Colloids and Surfaces A 527 (2017) 23–33

Contents lists available at ScienceDirect

Colloids and Surfaces A

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

A facile synthesis of broad plasmon wavelength tunable silver nanoparticles in citrate aqueous solutions by laser ablation and light irradiation

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ARTICLE INFO

Keywords:
Silver nanoparticles
Liquid phase laser ablation
Photo-mediated shape transformation
Plasmon resonance

ABSTRACT

A complete light based synthesis of silver nanoparticles of different shapes exhibiting strong and broad band plasmon resonances is demonstrated in aqueous solutions of single reagent tri-sodium citrate (TSC). This method involves synthesis of almost spherical nanoparticles using liquid phase pulsed laser ablation (LPPLA) followed by their photo-mediated shape transformation into triangular nanoplates by visible light irradiation. UV–vis spectroscopy and Mie theory based analytical calculations show that this method can produce high concentrations of nanoparticles at optimum TSC concentration. LPPLA method is shown to be potential for producing relatively smaller size, isolated spherical silver nanoparticles at optimum TSC concentration without aid of strong reducing agents like borohydrides. This method has also resulted interconnected nanoparticle networks in pure water or at very low TSC concentrations. These isolated spherical nanoparticles were further shown to act as seed particles for high yield synthesis of nanoplates. The concentration of TSC played a vital role in producing both highly stable spherical nanoparticles and their photo-mediated shape transformation into triangular nanoplates. At the optimum TSC concentration of about 10 mM, pH about 7.5 and visible light irradiation of about 24 h, the produced triangular nanoplates have shown strong plasmon absorption in visible to near NIR region, useful for solar light harvesting applications. Further during the light irradiation, presence of additional silver ions in the nanoparticle solution initially increased the growth of spherical nanoparticles which finally resulted in high yield formation of triangular nanoplates.

1. Introduction

Silver nanoparticles (SNPs) exhibit strong absorption and scattering of light due to excitation of localized surface plasmon resonance (LSPR). The important feature of LSPR response is tunability of the resonance wavelength with shape and size of nanoparticles and surrounding medium dielectric constant. For SNPs, the LSPR is significantly strong and can be tuned in the entire visible and near infrared regions as a result, these nanoparticles have found many useful emerging applications [1–5]. The extent of LSPR response and its wavelength tuning can be enhanced with anisotropic shaped nanoparticles like rods, cubes, plates etc [4–7]. Because of this, synthesis of different shapes of SNPs has received considerable attention in recent years [4–7]. For triangular shape silver nanoplates synthesis, different solution-based approaches mainly chemical reduction [4,8–10], photochemical [11–15], electrochemical [16] etc methods have been realized. It may be noted that formation of anisotropic shapes occurs under specific conditions, since these are not thermodynamically favorable shapes. The most reliable approach is based on face blocking theory [4,17] in which a surface capping agent adheres to a particular facet of the seed nanoparticle and directs anisotropic growth. The photo-response nature of silver is found to be effective for controlled photo-mediated growth of triangular nanoplates [15,18] and also minimizes additional chemical reagents as required for kinetic controlled growth in chemical reduction methods. The wavelength of light used for irradiation was found to control the size and associated optical response of the nanoplates [18,19]. In this photo-mediated process, seed SNPs are required at the initial stage to transform them into triangular nanoplates at later stage. The seed nanoparticles are prepared with strong reducing agents like $NaBH_4$ [20–22]. However, for the later step of shape conversion, tri-sodium citrate (TSC) being a weak reducing agent was found to be one of the effective reagent for producing high yield of nanoplates [17,20–22]. Further the concentration of involved different reagents, reaction temperature, order of mixing etc are critical in obtaining nanoplates of desired LSPR response [8,9,23]. Also the formed nanoplates solutions contain different extraneous species or

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http://dx.doi.org/10.1016/j.colsurfa.2017.05.003
Received 23 March 2017; Received in revised form 30 April 2017; Accepted 2 May 2017
Available online 06 May 2017
0927-7757/

ions which are added during the synthesis to control the growth process.

In comparison to this, liquid phase pulsed laser ablation (LPPLA) method is a hybrid physico-chemical process producing nanoparticles either in pure solvents (both aqueous and organic) or in solutions of desired capping agents [24]. This process involves ablation of pure metal target with a pulsed laser beam and confinement of the metal vapor/droplets by its surrounding liquid, allowing growth of nanoparticles from the ablated material. The laser ablation and nanoparticle formation depend on optical and thermal properties of the target and surrounding liquid [24,25]. In LPPLA, since the nanoparticles are formed by top-down approach from a pure metal target, the capping action of reagents present in the solution is more important than their chemical reduction capacity. As a result of this, it has become one of the promising methods for the growth of plasmonic metal nanoparticles with different capping agents including TSC [24–27]. Synthesis of SNPs in TSC by LPPLA and subsequent light irradiation for growth of triangular nanoplates without addition of other chemical reagents is a unique way of realizing different shapes of SNPs in a single reagent solution. So far, the literature on SNPs synthesis by this hybrid process is scanty [28]. Particularly role of important parameters mainly citrate concentration, solution pH and ablation/irradiation time in LPPLA and subsequent light irradiation processes for synthesis of SNPs exhibiting broad LSPR response is not addressed. This completely light based synthesis method is novel in terms of producing smaller size spherical SNPs in TSC alone by eliminating contamination of strong reducing agents like borohydrides, as mostly employed in chemical reduction methods. Therefore, it is important to study and understand the effect of different process parameters involved in this hybrid light based synthesis process. This paper addresses the effect of TSC concentration, laser ablation time and pH in LPPLA for producing stable SNPs with strong LSPR response, since these process parameters play a vital role in obtaining stable and high concentration of SNPs during laser ablation. Further in photo mediated shape transformation of SNPs, reduction of Ag^+ ions in presence of TSC is one of the major steps allowing the growth of anisotropic nanoparticles. Therefore, light irradiation induced changes in nanoparticles morphology and associated LSPR characteristics was studied at different TSC concentrations, both in absence and presence of additional Ag^+ ions. The main objective of this study is to optimize the process parameters for obtaining different shapes of stable SNPs with wide wavelength band LSPR useful for plasmonic photo-catalytic and photovoltaic applications.

2. Experimental

2.1. Materials and methods

2.1.1. LPPLA synthesis of SNPs

Using a second harmonic Nd:YAG laser (YG980, Quantel), wavelength: 532 nm; pulse duration: 9 ns; and pulse repetition rate: 10 Hz; a high purity (99.99%) silver metal target (coin) was ablated in 10 mL of both de-ionized (DI) water and tri-sodium citrate (TSC) solutions of different concentrations in the range of 0.05–100 mM. During the laser ablation, the glass beaker containing liquid and metal target at bottom was continuously rotated for uniform ablation of the target by avoiding crater formation on the target. This also helped in easy dispersion of the formed nanoparticles in the solution. The pH of the solution was adjusted by controlled addition of either NaOH or HCl. With laser pulse energy of about 100 mJ and fluence of about 5 J/cm^2, ablation of the target in the above mentioned solutions was carried out for 30 min duration. The produced SNPs solutions were stored in dark till further use.

2.1.2. Light irradiation of SNPs

Photo-mediated shape transformation of the LPPLA grown SNPs in different concentrations of TSC was studied. For this, the SNPs solutions were irradiated under visible light from a conventional lamp source (Cromton Greaves, 150W) up to 24 h. During light irradiation, the samples were placed at about 15 cm from the lamp.

2.1.3. Preparation of samples with additional Ag^+ ions

The effect of presence of additional Ag^+ ions during light irradiation on the shape conversion process was studied. For this the SNPs grown in different TSC concentrations were added with 10 mM $AgNO_3$ to obtain 0.1 and 0.2 mM final concentration and then irradiated with the light.

3. Characterization

3.1. Optical absorbance

Optical absorption spectra in 250–1100 nm wavelength range were recorded using a fiber spectrometer consisting of a CCD spectrograph (AvaSpec-3068) and a balanced deuterium halogen light source (DH-S-BAL, Avantes). All the measurements were carried out with quartz cuvette of 2 mm path length and DI water as reference. Nanoparticles growth during the laser ablation and also SNPs shape transformation during light irradiation was monitored from optical absorption spectra measured at regular intervals of every 3 min and 2 h respectively.

3.2. Morphological characterization

Morphology of the grown nanoparticles was determined from transmission electron microscopy (TEM) imaging in bright field mode (Zeiss) at 200 kV. For TEM characterization, the samples were prepared by solvent evaporation of few drops of SNPs solution on to formvar coated copper grids.

3.3. XRD and zeta-potential measurements

The structural characteristics of the grown nanoparticles before and after light irradiation were measured using X-ray diffractometer (Discover 8, Bruker) with Cu Kα radiation source. For this, samples were prepared in film form on thoroughly cleaned *epi*-polished silicon substrates by repetitive drop casting and solvent evaporation. The nanoparticles surface charge characteristics was analyzed using Zeta potential measurements through a zeta-analyzer (MPT-2, Malvern).

4. Results and discussions

4.1. LPPLA growth of SNPs

4.1.1. Effect of TSC concentration on optical absorbance

Formation of SNPs by laser ablation of silver target in pure DI water and different concentrations of TSC was studied from optical absorbance. Fig. 1(a–d) presents the variation of absorbance of SNPs at different laser ablation periods up to 30 min, produced in DI water and aqueous solutions of TSC at 0.5, 10 and 100 mM concentrations respectively. In these spectra, absorption peak at about 400 nm wavelength corresponds to dipolar mode LSPR excitation of SNPs [2,4]. In all the cases, formation of SNPs is evident from this LSPR peak, however the absorbance and its variation is different. For SNPs grown in DI water, with increasing ablation time, the LSPR peak absorbance marginally increased along with asymmetric broadening extended up to 900 nm wavelength. This shows that SNPs in the solution are not in isolated form rather coalesced, contributing to the absorbance at longer wavelengths [29]. In contrast to this, the SNPs grown in TSC solutions have shown systematic and monotonously increased absorbance with ablation time, without much broadening of the LSPR peak. The increased absorbance, without change in LSPR peak wavelength and broadening, is attributed to increased concentration of nanoparticles with ablation time. This is attributed to efficient surface capping of SNPs by TSC due to matching of citrate ion ligand size with