Influence of Synthesis Temperature on Growth of Silver Nanorods

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Abstract— Silver nanorods (Ag NR) have been successfully synthesized by wet chemical method (seed-mediated growth) utilizing 10 nm silver nanospheres as a seed material and subsequent reduction of silver precursor with a weak reducing agent (ascorbic acid) along with a directing surfactant. The effect of synthesis temperature on the structure, morphology, composition and optical properties were investigated through X-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, UV-Vis and FTIR spectroscopy. Both XRD and SAED patterns demonstrate that silver nanorods are crystallized in face centered cubic symmetry. The synthesis temperature significantly influences the morphology of the nanorods. Absorbance spectra confirm the nanorods formation with two SPR bands, one at lower wavelength side and another at higher wavelength side. The results show that increase of synthesis temperature led to decrease of aspect ratio of nanorods.

Index Terms— Silver nanorods, synthesis temperature, crystal structure, particle size, morphology, composition, absorbance

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1 INTRODUCTION

Recently, one-dimensional 1D structures having diameter in nanoscale, such as nanorod and nanotube, have become the focus of intensive research due to their peculiar properties [1], [2] which results in unique applications in mesoscopic physics and fabrication of nanoscale devices [3], [4]. Compared with micrometer-diameter whiskers, they are expected to exhibit remarkable mechanical properties, including electrical, optical and magnetic properties. Nanosized particles of noble metals have attracted immense interest in various fields of physics and chemistry due to their conspicuous physicochemical catalytic properties and their potential applications in microelectronics, optical, electronic, magnetic devices [5], [6]. These properties are strongly dependent on the size and shape of the particles [7], [8] and therefore it could be critical to develop an effective preparation method through which we can attain control over the morphology of the nanomaterials.

In particular, optical properties of metallic nanoparticles depend on the shape [9]. In case of spherical ones, only one absorption band can be observed. Where as, in nanorods the absorption of visible light is along the length of the nanorod (longitudinal plasmon band) and also along the width of the nanorod (transverse plasmon band). The larger aspect ratio causes the more red-shifted in the longitudinal plasmon band [10], [11]. Spheres comprise an aspect ratio of 1. Usually, capping agents usage in synthesis process leads to spheres formation, but occasionally results in shapes other than spheres. The mechanism of such shape control has recently been studied by El-Sayed and coworkers and Reetz and coworkers [12], [13].

Among all metals, silver nanorods and nanowires should be particularly interesting to fabricate and study because bulk silver exhibits the highest electrical and thermal conductivies. Silver nanomaterials have also been used to serve as sacrificial templates for generating other nanoaprticles that are more difficult to fabricate [14], [15]. Silver has also been used in a rich variety of commercial applications, and the performance of silver in these applications could be potentially enhanced by processing silver into 1D nanostructures with well-controlled dimensions and aspect ratios [16], [17]. However preparation of silver nanoparticles by chemical reduction methods generally yields a wide range of sizes and morphologies.

In general, the solution phase chemical method is preffered one for fabricating nanomaterials which is again classified into hard templates [14], [18] or soft templates [19], [20]. In the hard templates, the metal ions are reduced inside cylindrical pores of oxide or polymeric membranes. In the soft templates method, neutral or charged surfactants are used for the growth of nanoparticles. Most of the hard templates are tedious to fabricate and media (corrosive) used for the dissolution of the template may destroy the synthesized nanomaterials. However, soft templates are versatile and advantageous for the small diameter nanorods fabrication with high aspect ratios. This process is simple, efficient and usually gives high yields. In preparing gold and silver nanorods using surfactants, three different approaches are available: the electro-chemical [9], [21], seed-mediated growth [10], [11], [22], [23] and ultraviolet irradiation–photoreduction [4], [24] methods.

We used the seed-mediated growth approach to make metallic nanorods in homogeneous solution, following the procedures recently described by Jana et al. [11], [12], [23]. In seed-mediated growth methods, first small metal particles are prepared and later used as seeds for the growth of nanorods. This process is readily amenable to scaling up. The particle size can be varied simply by altering the ratio of seed to metal salt, providing a controlled number of preformed seeds and a growth condition which avoids the secondary nucleation. However, the difficulty in finding a suitable growth condition that inhibits additional nucleation during the growth stage limits the application of such methods. In general, these conditions in-

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clude using a reducing agent too weak to reduce the metal salt without the presence of seeds. Initial addition of preformed seeds has two advantages [11]: first, it increased the overall reduction rate, and hence the growth rate: second, the particles size is controlled by varying the ratio of metal salt to seed, thus restricting the particle size to nanometer regime.

In this paper, we used synthesized silver particles of 10 nm size to prepare silver nanorods of the high aspect ratios that are relatively uniform as seed material. The silver seeds were prepared through reduction of silver nitrate with sodium borohydride at 70°C. Secondary nucleation during the growth stage was inhibited by carefully controlling the growth conditions using a weak reducing agent (ascorbic acid) and CTAB in aqueous solution. Here, the synthesis temperature was varied to control the aspect ratio and uniformity of the rods formation.

2 EXPERIMENTAL SECTION

2.1 Chemicals and materials

Silver nitrate ($AgNO_3$, 99.8%), Sodium borohydride (99%), Sodium citrate dihydrate (99%), Sodium hydroxide (NaOH, 96%), Cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, CTAB, 99%) were obtained from Sigma-Aldrich, Millipore (Milli-Q) water was used throughout the preparation of all samples.

2.2 Silver seeds synthesis

At first, a 10 ml aqueous solution containing 0.5 mM $AgNO_3$ and 0.5 mM sodium citrate dihydrate were prepared. Then, 50 µl of 0.2 M Sodium borohydride (reducing agent) solution was injected to the above solution all at once while stirring vigorously. Then instantaneously, we observed the colour change of solution to light yellow. The entire solution was heated at 70°C for 30 min under continuous stirring on magnetic stirrer. Sodium citrate dihydrate acts as stabiliser [23]. The average particle size was measured through SEM and found to be ca. 10 nm. This solution was used as a stock silver seed solution. The solution should be utilised within 24 hrs of its preparation otherwise, particles will be aggregated.

2.3 Procedure of silver nanorods growth

A 20 ml aqueous solution containing 0.2 M CTAB was prepared through heating at 40°C while stirring on magnetic stirrer for dissolution of CTAB. Then after cooling to room temperature it is used for further experiment. Next, 500 µl of 0.1 M $AgNO_3$ and 1000 µl of 0.2 M ascorbic acid solution were added. And then, 500 µl of seed solution was added and at last few drops of 1 M NaOH was added to maintain constant pH and stirred well for 20 min. Within 3 min, we can observe the greyish green colour solution formation. The synthesis temperature was varied from 30°C to 70°C. After that, the solution was centrifuged at 3000 rpm for 10 min and separated from spheres and surfactants. Then all the samples were washed for two times with Milli-Q water and nanorods were collected and stored for analysis.

2.4 Characterization of the synthesized Ag NPs

The as-synthesized Ag NR were characterized by various instrumental analyses. Crystalline metallic silver was examined by Seifert 3003TT X-ray diffractometer, using Cu Kα radiation (λ=0.1546 nm). The morphology of Ag NR was observed using Carl Zeiss EVO MA 15 scanning electron microscopy (SEM) measurements. The particle size and structure confirmations were analysed by Phillips TECHNAI FE 12, transmission electron microscopy (TEM). Elemental compositional study was investigated through energy dispersive spectroscopy (EDS) by using Oxford Inca Penta FET x3 EDS instrument coupled with SEM. UV-visible absorption studies were carried out by a Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer with a wavelength resolution better than ±0.2 nm. Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded with ATR-FTIR using Bruker Vertex-80 spectrometer.All the measurements were done at room temperature.

3 RESULTS AND DISCUSSION

3.1 Structural analysis

X-ray diffraction pattern of silver seeds and the as-synthesized silver nanorods at synthesis temperature of 50°C is shown in Fig. 1. The diffraction peaks corresponds to (111), (200), (220) and (311) planes assigned to face centered cubic (fcc) structure (JCPDS No: 04-0783). Absence of impurity peaks reveals the purity of the sample. Broadened peaks were due to nanosized effect. The crystallite size of Ag seeds and nano rods formed in the reduction process is calculated using Scherrer's equation [25]. The crystallite size was calculated from (111) preferred orientation and is found to be 9 nm for silver seeds and 12 nm for Ag NR synthesized at 50°C reaction temperature.

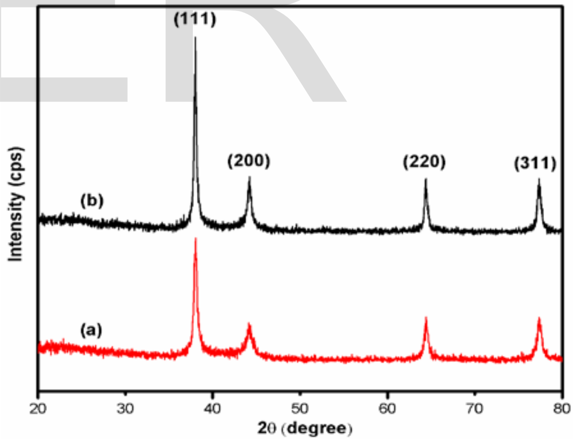

Fig. 1 XRD profile of (a) silver seeds synthesized at 70°C and (b) silver nanorods at synthesis temperature of 50°C.

3.2 Morphological studies

SEM images of the as-prepared samples are pictured in Fig. 2. The figures clearly depict that silver seeds are spherical in shape with particle size ~10 nm (Fig. 2(a)) and all other samples prepared using silver seed have shown nanorods formation (Fig. 2(b,c,d)). The synthesis temperature strongly influences the morphology and aspect ratio of the nanorods. The aspect ratio of the nanorods decreased with increase of synthesis temperature. At synthesis temperature of 30°C, the nanorods are long and as synthesis temperature increased to 70°C the length of the nano rods decreased with light increase

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in width of the nanorods which is also evidenced by UV-Vis spectra. The aspect ratios of the nanorods synthesized at 30°C, 50°C and 70°C are 6, 4.2 and 3.1 respectively.

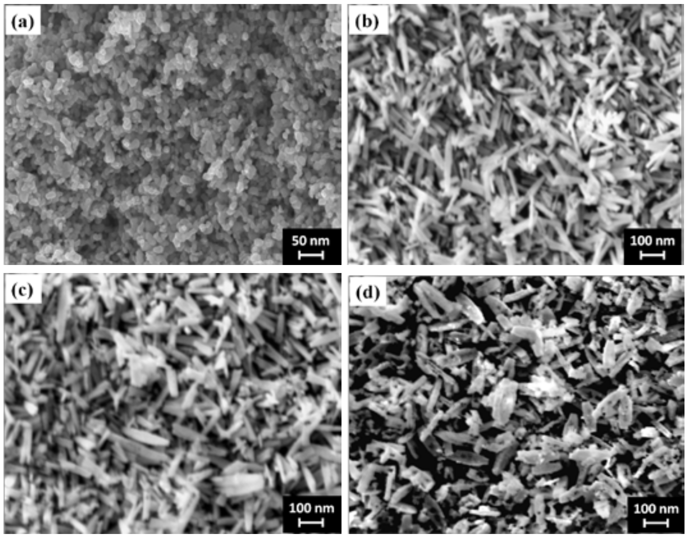

Fig. 2 SEM images of (a) silver seed and silver nanorods at different synthesis temperatures of (b) 30°C, (c) 50°C and (d) 70°C.

Fig. 3(a) shows the formation of silver nanorods through TEM analysis at reaction temperature of 50°C. The particle size of Ag NR from TEM micrograph is found to be around 14 nm. The selected area electron diffraction (SAED) pattern of Ag nanorods is pictured in Fig. 3(b), representing the four strong circular fringes (111), (200), (220) and (311) which corresponds to the characteristic peaks of face centered cubic crystalline structure and is supported by XRD results.

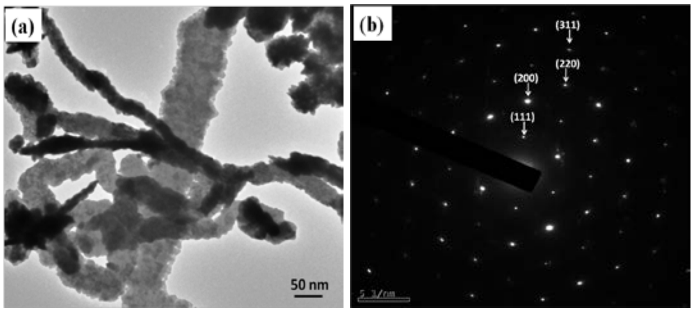

Fig. 3 Typical (a) TEM and (b) SAED pattern of silver nanorods at synthesis temperature of 50°C.

3.3 Composition analysis

Elemental analysis is carried by excitation of samples with electron beam of 20 kV. Fig. 4 shows the EDS spectrum of nanorods prepared at 50°C synthesis temperature. The spectrum shows the elemental peaks of Ag and C. Major emission peak for silver was appeared at 2.5-3.5 keV. Hence, from EDS spectra it was confirmed that there are no other impurities expect C. The appearance of C is due to the occurrence of surfactant coating on the surface of silver nanorods and carbon tape on the stud. Inset of the Fig. 4 shows the quantitative analysis of the silver nanorods at 50°C reaction temperature. This analysis enumerates that Ag was having higher weight percentage of 98.2% and the C having 1.8% weight percent.

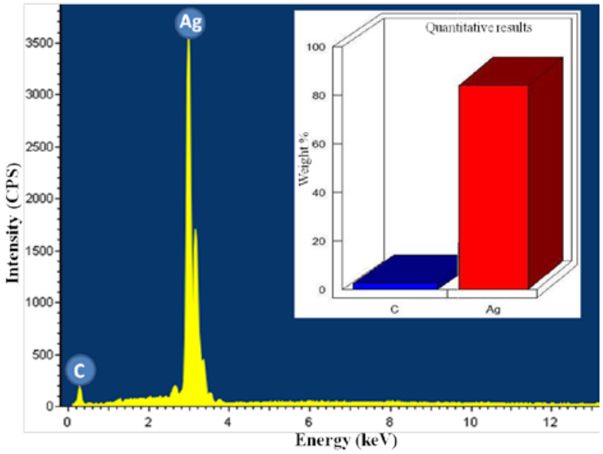

Fig. 4 Typical EDS spectrum of silver nanorods at synthesis temperature of 50°C.

3.4 UV-Vis spectroscopy

UV-Vis spectroscopic study is useful in tracking the morphological evolutions and optical properties because, silver nanostructures exhibits SPR depending on various shapes and sizes at different frequencies. Fig. 5 depicts the UV-Vis spectra of silver seed solution prepared and obtained solutions sampled at different synthesis temperatures (30°C, 70°C). Spherical nanoparticles will exhibit only one typical surface plasmon resonance (SPR) in the visible region. Whereas nanorods exhibit complex absorption pattern due to absorption of visible light along both the width of the nanorods (transverse plasmon band) and along the length of the nanorods (longitudinal plasmon band).

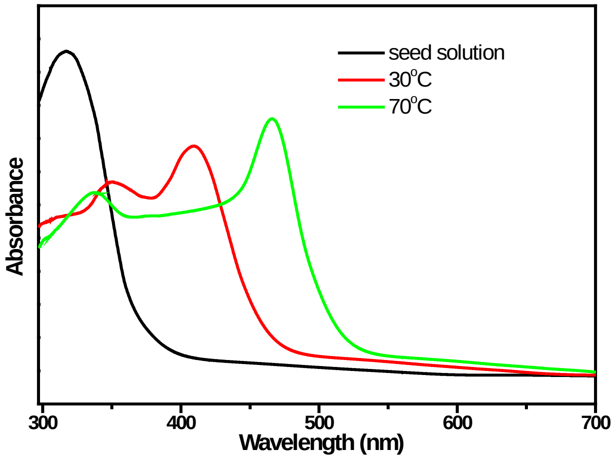

Fig. 5 Optical absorption spectra of silver seed solution and silver nanorods synthesized at 30°C and 70°C temperatures.

From UV-Vis spectra (Fig. 5), we can observe the appearance of single peak at 317 nm for silver seed solution and two peaks for silver nanorods, one at lower wavelength region and another at higher wavelength region. One band for 30°C and

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70°C reaction temperatures was displayed at 337 nm and 348 nm respectively, relevant to transverse plasmon bands. Another band at longer wavelength region obtained is longitudinal plasmon band. As the synthesis temperature is increased, the aspect ratio is decreased and this longitudinal plasmon band is red shifted. The longitudinal plasmon band of silver nanorods synthesized at different reaction temperatures appeared at 466 nm (30°C) and 409 nm (70°C) respectively. We observed that the aspect ratio of Ag nanorods was high at 30°C, the transverse plasmon band blue shifts to ~340 nm but, longitudinal plasmon band red shifts to ~470 nm. With increasing aspect ratio, the prominent red shift of the longitudinal plasmon band and the slight blue shift in the transverse plasmon band is a well known phenomenon [9].

3.5 FTIR spectroscopy

FTIR is a power tool for identifying types of chemical bonds in the samples and used for quantitative analysis. FTIR spectra of sodium citrate dihydrate and silver seeds, silver rods synthesized at 50°C are compared in Fig. 6. The figure shows that the spectrum of silver seeds (b) agrees closely allied with the spectrum of sodium citrate dihydrate (a) indicating citrate capped silver seeds formation and same composition. The whole spectra from (a-c) display broad intense bands at 3550–3200 cm^{-1} characteristic of stretching vibrations of surface OH groups (H_2O) and weak but distinct set of peaks at 2920–2840 cm^{-1} corresponding to v(CH) vibrations of CH_2 groups of citrate ion [26].

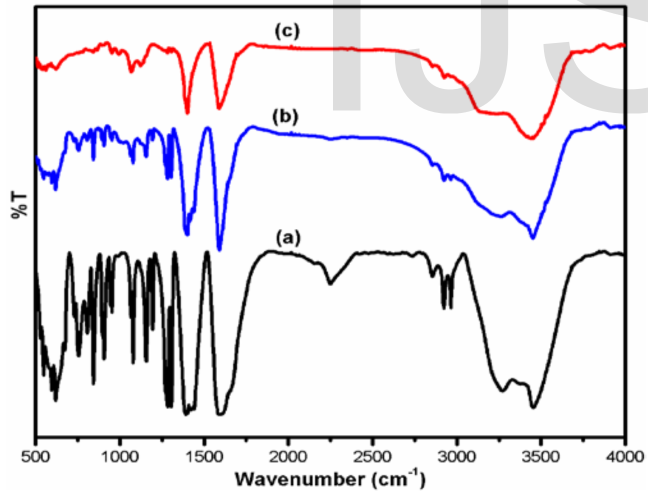

Fig. 6 FTIR spectra of (a) sodium citrate dihydrate (b) silver seeds and (c) silver nanorods synthesized at 50°C temperature.

All specrta are characterised by strong bands at 1580 and 1390 cm^{-1} (a-c), assigned to asymmetric and symmetric stretching vibrations of ionized carboxylic groups COO^{-} [26]. The absorption band at 1155 cm^{-1} (a) most probably correspond to bending vibrations δ(OH) of C–OH groups [26]. The absence of similar absorption band in (c) and less intense band in (b) presumably suggests that the alcoholic group of citrate ion is engaged in the coordination of silver. Small bands at 935-635 cm^{-1} of all spectra are related to C-H bending [27]. Thus, the FTIR spectra clearly demonstrate the participation of citrate ions in capping process of silver particles.

4 CONCLUSIONS

Silver nanorods have been successfully synthesized by a simple, wet chemical method. This technique is based on the seed-mediated CTAB directed growth of silver nanorods. We have studied the influence of synthesis temperature on variation of morphological and optical properties of silver nanorods. Reaction temperature plays an important role in controlling the diameters and aspect ratios of nanorods. Increase of reaction temperature resulted in decrease of aspect ratio of silver nanorods and an enhancement of mono-dispersed sizes and shapes. SAED and XRD patterns revealed the fcc symmetry of prepared nanorods. UV-Vis studies confirmed the nanorods formations with two SPR bands. FTIR results inferred the existence of citrate capped silver particles. The rod shaped silver may have many important applications especially in catalysis and this present technique may be extendable to synthesize other metal nanorods and exploitable for the scaled-up preparation of these nanomaterials.

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