in figure 4b where emission peak appears at 508 nm, the emission peak then was fixed at 508 nm for recording the excitation spectrum (figure 4a). Again the solution was excited with 340 nm and 360 nm where identical emissions were observed.

We strongly believe that the nanoparticles coalesce to form very small clusters from the explosions. When the filling factor is high, the clusters tend to coalesce with some interaction with the water molecules forming very thin oxide layer, which prevents the particles from further agglomeration. These processes will result in very small particles as well as agglomerated particles. The size can be controlled by adding some organic materials into water to avoid agglomeration. The fluorescence of the silver nanoparticles covering the region between 500 and 600 nm may be related to emissions from various small-sized clusters via direct radiative recombination of electrons with holes in the d bands around certain symmetry points being enhanced by the excitation of the SPR of these small clusters.

4. Conclusion

Fluorescent colloidal silver nanoparticles have been successfully generated via newly developed electro-exploding wire technique. The fluorescence is believed to be due to surface and volume enhancement of localized transitions around some symmetry points. The absorption was supported by the simulation and the excitation spectrum.
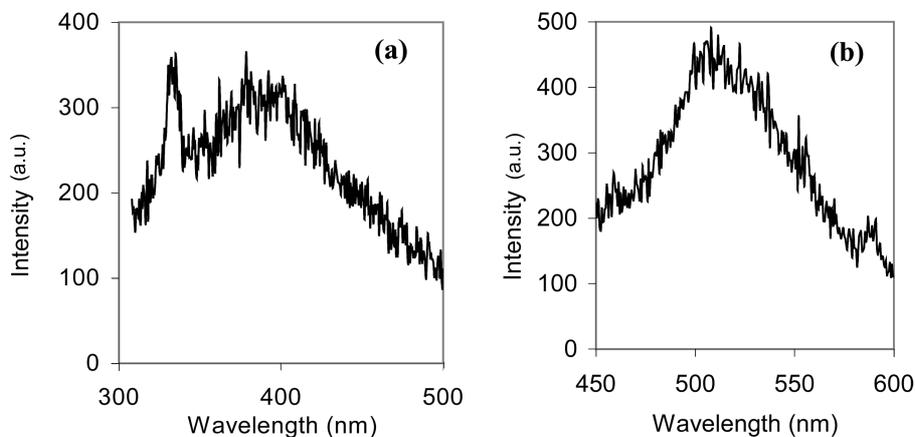
Figure 4. The fluorescence of silver nanoparticles. **(a)** Excitation and **(b)** emission (at 390 nm excitation) spectra.

Acknowledgement

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