



# Synthesis and fluorescence properties of Ag nanoparticles

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## ABSTRACT

Ag nanoparticles synthesized by employing an electro-exploding wire technique exist in face-centered cubic phase with average size  $\sim 10$  nm. A surface plasmon peak is observed at  $\sim 400$  nm. Study of fluorescence properties of Ag nanoparticles shows fluorescence peaks at  $\sim 300$  nm for excitation wavelength in the range 220–270 nm. In concomitant with these, resonant absorptions are observed at  $\sim 215$  nm and  $\sim 270$  nm, which allow us to establish the electronic levels operating in the Ag nanoparticles system. Also, intensity of fluorescence emission increases with increase in concentration of Ag nanoparticles till a critical concentration. For the first time, we report temperature dependence of fluorescence of the Ag nanoparticles in the temperature range 20–90 °C. Where, the intensity of the fluorescence peak at  $\sim 300$  nm decreases with increase in temperature. Also, in conformity with these, probability of resonant absorption decreases with increase of temperature and with change in position of emission wavelength from maximum intensity.

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## 1. Introduction

Metal nanoparticles [1–3] have been a source of immense interest because of their novel properties which arise due to their high surface area to volume ratio and the quantum size effect [4]. Noble metal nanoparticles dispersed in water phase have long fascinated scientists due to different bright colors displayed by them. Also, metal nanoparticles are useful in various fields besides their ability to promote surface enhanced optical phenomenon [5, 6]. Study of their fluorescence properties yields new insight into the energy band structure of the nanoparticles, prerequisite for their possible practical applications in integrated optical devices, in bio-labeling and as a sensor [1,7–9]. Hence, it is very important to synthesize pure metal nanoparticles and study their fluorescence properties. Fluorescence spectroscopy has proved as a very sensitive technique to study the fluorescence properties of nanoparticles. Various techniques have been employed for synthesis of noble metal nanoparticles [10–15]. We synthesize Ag nanoparticles by an electro-exploding wire (EEW) technique [16–19], a process in which high current density is passed through a metal in a wire-plate geometry.

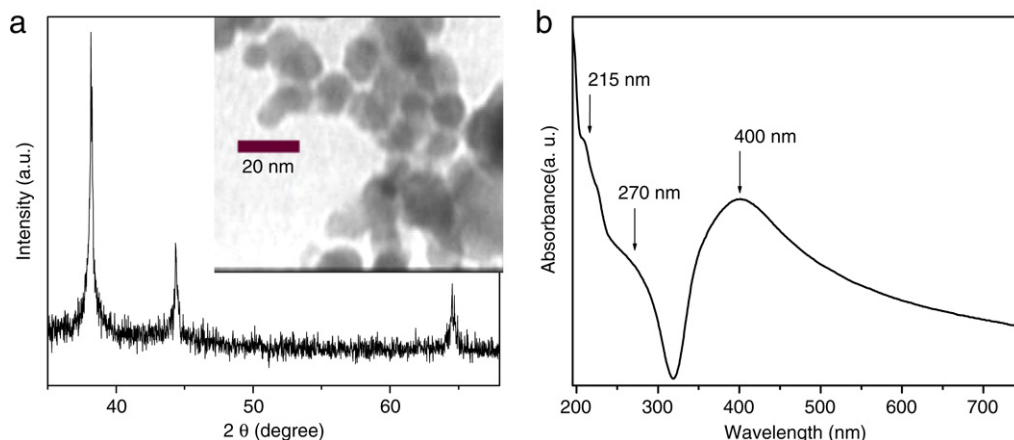
Fluorescence is defined as the light emission by a substance, after it has absorbed light. Also, it is well known that the process of fluorescence emission consists of photon absorption by an electron to go to an excited state, relaxation of the excited electron from higher vibrational levels of that state to the lowest

vibrational level, followed by fluorescence emission [20]. Recently, there are reports of fluorescence from Ag nanoparticles [3,14, 21]. Simple picture of photon absorption by Ag nanoparticles and subsequent re-emission of photons to give fluorescence seems to be quite straightforward. There are nonradiative processes, preceding/competing with photon emission, in fluorescence. The factors affecting the rate of radiationless deactivation of an excited state, when a fluorophore is dispersed in a solvent, are not well understood. Important factors in this regard are temperature, concentration of fluorophore and surrounding medium. To the best of our knowledge, publications related to fluorescence intensity dependence above room temperature is scant for any fluorophore. A few publications exist which correlate observed intensity variations with conformational changes, in systems studied above room temperature [22,23]. However, no publications exist where intensity changes are reported from pure radiationless transitions.

In this paper, we report a detailed study of fluorescence properties of the Ag nanoparticles dispersed in de-ionized water (henceforth referred as water). Pure Ag nanoparticles, used in this study, have been synthesized by employing a novel, physical, top-down technique of EEW, using only pure Ag metal. A surface plasmon peak at 400 nm has been observed in the UV–visible absorption spectrum. Fluorescence peaks have been observed at  $\sim 300$  nm at excitation wavelength ( $\lambda_{ex}$ ) in the range 220–270 nm. Further, resonant absorptions have been observed at  $\sim 215$  nm and  $\sim 270$  nm, evident from the excitation spectrum. The effect of concentration of the Ag nanoparticles and temperature on the fluorescence of Ag nanoparticles has been studied. Employing pure nanoparticles, it has been possible to demonstrate for the first time fluorescence intensity variation above room temperature

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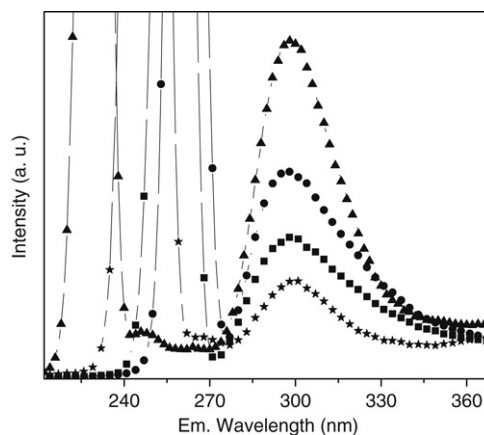
**Fig. 1.** (a) X-ray diffraction patterns of the Ag nanoparticles employed in this study; the inset shows the TEM image of a large collection of the Ag nanoparticles, (b) UV-visible absorption spectrum of the Ag nanoparticles dispersed in water.

where conformational changes are not active (same fluorescence emission position). Also, related to this, intensity of the excitation peaks at  $\sim 215$  and  $\sim 270$  nm decreases with increase of temperature and with change in emission wavelength ( $\lambda_{em}$ ) from the maximum intensity position.

## 2. Experimental details

Ag nanoparticles, reported here, have been synthesized by employing a novel, physical, top-down approach of EEW. In the EEW technique, a thin Ag wire is exploded on a thin Ag plate by passing a current density  $\sim 10^{10}$  A/m<sup>2</sup>; in a time  $\sim 10^{-6}$  s. In the EEW process, flow of current through the Ag wire–plate leads to heating at the point of contact, followed by melting. The melted Ag metal at the point of contact is further heated by the ever increasing current density due to increase in resistance, which leads to evaporation of the Ag metal and subsequent plasma formation. This plasma is contained by the self induced magnetic field. When the vapour pressure of the plasma overwhelms the self induced magnetic field, explosion occurs and plasma products are dispersed in the medium, which leads to Ag nanoparticles formation. Ag nanoparticles are thus synthesized by fragmentation of the parent Ag metal, in water medium, which simultaneously caps and collects the particles. Synthesized Ag nanoparticles are free from extraneous impurities, as no chemicals have been used in the nanoparticle synthesis. A schematic diagram and detail mechanism of the EEW process has already been published by us [16–19].

For preparing X-ray diffraction (XRD) samples, the powder is extracted by centrifugation of the Ag nanoparticles dispersed in water. XRD-patterns of the Ag nanopowder are recorded on a Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). For TEM investigations, a small drop of the Ag nanoparticles dispersed in water is put on a carbon coated copper grid. After drying the grid, TEM characterization is carried out employing a JEOL-2010F, UHR electron microscope operating at 200 kV. After ultrasonication (Ultrasonicator power = 35 W) for 10 min, UV-visible absorption spectrum of the Ag nanoparticles dispersed in water is recorded by employing a Hitachi 3300 UV-visible double beam spectrophotometer, after correcting the base line. With similar samples of the Ag nanoparticles dispersed in water, fluorescence measurements are done by using a Carey Eclipse fluorescence spectrophotometer from Varian, equipped with a Xenon light source, two Czerny–Turner monochromators for excitation and emission, and accessories to monitor and control sample temperature.



**Fig. 2.** Fluorescence emission spectrum of Ag nanoparticles dispersed in water at  $\lambda_{ex} = 225$  nm (triangles), 235 nm (stars), 255 nm (squares) and 260 nm (spheres), respectively.

## 3. Results and discussion

In Fig. 1(a), we show XRD patterns of the Ag nanoparticles. There are peaks at  $2\theta = 38.14^\circ$ ,  $44.34^\circ$  and  $64.54^\circ$  in the XRD data. The position of the XRD peaks of the Ag nanoparticles matches with those from metallic Ag in the face-centered cubic phase. Also, in the inset to Fig. 1(a), we show TEM image of a group of Ag nanoparticles. Average size of the particles is  $\sim 10$  nm and nanoparticles are spherical in shape. Fig. 1(b) shows the UV-visible absorption spectrum of these nanoparticles dispersed in water (concentration of the Ag nanoparticles is  $\sim 10^{18}$  atoms/cc). A peak at  $\sim 400$  nm, observed in the absorption spectrum, is assigned to surface plasmons, which arise due to collective oscillations of the valence electrons in the electromagnetic field of the incident light. A surface plasmon peak at  $\sim 400$  nm is characteristic of the Ag nanoparticles [24].

For metal nanoparticles, it is well known that the energy bands split into a series of energy levels as a result of the quantum size effect. Further, the splitting of energy levels will be more distinct as the size of the nanoparticles becomes smaller [4,25]. Hence, the energy level splitting makes electronic transitions abundant. With increasing excitation energy electrons will be excited into higher energy levels, which are discrete too. To substantiate this, we have studied in detail the fluorescence properties of the Ag nanoparticles dispersed in water. In Fig. 2, we show the fluorescence emission spectrum of the Ag nanoparticles dispersed in water (concentration of the Ag nanoparticles is  $\sim 10^{18}$  atoms/cc)

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