Journal of Luminescence 134 (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

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

Synthesis of silver hollow nanoparticles and observation of photoluminescence emission properties

H.S. Desarkar, P. Kumbhakar*, A.K. Mitra [1]

Nanoscience Laboratory, Department of Physics, National Institute of Technology Durgapur, Mahatma Gandhi Avenue, West Bengal 713209, India

ARTICLE INFO

Article history:
Received 21 April 2012
Received in revised form
22 September 2012
Accepted 5 October 2012
Available online 16 October 2012

Keywords:
Hollow nanoparticles
Laser ablation in liquid
Silver nanoparticles
Surface plasma resonance
Interband transition
Photoluminescence

ABSTRACT

Preparation of hollow silver nanoparticles (HSNs) along-with solid silver nanoparticles are reported by Nd:YAG laser ablation of solid silver target immersed in water medium with a laser ablation time (LAT) duration of 50 min and with the incident laser fluence of 151 J/cm^2. It is found that only solid silver nanoparticles are produced when the experiment is carried out with smaller values of LAT duration. The synthesized samples are characterized by using transmission electron microscopy and UV–Visible absorption spectroscopy. The UV–Visible absorption spectra of the samples show sharp absorptions in the ultraviolet and in visible regions due to interband transition and surface plasmon resonance oscillations in Ag nanoparticles, respectively. It is found that all samples exhibit photoluminescence (PL) emission, at room temperature, in the UV–Visible region peaked at ~346 nm, due to the recombination of electrons with holes from sp conduction band to d band of Ag. The sample containing HSNs exhibits strong PL emission and the value of peak PL emission intensity is enhanced by the factor of 2.4 in comparison to that obtained from the sample synthesized with LAT duration of 20 min. The synthesized HSNs may find applications in catalysis and in chemical sensing.

1. Introduction

In the last two decades, noble metal nanoparticles have attracted attention of the researchers because of their size dependent electronic, catalytic, magnetic and optical properties [1–3]. And recently, a lot of focuses on research activities on Ag nanoparticles have been given as its bulk counterpart has the highest electrical and thermal conductivities in comparison to those of all other noble metals [4]. The properties of nanoparticles are strongly dependent on its size and shape. Hence, by precise control of the size and shape it is possible to tune the chemical and physical properties of materials and some unique properties of nanomaterials can be explored. Shape-controlled synthesis of different nanostructures of Ag, such as cubes [5], rice [6] and wire [7], have been reported earlier by using various synthesis techniques.

Recently, hollow nanoparticles have attracted tremendous attention of the researchers because of their specific structures and properties. Due to their high surface to volume ratio and low density they are widely desirable in drug delivery system [8], biotechnology [9] and as photo catalyst [10]. Hollow nanoparticles offer some advantages over their solid counterparts in terms of their light weight and reduced cost, as fewer amounts of materials are required [11]. The fabrication of hollow Ag spheres at room temperature has been reported by Chen et al. by using the convenient and versatile wet chemical method [4]. Another most popular method of synthesizing hollow nanoparticle is template mediated approach. In the template mediated approach, the surface of the template is coated with the desired material and then the template is removed by a post treatment to produce hollow nanoparticles [12].

Laser ablation in liquid (LAL) is a highly promising and recent technique for preparing solid nanoparticles from solid targets [13–15]. Also by using LAL technique, the shape and size of the nanoparticles can be modified by varying the incident laser wavelength, fluence, ablation time as well as the liquid environment. During laser ablation experiment, ejection of particles from the target is occurred followed by the formation of the bubbles. As the laser radiations are incident on the metal target, the surface temperature of the target may increase even above the boiling temperature of the liquid. Thus the formation of bubbles takes place at the solid–liquid interface. The laser induced bubbles trap the produced nanoparticles, which results in the formation of hollow nanoparticles. Yan et al. has reported the preparation of platinum [16], Al_2O_3 [17] and Zn [18] hollow nanoparticles by utilizing such mechanism. But in most of the earlier reports the size of the prepared hollow nanoparticles are larger than 100 nm

* Corresponding author. Tel.: +91 343 2546808; fax: +91 343 2547375.
E-mail addresses: nitdgpkumbhakar@yahoo.com, pathik.kumbhakar@phy.nitdgp.ac.in (P. Kumbhakar).
[1] Presently retired.

0022-2313/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2012.10.007

and preparation of hollow nanoparticles with size smaller than 100 nm are rarely reported [16,17].

However, here we have reported the preparation of hollow silver nanoparticles (HSNs) having sizes (diameters) lying in 15–60 nm range along-with solid silver nanoparticles having average size (diameter) of ~11 nm by laser ablation of Ag target kept in water medium. The wavelength of the used laser radiation is 1064 nm, emitted from a Q-switched Nd:YAG laser source, having pulsed duration of 10 ns. The used value of the laser ablation time (LAT) and the laser fluence are 50 min and 151 J/cm^2, respectively. We have performed the experiment also with the LAT durations of 20 and 40 min with the same laser fluence of 151 J/cm^2 and in these cases the formations of HSNs are not observed, but solid nanoparticles with broader size distributions are found. The reason for not creation of HSNs at lower values of LAT durations has been explained later. The UV–Visible spectra of all the samples show the appearances of strong and sharp interband absorption in the ultraviolet region at ~260 nm (~4.77 eV) as well as SPR absorptions in the visible region (391–400 nm). Photoluminescence (PL) emissions from noble metal nanoparticles have received less attention because most of the emission processes have low efficiency [19]. Visible PL from gold and copper nanoparticles are first observed by Mooradian [19]. Boyd et al. have reported single and multiphoton PL spectra from clean samples of gold, silver and copper with both smoothed and rough surface [20]. However, here we have reported PL emissions characteristics of all samples and it is found that all samples exhibit PL emissions covering the whole visible region peaked at an UV wavelength of ~346 nm which is attributed to recombination of electrons from sp conduction band to d band of Ag. The PL peak emission intensity at ~346 nm is enhanced by the factor of ~2.4 in the sample prepared with 50 min of LAT in comparison to that obtained in the sample prepared with 20 min of LAT. Despite the complex mechanism of laser-matter interaction, laser ablation in liquid technique provides a simple, flexible and less expensive way for formation of HSNs.

2. Experimental details

A solid Ag target of ~10 mm thick and of purity of 99.99% is kept in a Petri dish containing 10 ml of water. The laser radiation at 1064 nm wavelength coming from a Q-switched Nd:YAG laser is focused using a lens of 30 cm focal length. The laser source is operated at a repetition rate of 10 Hz and having pulse duration of 10 ns. In order to avoid formation of craters [21] we have translated the Petri dish containing the Ag target during the laser ablation experiment. The morphology and structure of the synthesized samples are characterized with a transmission electron microscope (TEM, FIB-20), selected area electron diffraction (SAED) and energy-dispersive X-ray analysis (EDXA). UV–Visible absorption characteristics have been recorded in the range of 200–800 nm with the help of UV–Visible spectrophotometer (Hitachi, U 3010) and for these measurements nanocolloids are kept in a quartz cuvette of path length of 10 mm. Photoluminescence (PL) emission spectra from all samples are collected at room temperature by using a luminescence spectrometer (Perkin Elmer LS55) and by keeping the nanocolloids in a four side polished PL cuvette of path length of 10 mm.

3. Results and discussions

Fig. 1(a) and (b) shows the TEM images taken at two different regions of the same sample S1. The sample S1 has been prepared with 50 min of LAT with the laser fluence of 151 J/cm^2. For obtaining TEM image, the sample is dried on a TEM grid consisting of copper meshes with a heavy layer of carbon film. It is found from Fig. 1(a) that the majority of the particles are solid nanospheres and a small proportion of the particles are HSNs as indicated by arrows. From Fig. 1(b) it is found that some bigger size HSNs are also present in the sample S1. The contrast variations in the center of particles indicate the presence of hollow particles. Beside spherical shape, oval shaped and irregular shaped HSNs are also observed in the synthesized product, indicated by arrows in Fig. 1(b). Fig. 1(c) shows the size distributions of all particles (solid and hollow ones) as obtained by analyzing TEM images as shown in Fig. 1(a) and (b). It is found from Fig. 1(c) that the average size of the prepared solid nanoparticles is ~11 nm whereas the size of the hollow nanoparticles varies between 15 and 60 nm and the proportion of HSNs is increased with the increase in size of the synthesized particles, i.e. larger particles are more likely to become hollow. The magnified images of some selected HSNs present in the sample S1 are also shown in the inset of Fig. 1c, which clearly demonstrates the formation of hollow nanoparticles. The EDXA spectrum of the sample S1 is shown in Fig. 1d, which shows the presence of Ag as a principal element.

Structural information from an assembly of HSNs is obtained using a SAED pattern as shown in Fig. 1e, viz., for sample S1. From Fig. 1e it is found that the SAED pattern consists of six concentric rings. The lattice spacing from the six different rings in the SAED pattern are calculated and compared with the standard lattice spacing of Ag (JCPDS 04-784) and Ag_2O (JCPDS 43-0997) along with their respective (*hkl*) indices and the results are summarized in the Table 1. From the Table 1 it is found that our calculated values matches exactly well with those of standard values of Ag and Ag_2O and this proved the coexistence of both Ag and Ag_2O in the sample. In order to clarify the fact that if there is any increase in Ag_2O formation with increase in LAT, we have carefully studied the SAED patterns taken for all the samples. It is found by analyzing the SAED patterns (not shown here) of the samples produced with LAT of 20 and 40 min that all diffraction rings those are appearing in these samples are due to Ag only. Weak oxidization of Ag during this smaller LAT duration may be possible but we could not identify it experimentally here. Actually due to strong confinement effect of water with increase in LAT, nanoparticles which are ejected from the Ag target are accumulated near the laser spot. When the number of these accumulated nanoparticles is sufficiently large and reaches a certain critical value, they shield the incident laser radiation. As a result, the incident laser light is now incident on the nanoparticles prepared in earlier steps and causes fragmentation and melting of nanoparticles. Melting may increase the tendency of the nanoparticles to get oxidized at longer values of LAT.

The oxidation of Ag nanoparticles generated by laser ablation in water is usually inherent due to soluble oxygen or reaction of Ag with water. Ag^+ ions are also generated during laser ablation of bulk Ag. Photo-ionization of Ag clusters in water [22] can be described as

$$Ag \xrightarrow{h\nu} Ag^+ + e^-.$$

The dissociated electrons may recombine with Ag^+ ions to form Ag atoms or may produce OH^- from water molecule as described below

$$H_2O + e^- \rightarrow OH^- + H^+.$$

TheAg_2O molecule is formed by the following reaction [22]:

$$2Ag^+(aq) + 2OH^- \rightarrow Ag_2O(s) + H_2O.$$

A bright field (BF) HRTEM image of an isolated Ag nanoparticle is shown in Fig. 1f, in which the formations of lattice fringes are