JOURNAL OF MATERIALS SCIENCE **37** (2002) 5083 – 5087

Deposition of silver nanoparticles on montmorillonite platelets by chemical plating

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A method for directional deposition of silver nanoparticles on montmorillonite platelets was developed. In order to utilize the elemental layer sheets of montmorillonite as substrate for chemical plating, the clay was modified with dodecyl benzyl dimethyl ammonium chloride, and then exfoliated in toluene with the aid of ultrasonic. Silver deposition in dimethyl formamide with PVP as stabilizer was nucleated at the montmorillonite surface and in the solution. Directional deposition was successful through sensitization with stannous isooctoate and reduction of silver nitrate with Tin(II) ions.

1. Introduction

Synthesis of nanoparticles is an interesting field in solid states chemistry. Recently, much interest has been shown for ultrafine metal particles because they have unique properties that are different from bulk metals in optical property, catalytic activity, magnetic property, and so on [1–5]. In particular, many studies have been devoted to silver, gold and copper colloids. Usually nanoparticles are spherical in shape. The preparation of nano scale flake-shaped metal particles, however, has not been found in the known literatures. Nano scale metal flakes are very interesting in electronics, mechanics, electromagnetics, communication and stealth technology.

Preparation of silver particles is attracting a great deal of attention because of its unique properties, such as extremely high electric conductivity and extremely low emission coefficient. Organized structures of silver nanoparticles have been prepared on different substrates for various applications, such as surface-enhanced Raman spectroscopy (SERS) [6], nanoelectrode [7], and modulation of optical properties [8]. Techniques used for deposition of metal nanoparticles on particular substrates involve the use of bifunctional molecules, which can attach to both the substrate and the metal [9, 10].

Electroless plating has recently been used for modification of carbon nanotubes [11, 12] and spherical SiO_2 colloids [13]. In the later process, the surface of the silica spheres was modified with Sn^{2+} ions and then a redox reaction was carried out, in which the Sn^{2+} was oxidized to Sn^{4+} and at the same time Ag^+ ions was reduced to metallic Ag.

Layered silicates, e.g., montmorillonite, have been used in polymer nanocomposites with significant improvement in mechanical properties [14, 15]. Montmorillonite possesses a 2-to-1 layered structure with a single octahedral aluminum layer located between two layers of silicon tetrahedral [16]. Each layer is about 1nm thick with lateral dimension of 100–1000 nm [17]. The clay can be delaminated into elemental sheets without difficulty. It is therefore tempting to utilize these sheets as the substrate for the preparation of nano scale metal flakes by means of electroless plating.

In the present article, we report the deposition of silver nano particles on discrete montmorillonite platelets based on a common procedure of electroless plating. Through sensitization, directional growth of silver particle on the surface of platelets has been achieved, instead of random nucleation in the solution. The process can be used for the preparation of nano scale flakes deposited with silver particles, and for the observation of montmorillonite platelets by transmission electron microscopy in solutions as well.

2. Experimental section

2.1. Materials

$AgNO_3$, toluene, methanol and nitric acid were all analytic reagents supplied by Beijing Chemical Factory. Polyvinylpyrrolidone (PVP, molecule weight 30,000) was supplied by Beijing Chemical Reagents Co. Trifluoroacetic acid and DMF were anhydrous chemical agents respectively from Beijing Jinlong Chemical Reagents Co. and Beijing Yili Fine Chemical Co. Stannous isooctoate was supplied by Beijing Elf Atomchem Polystab Co. Dodecyl benzyl dimethyl ammonium chloride (DBDA) was prepared in this laboratory, and Na-based montmorillonite (MMT, Cation exchange capacity 1 meq/g), was supplied by the Engineering plastics Laboratory of Institute of Chemistry, CAS.

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2.2. Preparations

2.2.1. Organophilic montmorillonite

Na-montmorillonite was added to deionized water. The mixture was stirred vigorously at room temperature to form a uniform 5 wt% suspension. Then a DBDA nitric acid solution of 2 wt% concentration (the mole ratio of DBDA to nitric acid was 1 : 1) was dropped. DBDA was 20% in excess for exchange of the Na^+ cations. Then the temperature was raised to 80°C and kept at the temperature for 24 hours. The solid was separated with a centrifuge, and was washed with deionized water to neutrality. The neutral organophilic montmorillonite (DBDA-MMT) was dried in vacuo, and pulverized to pass 500 meshes sieve.

2.2.2. Deposition of silver

0.05 g DBDA-MMT was added to 100 cm^3 toluene. The mixture was treated in a 380 w ultrasonic generator for 3 minutes. As DBDA-MMT was exfoliated with the aid of ultrasonic, the mixture became practically transparent.

To 15 cm^3 of the above DBDA-MMT-toluene mixture, 11 cm^3 of a solution of stannous isooctoate (containing 1.20 mmol Sn^{2+}) and CF_3COOH (1.80 mmol) in a 50% (v/v) methanol-toluene mixture was added. This resulted in deposition of Sn^{2+} on to the surface of the platelets. After 1 h at room temperature, 40 ml of a solution of $AgNO_3$ (4.0 mmol) in a methanol/toluene (50% v/v) mixture was introduced, and stirred for 24 hours. PVP was used as stabilizer at the molar ratio of vinylpyrrolidone unit to $AgNO_3$ 10/1. This resulted in directional deposition of Ag nanoparticles on the surface of DBDA-MMT platelets.

2.3. Characterization

2.3.1. Electron microscopy

A drop of the solution containing platelets was placed on a carbon-covered copper grid. After the solvents were dried, transmission electron microscopic (TEM) study was carried out on a Hitachi H-800 transmission electron microscope. For the calculation of average diameter and standard deviation, 300 silver particles in a TEM micrograph were measured at random.

2.3.2. Spectroscopic studies

UV-visible spectra were recorded on a Shimadzu UV-1601 PC spectrophotometer, using quartz cuvettes of 1-mm thickness.

X-ray diffraction (XRD) measurements were conducted on a Japan D/max 2400 Diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm) with a generator voltage of 40 kv and a generator current of 100 mA. The scan started from a 2Theta value of 1.5°. The scanning rate was 2°/min. The basal spacing d_{001} was calculated according to Bragg equation $2d \sin\theta = \lambda$.

X-ray photoelectron spectra (XPS) were taken at an angle of 0° using ESCA Lab 220i-XL system. As the X-ray source, the Al K_α (15 kV × 20 mA) line was used, with spectrophotometer step energy of 1486.6 and 0.05-eV resolution.

3. Results and discussion

3.1. Exfoliation of montmorillonite

Montmorillonite modified with long chain quarternary ammonium salt (DBDA) exfoliated in toluene easily with the aid of ultrasonic. The course brought about a dramatically raising of viscosity. When a mixture of 2.5 wt% DBDA-MMT in toluene was treated in the ultrasonic generator, the system became a transparent gel in one minute.

The exfoliation of DBDA-MMT in toluene was studied by XRD in usual way [18–22]. In Fig. 1, XRD traces are shown. The basal spacing of Na-MMT was 1.24 nm. Through modification with DBDA, the basal spacing was expended to 2.88 nm. After ultrasonic treatment, the 001 diffraction was almost disappeared, indicating the loss of the structure registry.

In the TEM photographs, individual platelets of DBDA-MMT could not be clearly observed (Fig. 3a) because thin platelets did not give rise to a high enough contrast.

3.2. Deposition of silver in DMF

For the synthesis of silver nano particles, organic substances, such as ethanol, N,N′-dimethylformamide (DMF) and formaldehyde, can be used to reduce silver nitrate. DMF is a moderate reducing agent. Silver cation was reduced and the formed carbarmic acid decomposes easily [23]:

$$\begin{aligned} &\mathrm{HCONMe_2} + 2\mathrm{Ag}^+ + \mathrm{H_2O} \rightarrow 2\mathrm{Ag}^0 \\ &\quad + \mathrm{Me_2NCOOH} + 2\mathrm{H}^+ \\ &\mathrm{Me_2NCOOH} \rightarrow \mathrm{CO_2} + \mathrm{Me_2NH} \end{aligned}$$

The reaction proceeds at a meaningful rate even at room temperature and in the dark. Moreover, the reaction can be conducted without taking any special care with regard to the presence of oxygen.

Reduction of silver nitrate in DMF was readily observed by the showing up of a yellow color, which deepened to greenish black as the time went by. In the UV-vis spectrum (Fig. 2) a characteristic peak for Ag^0 at 415 nm appeared with the reduction of Ag^+ by DMF.

PVP (the molar ratio of vinylpyrrolidone unit to $AgNO_3$ 10/1) was used as stabilizer. The Ag^+ ions and

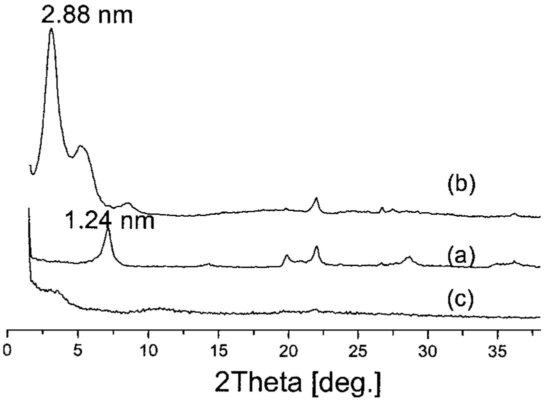

Figure 1 XRD patterns for (a) Na-MMT, (b) DBDA-MMT and (c) DBDA-MMT after ultrasonic treatment in toluene.

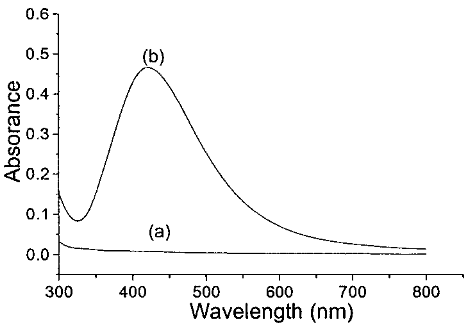

Figure 2 UV- vis spectra for (a) $AgNO_3$-DMF system and (b) after 12 h at 60°C.

Ag particles were loosely bonded to the chain of PVP to make the system stable. It was found that the average diameter of silver particles changed with the ratio of vinylpyrrolidione unit/Ag^+. However, the stabilizer did not bring about directional growth of silver particles on the surface of DBDA-MMT platelets.

For example, to 15 cm^3 of the 0.05 wt% exfoliated DBDA-MMT-toluene mixture, 30 cm^3 of a solution of $AgNO_3$ (4.0 mmol) in DMF was introduced. The mixture was heated at 60°C for 12 h to effect the reduction of silver nitrate. As demonstrated by the TEM micrograph (Fig. 3b), silver particles were in the range of 10–30 nm formed uniformly in the solution in the absence of MMT plates. It is seen that along with deposition of silver on the DBDA-MMT plates, the contour of the MMT platelets became clear (Fig. 3c). Although more particles were found on the surface of MMT platelets, the difference in number density on the surface of DBDA-MMT platelets and in the solution was insignificant. That is to say, nucleation took place not only at the surface but also in the solution.

3.3. Directional deposition of silver particles

In order to achieve directional deposition of silver particles on the MMT platelets, sensitization of the surface was studied. The procedure used for the present work was similar to that used in the industry for silver-plating of plastics [24].

The sensitization treatment brings Tin(II) ions to the surface of MMT platelets. In the procedure, stannous isooctoate was used as the resource of Tin(II), and trifluoroacetic acid was used to facilitate the dissolution.

Adsorption of stannous ions on the MMT platelets was confirmed by XPS, as shown in Fig. 4. After the sensitization treatment, MMT was separated and washed thoroughly. In the spectrum for DBDA-MMT after sensitization (Fig. 4b), the peak of Sn_{3d} is remarkable. According to the literature [25], the 3d peak for Tin(II) should be positioned around 486.7 eV. In Fig. 4b, the peak at 487.0 eV should be designated to Sn_{3d} of Tin(II). The presence of isooctoate anion made a slight change in the binding energy.

After sensitization, reduction of silver nitrate was effected with Tin(II) ions in methanol/toluene system at room temperature. Formation of silver particles was again demonstrated by the adsorption at 410 nm in the UV-vis spectrum.

By means of sensitization, directional deposition on MMT platelets was successful. It is seen in the TEM photographs (Fig. 5) that flakes of dimension ca. 100–300 nm were densely deposited with silver particles, and very few silver particles were formed in the solution.

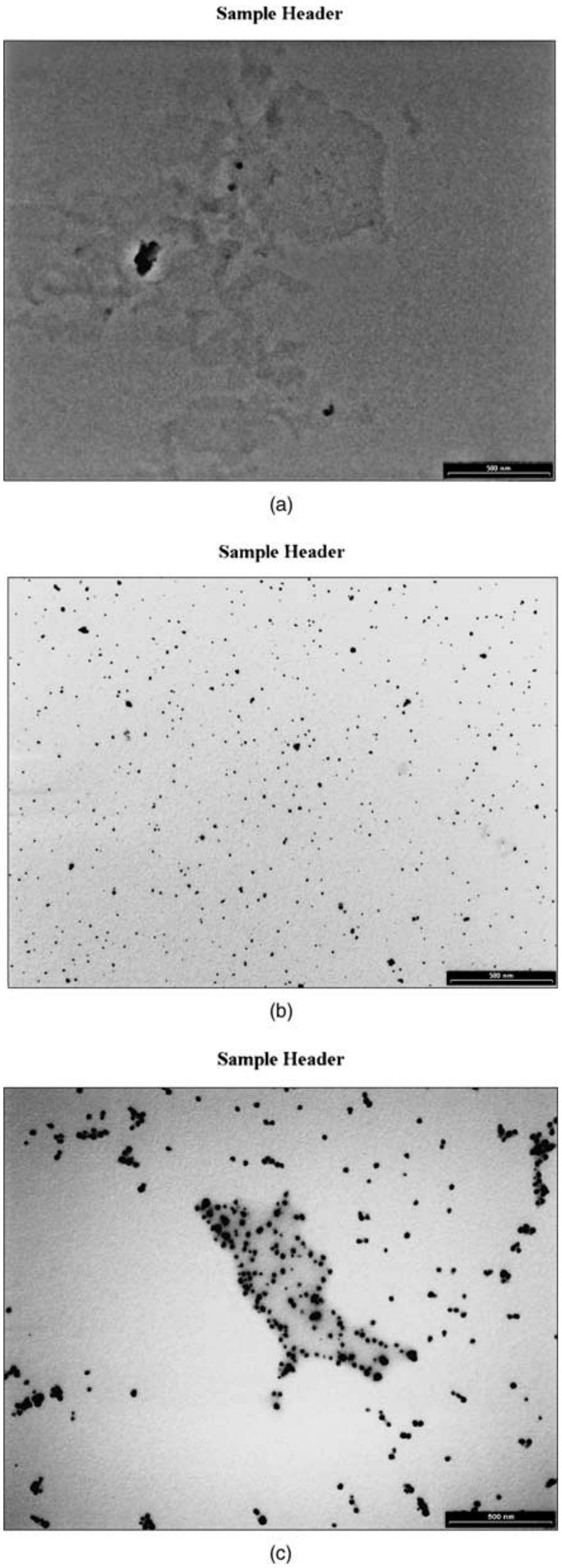

Figure 3 TEM micrographs for (a) DBDA-MMT platelets in toluene; (b) silver particles formed in DMF stabilized with PVP in the absence of DBDA-MMT platelets; (c) silver particles formed in DMF in the presence of DBDA-MMT platelets stabilized with PVP.

It was found that the moral ratios of $[Ag^+]/[Sn^{2+}]$ in the reaction system made a significant influence

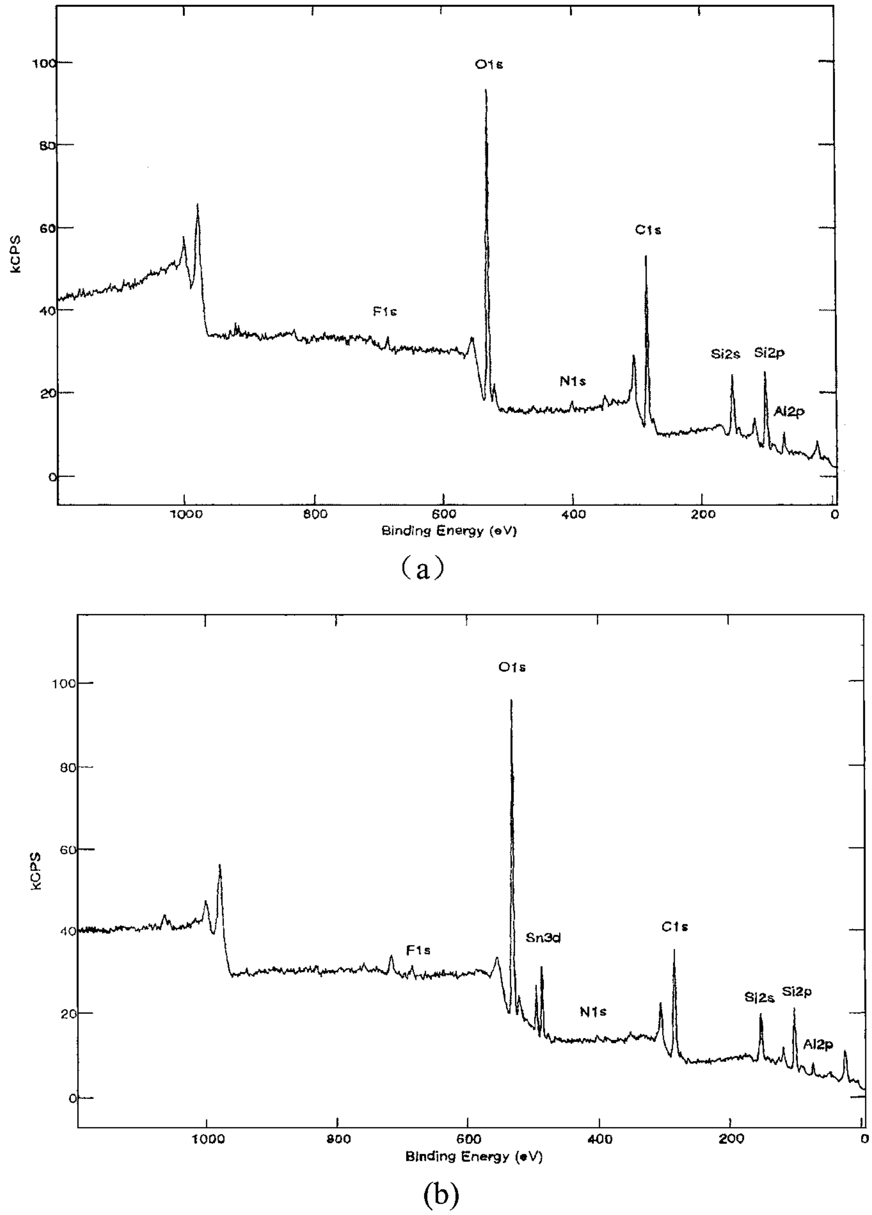

Figure 4 XPS spectra for (a) DBDA-MMT and (b) DBDA-MMT after sensitization.

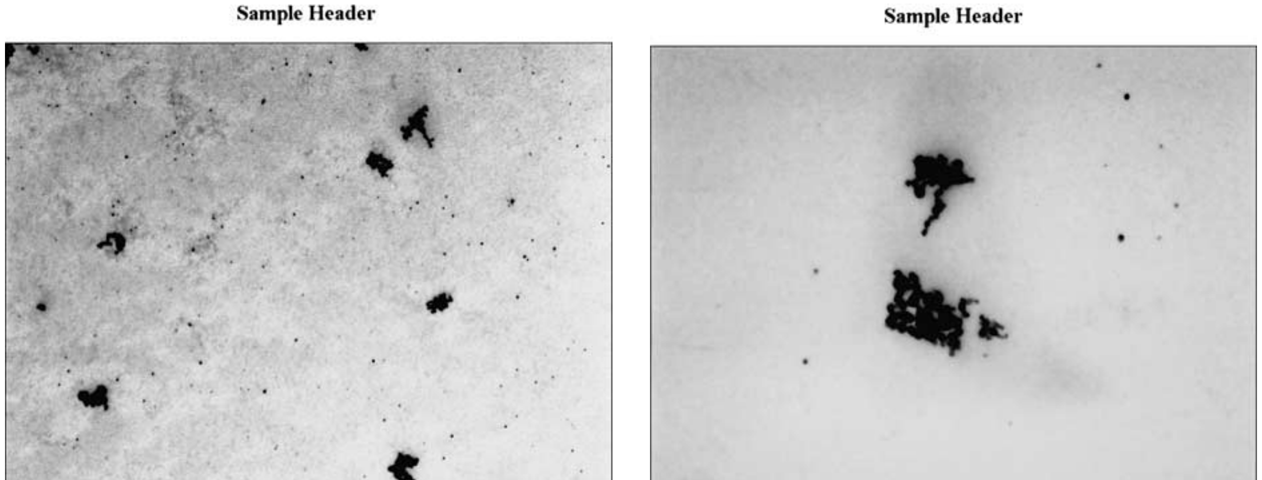

Figure 5 TEM photographs for MMT platelets after directional deposition of silver particles: (a) magnification 10,000 and (b) magnification 150,000.

TABLE I Effect of Ag^+/Sn^{2+} molar ratio on the silver particle deposition

Ag^+/Sn^{2+} molar ratio	Range of diameter (nm)	Average diameter (nm)	Standard deviation (nm)
18/1	8.4–27.4	15.7	3.9
16/1	9.7–11.7	21.1	3.3
14/1	2.9–23.2	10.8	2.8
12/1	4.2–16.9	9.7	2.2
10/1	7.6–25.3	8.6	2.4
8/1	4.2–19.0	11.4	2.8
4/1	5.5–11.4	9.3	1.9
2/1	6.3–21.1	11.3	2.7
1/1	6.4–22.5	11.8	2.8
1/2	6.8–31.7	15.1	4.0

on silver deposition. As shown by the data collected in Table I, lowest average particle size and narrowest size distribution were achieved in the system of $[Ag^+]/[Sn^{2+}]$ ratio 4/1, where silver nano particles of 9.3 nm in average were deposited on the DBDA-MMT platelets. Moreover, all silver particles were deposited on the surface of MMT platelets in the case of $[Ag^+]/[Sn^{2+}]$ ratio 4/1. When the $[Ag^+]/[Sn^{2+}]$ ratio was lower than 2/1, some silver particles were formed in the solution rather than on the platelets. In this case Sn^{2+} was not completely adsorped by the platelets, and reduction of Ag^+ took place not only on the surface of platelets but also in solution.

4. Conclusions

Organophilic DBDA-MMT was delaminated in toluene with the aid of ultrasonic. MMT platelets were used as substrate for deposition of silver particles. In DMF without sensitization, silver particles were nucleated both at the MMT surface and in the solution. Directional deposition of silver on MMT platelets was achieved when the substrate was sensitized with stannous isooctoate first and the reductin was effected in methanol/toluene system. This process opened up an approach for the preparation of nano scale flakes deposited with silver.

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Received 31 December 2001
and accepted 20 August 2002