Synthesis of Silver Nanosheets onto Solid Substrates by using Seed-Mediated Growth Method

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Abstract. Silver nanosheets, with average size tunable from 30 to 100 nm, have been synthesized onto solid substrates by using seed-mediated growth method. The growth of silver nanosheets have been carried out at temperature of 30°C in the presence of a binary surfactant mixture: cetyl trimethyl ammonium bromide (CTAB) and poly-vinyl pyrrolidone (PVP) with their various concentrations. The effect of concentration of the surfactants on the grown silver nanosheets were evaluated. Characterizations of the samples have been performed by using UV-Vis spectroscopy, X-ray diffraction (XRD) and field-emission scanning electron microscope (FESEM). UV-Vis spectra showed that the silver nanoparticles have grown with a various geometrical forms. XRD results confirmed that the presence of two peaks at 2θ: 38.119° and 44.305° indicated the silver nanosheets, with their crystal orientation of (111) and (200). FESEM images of the best samples showed the edge-length size of silver nanosheets was dominated in the range of 30-100 nm, with various morphologies of nanosheets, such as triangular, hexagonal and spherical shapes.

Keywords: Silver nanosheets, structure, UV-Vis, XRD, FESEM.
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INTRODUCTION

Silver nanoparticles of different shapes, such as cubes and octahedrons [1,2], tetrahedrons [3], wires/rods [4,5] and plates/sheets) have attracted high research interest, due to their unique and tunable optical properties, as well as their wide potential applications, such as optical probes, optical labels, chemical and biological sensors [6]. Among them, two-dimensional (2-D) silver nanosheets have special attracted attention in the past decade [7], including triangular plates/sheets [8], nanodisc [9], and hexagonal plates. The morphology and size of silver nanoparticles are important aspects that relate to their properties and applications. Hence, the study of size and morphology of silver nanoparticles become one of focusing aspect of research on the materials.

Synthesis of nanoplates is generally performed by transformation of spherical nanoparticles into nanoplates by using photo-induced methods [10]. Simpler method used to synthesis of nanoplates is seed-mediated growth method [11,12]. Hexagonal silver nanoplates have grown by using sulphuric acid [13] and urea [14] as a modifier. In this current work, we use ascorbic acid and binary surfactants: Polyvinylpyrrolidone (PVP) and *Cetyl-trimethyl-ammonium bromide* (CTAB) in order to vary shapes of silver nanoplates/nanosheets.

EXPERIMENTAL PROCEDURES

Materials

Silver nitrate ($AgNO_3$), trisodium citrate ($C_6H_5Na_3O_7$), sodium borohydride ($NaBH_4$), ascorbic acid ($C_6H_8O_6$), Poly-vinyl-pyrrolidone (PVP) and *Cetyl-trimethyl-ammonium bromide* (CTAB) were all purchased from Sigma-Aldrich. In order to synthesis of silver nanosheets, all the chemicals were made into solution. All the solutions were prepared using deionized (DI) water.

Preparation of Silver-Seed

A standard procedure for the synthesis of silver-seed was as follows: 0.5 mL 0.01 M AgNO3 solution and 0.5 mL 0.01 M trisodium citrate were added to 20 mL DI water, solid substrate then was immersed into the seed-solution and the solution was kept under cold condition for about 30 min. After that, 0.5 mL of 0.1 M $NaBH_4$ solution was added to the mix solution, and then kept them for about 1 h before using as seed.

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From this approach, spherical nanoseed of size ca. 3-5 nm can be grown on the substrate surface. The shape and size stability was achieved by the presence of trisodium citrate capping agent.

Preparation of Silver-Nanosheets

Growth solution of silver nanosheets consists of 0.01 M $AgNO_3$ (a variety volumes), 0.1 mL 0.1M ascorbic acid, 10 mL CTAB (a variety concentrations) and 10 mL PVP (a variety concentrations). Then 20 µL NH_3 was added to the solution. These solutions were then kept at room temperature for about 4h.

The growth process of silver nanosheets on the solid substrates was performed by immersing the substrates into a glass tube that contained the growth solution for about 4 h. The CTAB and PVP here are the surfactants molecules that have function both as morphology and aggregation controllers.

Characterizations

The UV-Visible optical absorption spectroscopy was performed using UV-160 Lamda 900 (Perkin Elmer) spectrophotometer. In order to characterize the structural growth of the silver nanosheets on the solid substrates, the X-ray diffraction methods using an XRD D8 Advance (Bruker) with Cu KR irradiation operated at 50 kV and 300 mA and a scan rate as low as 2 degrees per minute were performed. The morphology of the silver nanosheets growth was characterized using a field-emission scanning electron microscopy (FESEM) with SUPRA 55VP instrument.

RESULTS AND DISCUSSION

Morphology and Structure of Silver-Nanosheets

Prior to studying the surfactant effect, the optimum $AgNO_3$ concentration for Ag nanosheet formation was sought. The morphologies of the silver-nanosheets were observed by field-emission scanning electron microscopy (FESEM). The FESEM images of the silver-nanosheets grown on the ITO substrates that prepared using the seed-mediated growth are shown in Fig. 1. It was clearly shown that almost all of the surface area of substrate (more than 85%) was covered by silver nanosheets in all samples with different volume (0.5 mL, 0.8 mL, 1 mL and 1.5 mL) of silver ($AgNO_3$) solutions. The plate/sheets-like morphology of the samples, including triangular, hexagonal, truncated-hexagonal, trapezium, circular and irregular-sheets were also observed.

Fig. 2 shows the high-magnification (50.000X) FESEM images of the samples. It was found clear shapes of triangular, hexagonal, truncated-hexagonal, trapezium, circular and irregular-nanosheets observed in all samples. It was also shown that among the samples, the sample (b) of 0.8 mL silver solution has the most number of particles compared to other samples. The edge-length size of the silver nanosheets/plates was observed to be in the range of 30 - 200 nm for the samples of 0.8 and 1.0 mL silver solution (sample B and C). Whereas, bigger particles with the edge-length size in the range of 200-400 nm were obtained from the samples of 0.5 and 1.5 mL of silver solutions (sample A and D).

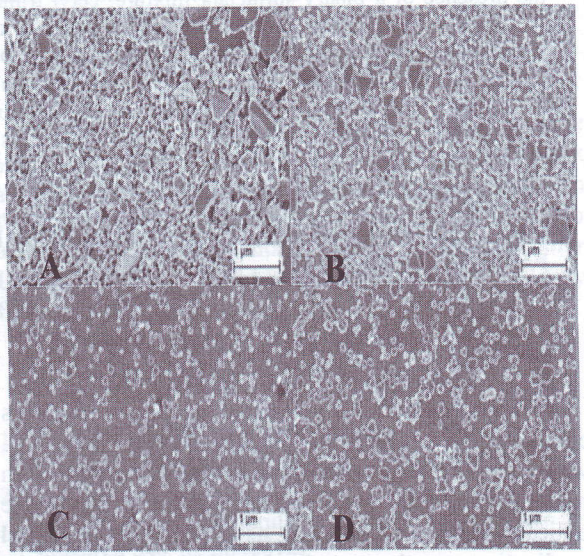

FIGURE 1. FESEM images of the silver nanosheets grown on ITO with volume of $AgNO_3$ (A) 0.5 mL, (B) 0.8 mL, (C) 1.0 mL and (D) 1.5 mL.

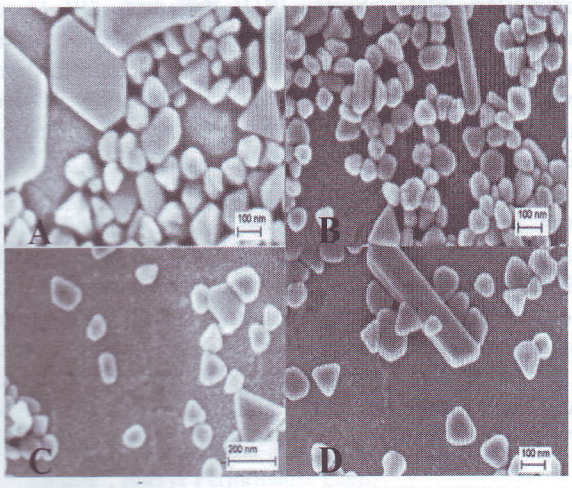

FIGURE 2. High-magnification (50.000X) FESEM images of the samples with volume of $AgNO_3$ (A) 0.5 mL, (B) 0.8 mL, (C) 1 mL and (D) 1.5 mL.

Individual silver-nanosheets of triangular, hexagonal, truncated-hexagonal, trapezium, circular and irregular-sheets are shown in Fig. 3. As can be seen that the size of the triangular, truncated-hexagonal, trapezium and irregular-sheets is about 100-200 nm in the edge-length. Whereas, more bigger size of silver nanosheets was observed to be the hexagonal-sheets, which was more than 500 nm in the edge-length.

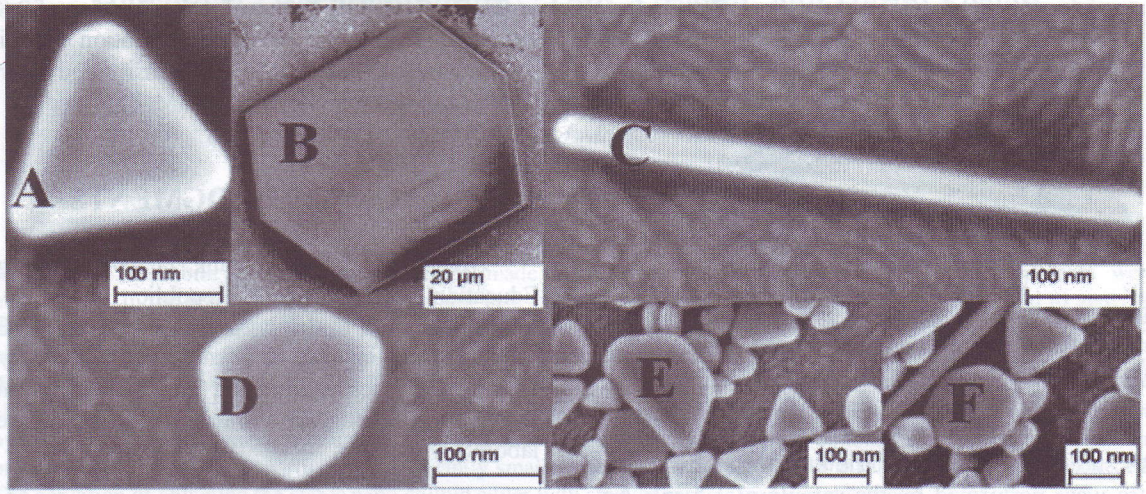

FIGURE 3. Individual silver-nanosheets (A) triangular (B) hexagonal (C) truncated-hexagonal (D) irregular-sheet (E) trapezium (F) circular.

The X-ray diffraction was carried out in order to determine the phase and purity of the samples. X-ray diffraction pattern of the silver-nanosheets (Fig. 4) shows that the peaks (38.119° and 44.305°) are assigned to the diffractions from the (111) and (200) planes of face-centre cubic symmetry of Ag (JCPDS No. 01-087-0717), respectively. In addition, there was no other impurity phase that was detected.

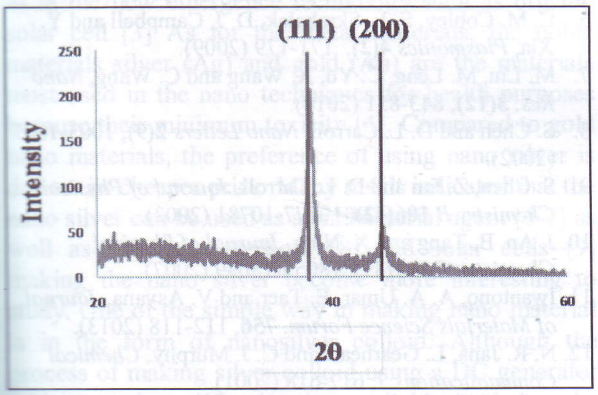

FIGURE 4. XRD pattern of the silver-sheets grown on ITO.

Effect of Surfactant on the Morphology and Structure of Silver-Nanosheets

The effect of concentration of surfactants on the morphology and structure of the products was evaluated by UV-VIS spectroscopy. Fig. 5 shows the UV-Vis spectra of the samples of silver nanosheets with different concentration of CTAB (150, 120, 100, 80 and 50 mM) at the same concentration of 0.8 mM PVP. The figure exhibits two peaks absorptions obtained from all samples, although the sample of 150 mM (a) shows weak peaks. Among them, the 50 mM CTAB sample produces the strongest absorption peaks, and this then was chosen as the best sample for further treatment.

The two absorption peaks at about 420 nm and 520 nm are contrary to a single SPR band for spherical silver nanoparticles. These two peaks are attributed to sheets-like silver nanoparticles. The number of peaks correlate with the number of ways the free electron oscillated. The strong peak at 420 nm is related to the Transverse Surface Plasmon Resonance (T-SPR), resonance toward the short axis, meanwhile the broad peaks at around 520 nm are due to Longitudinal Plasmon Resonance (L-SPR), a resonance toward the longer axis.

As can be seen from the Fig. 5, the spectrum of 50 mM CTAB sample has strongest absorption peak, due to the highest density of silver nanosheets compared to the other samples. On the other hand, the weakest peak of absorption spectrum from 150 mM CTAB sample, indicate the lowest density of silver nanoparticles grown on the sample.

UV-Vis spectra of the silver nanosheets with different volume of silver solution (0.5 mL, 0.8 mL, 1.0 mL and 1.5 mL) at the best concentration of binary surfactants of 0.8 mM PVP and 50 mM CTAB are shown in Fig. 6.

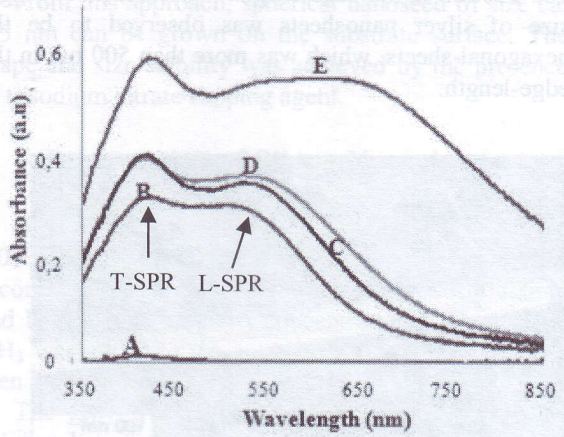

FIGURE 5. UV-Vis spectra of the silver nanosheets with 0.8 mM PVP and various concentrations of CTAB. (A) 150 mM (B) 120 mM (C) 100 mM (D) 80 mM (E) 50 mM.

As shown in the figure, the strongest absorption spectra were performed by the sample of 1.5 mL Ag solution and 0.8 mL silver solution. These strong peaks represent to high number of the silver nanosheets and high area covered by the nanosheets.

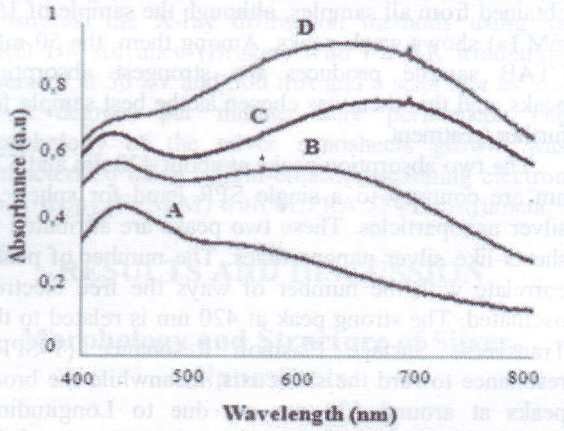

FIGURE 6. UV-Vis spectra of the silver-sheets at 0.8 mM PVP and 50 mM CTAB with volume of Ag solution of (A) 0.5 mL (B) 1.0 mL (C) 0.8 mL (D) 1.5 mL.

CONCLUSION

The current method of seed-mediated growth using a binary surfactant of CTAB and PVP has successfully grown a variety shapes of silver-nanosheets., including triangular, hexagonal, truncated-hexagonal, trapezium, circular and irregular-nanosheets. XRD pattern of the silver-nanosheets shows that the peaks (38.119° and 44.305°) are related to the diffractions from the (111) and (200) planes of fcc symmetry of silver nanosheets (JCPDS No. 01-087-0717), respectively.

The FESEM images of the silver-nanosheets grown on the ITO were clearly shown that almost all of the surface area of substrate (more than 85%) was covered by silver nanosheets in all samples. The edge-length size of the silver nanosheets/plates was observed to be in the range of 30 - 200 nm for the samples of 0.8 and 1.0 mL silver. The best concentration of binary surfactants that resulted highest density and strongest absorption spectra was of 0.8 mM PVP and 50 mM CTAB.

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