

## SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPATES BY A SEED-MEDIATED METHOD

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**Abstract.** *Silver nanoplates (SNPs) having different size were synthesized by a seed-mediated method. The seeds-silver nanoparticles with 4–6 nm diameters were synthesized first by reducing silver nitrate with sodium borohydride in the present of Trisodium Citrate and Hydrogen peroxide. Then these seeds were developed by continue reducing Ag<sup>+</sup> ions with various amount of L-Ascorbic acid to form SNPs. Our analysis showed that the concentration of L-Ascorbic acid, a secondary reducing agent, played an important role to form SNPs. In addition, the size and in-plane dipole plasmon resonance wavelength of silver nanoplates were increased when the concentration of added silver nitrate increased. The characterization of SNPs were studied by UV-Vis, FE-SEM, EDS and TEM methods.*

**Keywords:** silver nanoplate; seed-mediated; plasmon resonance; L-Ascorbic acid.

**Classification numbers:** 61.46.-w, 62.23.Kn.

## I. INTRODUCTION

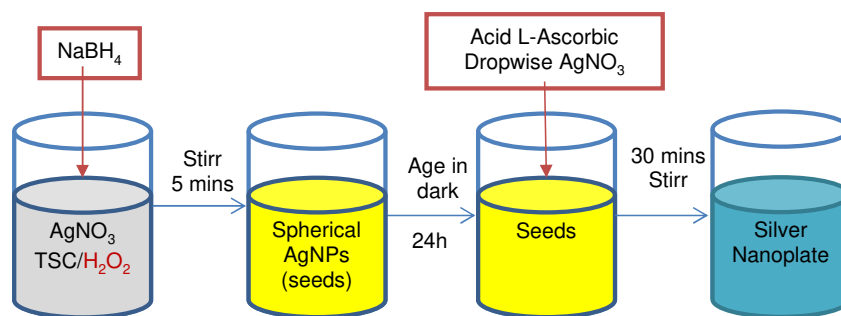
Metallic nanomaterials (gold and silver) are interesting objects of many scientists around the world because of their special optical properties such as the surface plasmon resonance (SPR) [1,2] or the Raman enhances surface scattering (SERS) [3]. The optical properties of silver nanoparticles depend on their shape and size [1,2]. Spherical silver nanoparticles have only one SPR absorption at 390 - 410 nm whereas silver nanoplates have three SPR absorptions due to their anisotropic properties, including out-of-plane quadrupole SPR at 330-350 nm, in-plane quadrupole SPR at 400-450 nm and in-plane dipole SPR from 450 to 900 nm [1–3], this special optical property makes the silver nanoplates red, orange, blue, green while spherical nano silver are yellow.

Silver nanoplates can be synthesized by single step reduction of  $\text{Ag}^+$  ions [4] or through 2 steps with small silver nanoparticles played as seeds, is further developed into a plate under the effect of secondary reducing agents such as Ascorbic Acid or the effect of light [5]. An advantage of the seed-mediated method is that it controls the size of the silver nanoplates formed by the size of the plate depending on the size of the germ. B. Ajitha and his colleagues made silver nanoplates by mediating with Ascorbic Acid as the secondary substance. These authors focus on the ratio of germ and the protective agent, regardless of the effect of Ascorbic Acid [5]. Jie Zeng and colleagues focus on the role of trisodium citrate in the formation of silver nanoparticles [6]. Jason M. Haber and his colleagues also studied the formation of silver nanoparticles with this method but have not yet investigated the effect of Ascorbic Acid on the size of the nanoplate [7].

In our research, silver nanoplates are made by a seed-mediated method according to Jason M. Haber with some modifications. We investigated the effect of L-Ascorbic Acid on the formation of silver nanoplates and investigated their surface plasmonics.

## II. EXPERIMENT

Silver nanoplates (SNPs) were synthesized in two steps: synthesized small spherical silver nanoparticles played “seeds” and developed those seeds to form SNPs.



**Fig. 1.** (Color online) Schematic illustration of synthesis of SNPs.

### Fabrication of Silver nanoparticles

Firstly, 0.93 mL of 10 mM  $\text{AgNO}_3$  solution (Sigma), 10 mL of 75 mM Trisodium Citrate (TSC, Normapur) and 132  $\mu\text{L}$  of 0.6% Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and Milli-Q water (Millipore)

were added into a beaker and stirred for 5 minutes. The total volume of the reaction solution was fixed at 200 mL. Then 0.92 mL of 100 mM NaBH<sub>4</sub> solution were rapidly added to initiate reduction, the color of solution immediately turned to yellow, demonstrating the formation of silver nanoparticles. Samples were stored in dark at room temperature for 24 hours.

#### **Fabrication of silver nanoplates**

20 mL of these seeds were poured in a 50 mL beaker, then 5 mM L-Ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, Sigma) were poured in the mixture with various volume from 0.475 mL to 7.6 mL. 1.9 mL of AgNO<sub>3</sub> 10 mM (Sigma) solution were dropped into the mixtures at a controlled rate ranging 60 μL/min. The color of solution was changed from orange → red → purple → green → blue depending on the amount of L-Ascorbic acid. The process was shown in Fig. 1.

#### **Characterisation**

The samples were analyzed by UV-Vis (Jacco V-670), FE-SEM in combination with EDS (Hitachi-S4800, Japan), TEM (JEM-1400, Japan).

For UV-Vis analysis, samples were diluted 10 times, using quartz cuvette to measure. For FE-SEM-EDS and TEM analysis, the samples were dripped on a 3 mm diameter copper grid and dried at room temperature, placed on conductive carbon tape and analyzed at the voltage 10kV for FE-SEM, 100kV for TEM.

### **III. RESULTS AND DISCUSSION**

#### **Silver nanoparticles preparation**

The UV-Vis spectra, the TEM image and the size distribution of silver nanoparticles were shown in Fig. 2. The UV-Vis spectra of M1 had a plasmon resonance (SPR) peak at the 390 nm, demonstrating the presence of spherical silver nanoparticles [1–4]. The TEM image of this sample showed spherical silver nanoparticles with 4-5 nm diameters, average particle size was 4.6 nm. On the other hand, H<sub>2</sub>O<sub>2</sub> was an agent that promotes development of planar twinned seeds which the anisotropic development necessary for nanoplates formation [7, 8].

#### **Fabrication of silver nanoplates**

The UV-Vis absorption spectra of SNPs prepared with different amounts of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> from 0.475 mL to 7.6 mL were shown in Fig. 3. The absorption peaks of the samples were given in Table 1. Our results showed that the SNPs prepared with 0.475 mL of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> gave two unclear peaks at 337 nm and 522 nm (Fig. 3a). It suggested that small silver nanoplates had begun to appear in this sample.

With increasing amounts of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> from 0.95 mL to 7.6 mL, the UV-Vis spectra of samples showed three SPR peaks, which was also the characteristic absorption spectrum for the SNPs [2–8]. All samples showed out-of-plane quadrupole peaks at 337 nm, characterized for the thickness of plates [8]. When the volume of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> increased from 0.475 mL to 1.9 mL, the in-plane dipole peaks were shifted to the red zone, from 522 nm to 600 nm, respectively (Table 1). We found that when the amount of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> increased, Ag<sup>+</sup> was reduced to Ag<sup>0</sup> faster so it would be arranged to create larger plates, leading to make red-shift of dipole peak of SNPs. It was suitable with other studies that in-plane dipole peak of the SNPs depends on their size [1, 2, 5, 7]. This was also consistent with our previous research [4] when silver nanoplates manufactured by

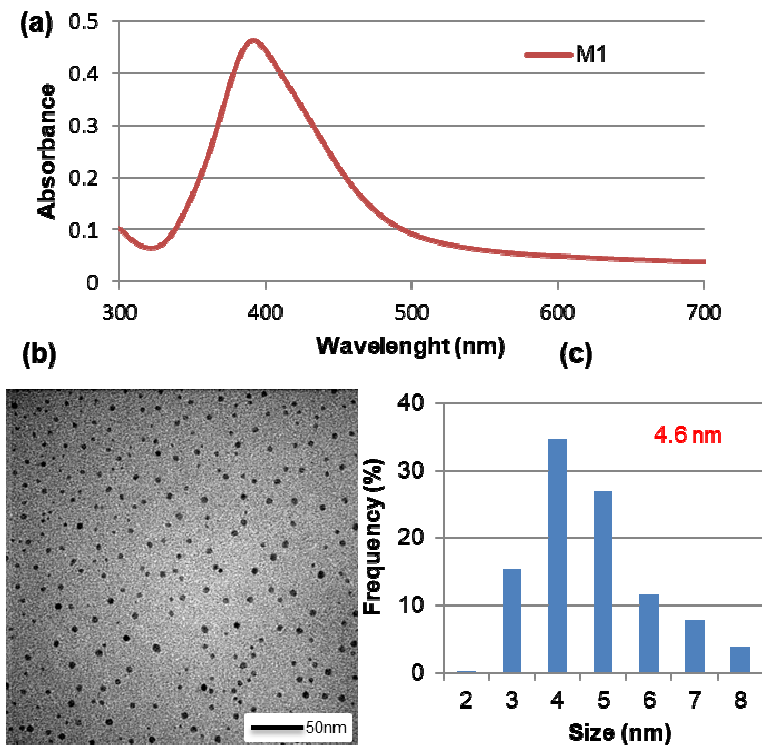


Fig. 2. UV-Vis spectra (a), TEM image (b) and size distribution diagram (c) of seeds.

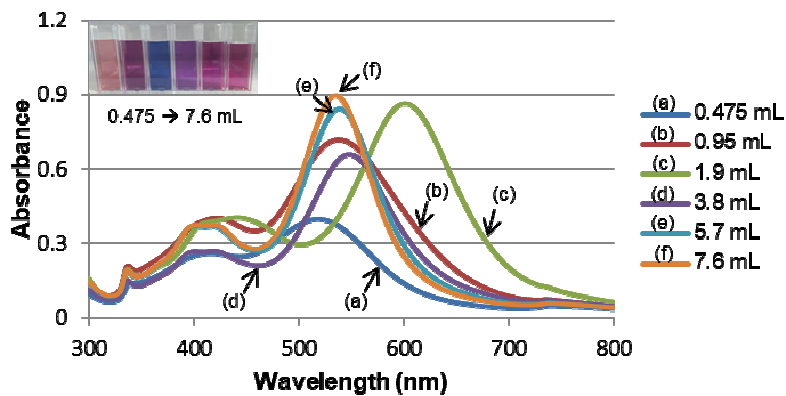
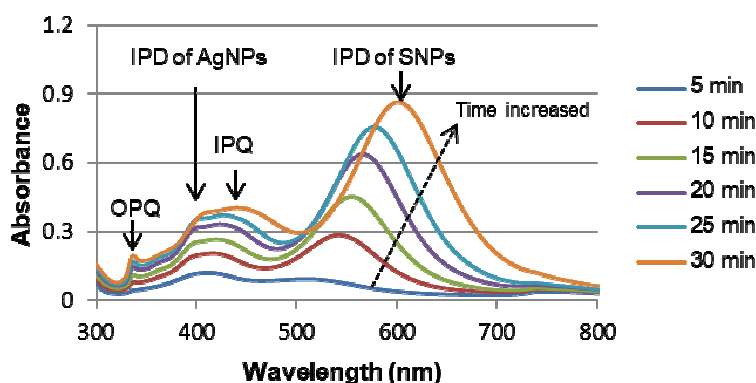


Fig. 3. UV-Vis spectra of SNPs with different L-Ascorbic acid volumes ranging from 0.475 to 7.6 mL.

a single step reduction method. On the other hand, TSC is necessary for making SNPs because it not only serves as a selective capping agents for (111) facets, but also acts as a strong coordination ligand with  $Ag^+$  ions [6].

However, by continuing to increase the volume of  $C_6H_8O_6$  from 3.8 mL to 7.6 mL the dipole peak wavelengths decreased from 558nm to 535nm, respectively (see Table 1). Therefore, we found that the amount of  $C_6H_8O_6$  increased as  $Ag^+$  was reduced to  $Ag^0$  faster, the new  $Ag^0$  atoms did not completely cling to the seeds to form a plate, that aggregated together to form spherical silver nanoparticles without joining and developing SNPs. So, in our study, the amount of 5 mM  $C_6H_8O_6$  is suitable to form largest SNPs was 1.9 mL.



**Fig. 4.** UV-Vis spectra of SNPs with 1.9 mL of  $C_6H_8O_6$  at different reaction times.

We chose a sample of 1.9 mL of  $C_6H_8O_6$  to study a quantitative investigation of the amount of  $AgNO_3$  added, corresponding to the different reaction times. The UV-Vis results were shown in Fig. 4 and Table 1.

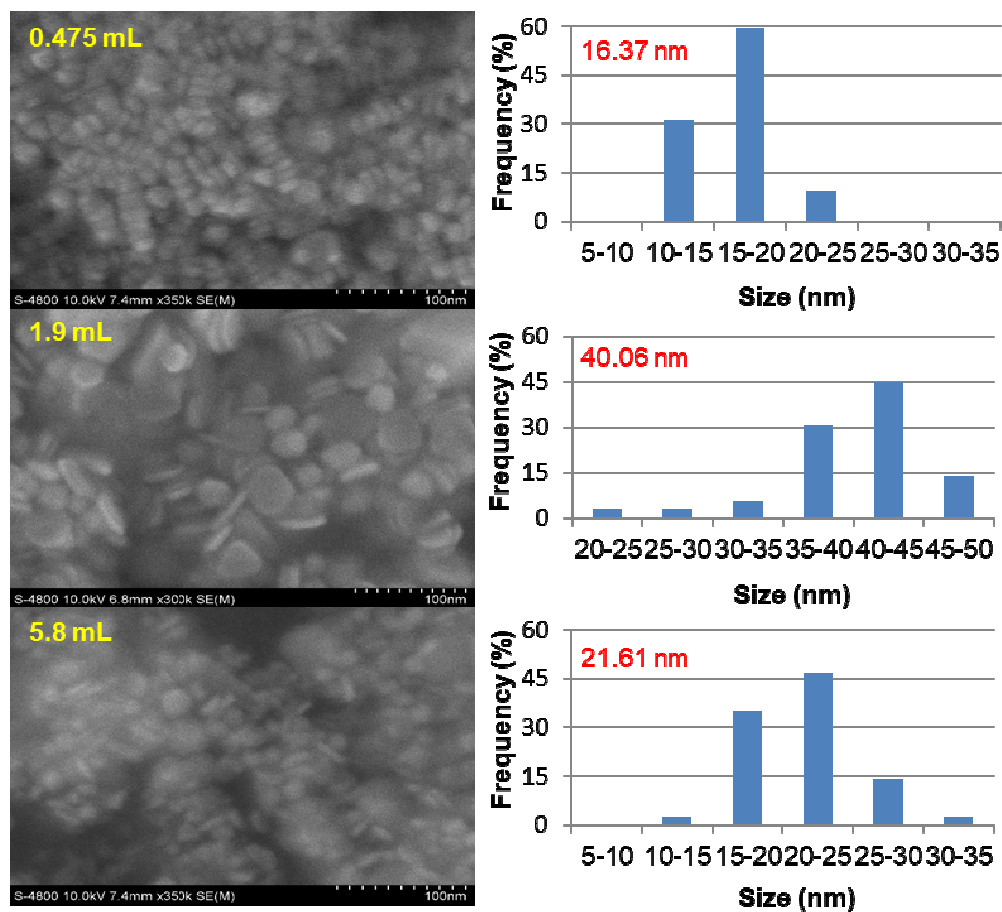
**Table 1.** Absorption peaks of SNPs with different L-Ascorbic acid volumes (left) and SNPs with 1.9 mL  $C_6H_8O_6$  at different reaction times (right).

Samples	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)	Samples	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)
0.475 mL	337	-	522	5 min	337	410	510
0.95 mL	337	410	544	10 min	337	418	542
1.9 mL	337	441	600	15 min	337	420	555
3.8 mL	337	421	558	20 min	337	423	567
5.7 mL	337	420	539	25 min	337	428	578
7.6 mL	337	420	535	30 min	337	441	600

After 5 minutes, the UV-Vis spectra at 5 min showed that there were three unclearly SPR peaks. From 10 minutes onwards, the shape of the peaks was clearer. The SPR of SNPs showed three peaks corresponding to the out-of-plane quadrupole (OPQ), in-plane quadrupole (IPQ) and in-plane dipole (IPD) resonance [10]. All samples had the first peak corresponding to the out-of-plane quadrupole SPR at 337 nm, which was characterized by the thickness of the plate [4–7] and did not change significant with the reaction time.

On the other hand, as the reaction time increased corresponding to the amount of  $\text{Ag}^+$  added, dipole SPR peak (peak 3) was shifted to the red zone: 5 minutes (510 nm), 10 minutes (542 nm), 15 minutes (555 nm), 20 minutes (567 nm), 25 minutes (578 nm) and the value at 30 minutes was 600 nm, demonstrated plate developed in size and more in number, resulting in absorption intensity also increased.

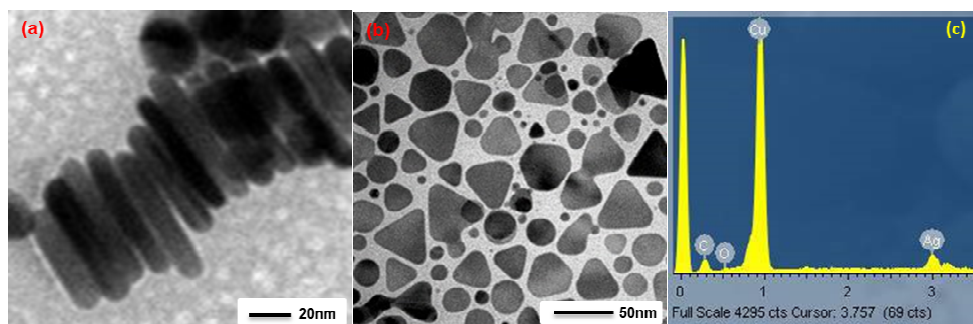
However, there was a unclearly weak peak at 400 nm corresponding to the in-plane dipole resonance of silver spherical nanoparticles. Because the absorbance of dipole peak of SNPs was extremely stronger than silver spherical nanoparticles, we suggested that the SNPs were formed by almost in this sample.



**Fig. 5.** FE-SEM images and the size distribution graphs of SNPs with different Ascorbic acid concentration.

The FE-SEM images and the size distribution of SNPs with various  $\text{C}_6\text{H}_8\text{O}_6$  content were presented in (Fig. 5). The sample with 0.475 mL  $\text{C}_6\text{H}_8\text{O}_6$  showed an existence of particles with a plate shape but it was unclear, the average size was 16.37 nm, the size distribution was stable in the range of 15 - 20 nm. With 1.9 mL of  $\text{C}_6\text{H}_8\text{O}_6$ , we found in the sample that the SNPs were

clear with the average size of 40.06 nm relatively uniform. When increasing to 5.7 mL of  $C_6H_8O_6$ , the size of SNPs was reduced by almost half, from 40.06 nm to 21.61 nm and their shapes were unclear and less uniform. This result was consistent with the findings from the UV-Vis results presented above. The suitable amount of  $C_6H_8O_6$  to form largest SNPs in our study was 1.9 mL.



**Fig. 6.** TEM images with two different orientations (a,b) and EDS result (c) of SNPs with 1.9 mL of  $C_6H_8O_6$ .

The TEM images (Fig.6a,b) showed SNPs with a clear plate shape and their sizes were about 40 nm, a uniform thickness of approximately 7-8 nm. The rod-like shape were SNPs that seen from the edge (Fig. 6a). Besides, there were some spherical silver nanoparticles with sizes of 10-15 nm. This result was consistent with UV-Vis and FE-SEM results.

On the other hand, the EDS spectra (Fig.6c) were studied by placing the sample on a copper grid and recording the scan signal, so that the Cu signal was relatively strong. The results of the EDS showed that the peak of silver was clear and that the peak of carbon element and oxygen element were in TSC.

#### IV. CONCLUSION

Successfully fabricated silver nanoplates by a seed-mediated method in which L-Ascorbic acid plays an important role in the formation of silver nanoplates. The UV-Vis chart shows three surface plasmon resonance peaks of silver nanoplates, including the out-of-plane quadrupole at 337 nm, which characterize plate thickness, in-plane quadrupole and in-plane dipole according to the size of silver nanoplates. The results of UV-Vis, FE-SEM and TEM analysis showed that the size of silver nanoplates depended on the concentration of L-Ascorbic acid and the suitable amount of L-Ascorbic acid to form largest silver nanoplates was 1.9 mL.

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