The Fabrication of Metal Nano Particle/Polymer Nanocomposite Thin Films By Layer-by-Layer Sequential Adsorption Method and Their Characterization

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Metal nano particle/polymer nanocomposite thin films were fabricated by layer-by-layer sequential adsorption method. Polymer coated metal nano particles were prepared by in-situ reduction of protective polymers. Polyelectrolytes were used as protective polymers. And carboxylate-modified metal nano particles were prepared by modifying the surface of metal nano particles with self-assembled monolayer. By modifying the surface of metal nano particles, the surface has negative charge. Polyelectrolytes and self-assembled monolayer prevent the agglomeration of these metal nano particles. The particle size and morphologies were characterized by transmission electron microscopy (TEM). These thin films were characterized by UV-visible spectroscopy, and atomic force microscope (AFM). The cross-sectional images were observed by TEM. From these measurements, it was found that metal nano particles were uniformly distributed in the thin film.

Key words: layer-by-layer, nano particles, self assembly, Ag,

1. INTRODUCTION

Recently, nano-technology has developed and plays an important role in industrial. Ultra thin films and nano particles are drawing attention for various applications. Nano particles have different properties from bulk properties. Arising from their small size, semiconductor and metal nano particles have quantum size effect. Therefore, the assembly of nano particles is important and has potential for optical, electronic, catalytic, and biocompatibility. We fabricated self-assembled thin films composed from polymer and metal nano particles by wet chemical process. Wet chemical approach can offer many advantages over conventional methods (dry process), and include low cost of instrumentation and convenience in use. We used layer-by-layer sequential adsorption method to fabricate self-assembled thin films. Layer-by-layer sequential adsorption method was presented by Decher and co-workers [1]. Layer-by-layer sequential adsorption method was often used for oppositely charged polymers. Sequential dipping causes material to be deposited on the surface because of electrostatic interaction between the charged surface and polyelectrolyte. Once deposited, the layer of polyelectrolyte inverts the surface charge of the material it is adsorbed to, enabling a subsequent layer of polymer to be deposited from the second solution. Since this method used electrostatic interaction between materials, it has also been successfully applied to thin films of all materials having electrical charges (For example: inorganic particles, dyes, clays, enzymes, virus, and protein) [2-3]. This method provides new opportunities for optical [4], electronic [5-8], magnetic [9], filtering [10-11], and sensing devices [12]. By changing the condition of pH and the concentration of salt, it was known that the thickness of the thin films can be controlled [13-14]. The controlling thickness and morphology at a molecular level offer the advantages for nano-technology. Thus, layer-by-layer sequential adsorption method has great potential for various application.

In this study, the preparation and characterization of polymer/metal nano particles composite films by layer-by-layer sequential adsorption method were described. We explored the growth conditions that metal nano particles were uniformly distributed in the thin film. Therefore, we studied the growth conditions, including the effect of the method to fabricate Ag nano particles, and dipping time in Ag nano particle solution.

2. EXPERIMENTAL

All H_2O used was ultra pure water of $18.2 M\Omega$. Substrates for thin film fabrication were silicon wafer, glass slide, and quartz crystal. The substrates were etched by KOH solution (a mixed solution of 5 g KOH and 300 ml ethanol and 200 ml ultra pure water) and rinsed with ultra pure water. The substrates were dried with a nitrogen gas before film deposition.

Polymer coated silver nano particles, described as particle (1), were prepared as follows. 5mM of $AgNO_3$ (Wako) was dissolved in $10^{-2}M$ poly acrylic acid (PAA: Polyscience M_W=90,000, 25% solution) solution. After stirring for few minutes, 0.3ml of $10^{-2}M$ sodium borohydride solution was dropped into PAA solution. The color of the solution turned to yellow. Then, the pH of the solution was changed by HNO_3 solution at 2.5.

Carboxylate-modified Ag nano particles, described as particle (2), were synthesized as follows [15]. 0.5 mmol of $AgNO_3$ (Wako) dissolved as 5 % (w/v) aqueous solution and 1.0 mmol of mercapto succinic acid (MSA : Wako) were mixed in 100 ml methanol, followed by the addition of 25 ml freshly prepared 0.2 M aqueous sodium

borohydride. After 1 h of further stirring, the dark-brown precipitate was collected under a centrifugation force, then washed twice with 20 % (v/v) water-methanol solution through ultrasonic re-dispersion centrifugation process. This process was repeated with using 99.8 % methanol. Finally, the precipitate was dispersed in ethanol and dried in vacuum at 30 °C.

The fabrication of polymer/metal nano particles multilayer thin films was carried out as follows (Fig. 1).
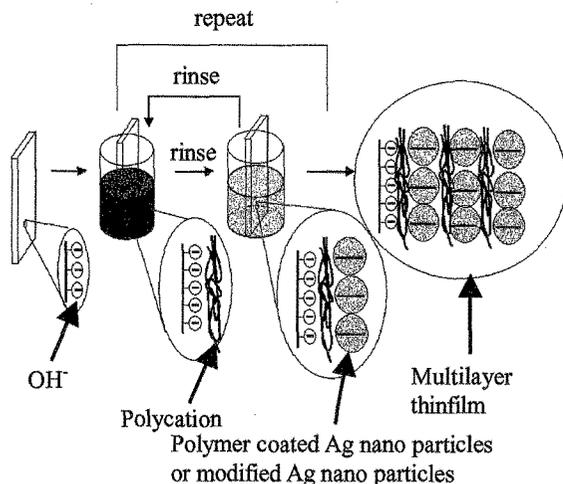
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Fig. 1: The scheme of layer-by-layer sequential adsorption method

(i) (PAH/Ag nano particles in PAA solution) film, described as (i) film

Polyallylamine hydrochloride (PAH:Aldrich M_W= 70,000) 10^{-2} M solution was used as cationic solution. PAA: Ag solution was used as anionic solution. Prior to deposition multilayer, a precursor polyelectrolyte multilayer film was assembled on the substrate. A pre-cleaned substrate was immersed in Poly (diallyldimethylammonium chloride) (PDDA:Aldrich M_w=200,000-350,000 20 Wt%) 10^{-2} M solution for 3 min, then rinsed with water for 2 min twice. Subsequently, the substrate was immersed into Poly (sodium 4-styrene sulfonate: M_W=70,000) PSS 10^{-2} M solution for 3 min, then rinsed with water for 2 min twice. This process was repeated three times. After that, (PAH/Ag nano particles in PAA solution) thin film was prepared on a precursor polyelectrolyte multilayer deposited substrate, similarly. This procedure was repeated twenty times for each layer, referred as (PAH/Ag nano particles in PAA solution)$_{20}$.

(ii) (PDDA/carboxylate-modified Ag nanoparticles) thin films, described as (ii) film

PDDA 10^{-2} M solution was used as cationic solution. Carboxylate-modified Ag nano particles solution were used as anionic solution (5.0×10^{-3} wt %). The deposition process was similar to above-mentioned method. After (PDDA/PSS)$_3$ layer was fabricated, (PDDA/ carboxylate -modified Ag nano particles) layer was fabricated. The films that were fabricated with the condition of the immersion time in Ag solution for 3 min, 10 min, 20min and 30 min were prepared. This procedure was repeated twenty times for each layer, referred as (PDDA/ carboxylate-modified Ag nano particles)$_{20}$. These films fabricated with the condition of the immersion time in Ag solution for 3 min, 10min, 20min and 30min were

respectively referred as (ii-a), (ii-b), (ii-c), and (ii-d).

These films were fabricated by using a mass controlled layer-by-layer adsorption apparatus (Nippon Laser & Electronics Lab., NL-SA10107)

The particles and film characterized by a field emission transmission microscope (FE-TEM: Philips, TECNAI F20) operated at 200kV.

For the observation by cross-sectional TEM, ultramicrotomed sections of the organic-inorganic multilayers formed on an anodic polystyrene substrate were prepared in the usual manner employing an ultramicrotome (RMC, MT-XL). Briefly, an encapsulated specimen was trimmed initially with a glass knife. Then electron transparent sections of about more than 50nm thick were prepared by cutting in the direction approximately parallel to the interface of the deposition film and the substrate using a NACC diamond knife (Micro Star Technologies).

The surface morphologies of prepared films observed by atomic force microscope (AFM: Digital Instruments Nano Scope IIIa).

UV-VIS adsorption spectra of the samples were recorded a Shimadzu UV-3150 spectrophotometer in the range 300-800nm with 2nm resolution.

3. RESULTS AND DISCUSSION

The particle sizes of polymer coated Ag nano particles and carboxylate-modified silver nano particles were estimated to about 4.0 nm and 7.0 nm in Fig. 2, respectively.
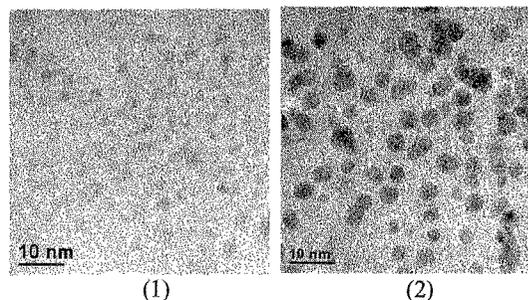

Fig. 2: TEM images of polymer coated Ag nano particles:(1) and carboxylate-modified Ag nano particles:(2)

Fig. 3 is UV-VIS adsorption spectrum of (PAH/Ag nanoparticles in PAA solution)$_{20}$ and (PDDA/ carboxylate-modified Ag nano particles)$_{20}$ thin films. The adsorption band near 430 nm attributes to surface plasmon resonance of Ag nano particles in the dispersion. Compared with the spectrum of (ii-a), the spectrum of (ii-d) shows red shift and broadening of the absorption band and the peak intensity of (ii-d) is larger than (ii-a). As immersion time in Ag solution is long, the peak intensity is larger and peak wavelength shift to long wavelength. These results show that carboxylate-modified Ag nano particles were agglomerated. Since the peak intensity of (ii-a) is larger than (i), the quantity of nano particles distributed in (ii-a) film is larger than (i) film. Therefore, it seems that particle (ii) film is better than particle (i) film.
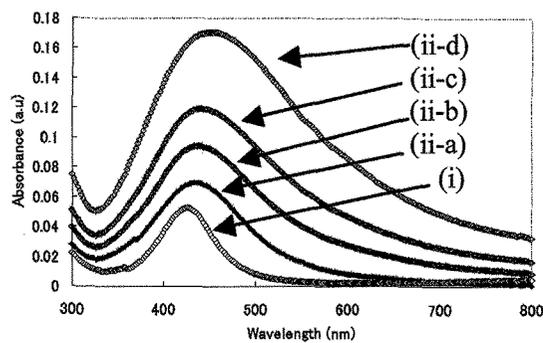
Fig. 3: UV-VIS spectra as (PAH/Ag nano particles in PAA solution)$_{20}$ thin film:(i) and (PDDA/carboxylate-modified Ag nano particles)$_{20}$ thin films:(ii)
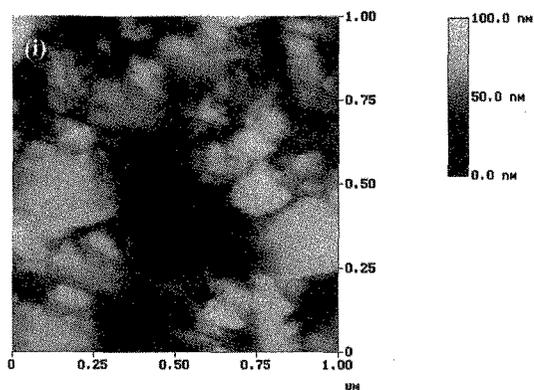

Fig. 4: AFM image as (PAH/Ag nano particles in PAA solution)$_{20}$ thin film:(i)

AFM images of (PAH/Ag nano particles in PAA solution)$_{20}$ thin film and (PDDA/carboxylate -modified Ag nano particles)$_{20}$ thin films on silicon wafers are shown in Fig. 4 and Fig. 5. It should be noted that, due to the size and shape of the tip used in AFM experiments, the particle sizes appear to be much larger than the results yielded with TEM. Fig. 4 reveals that Ag nano particles were agglomerated. Compared with Fig. 4, carboxylate-modified Ag nano particles were uniformly close packed and not agglomerated in the image (ii-a) of Fig. 5. Because PAH and PAA are weak polyelectrolytes, the polymer chains are loop. Additionally, in (ii) film, Ag nano particles were self assembled with polyelectrolyte directly (PDDA/Ag nano particles), but in (i) film, Ag nano particles with the condition that nano particles were mixed in polyelectrolyte solution were self assembled with polyelectrolyte (PAH/Ag nano particles in PAA solution). Therefore, it seems that the agglomeration was observed in Fig. 4. While, in Fig. 5, as immersion time in Ag solution was longer, island growth was remarkably observed. Comparing image (ii-a) and image (ii-b), in image (ii-b) Ag nano particles were uniformly close packed more than in image (ii-a). While, island growth of carboxylate-modified Ag nanoparticles was found in image (ii-c) and (ii-d). In layer-by-layer sequential adsorption method, it is known that nano particles were self assembled in the state of island [16]. It is seemed that Ag nano particles were agglomerated because of the van der-Waals force and hydrogen-bond
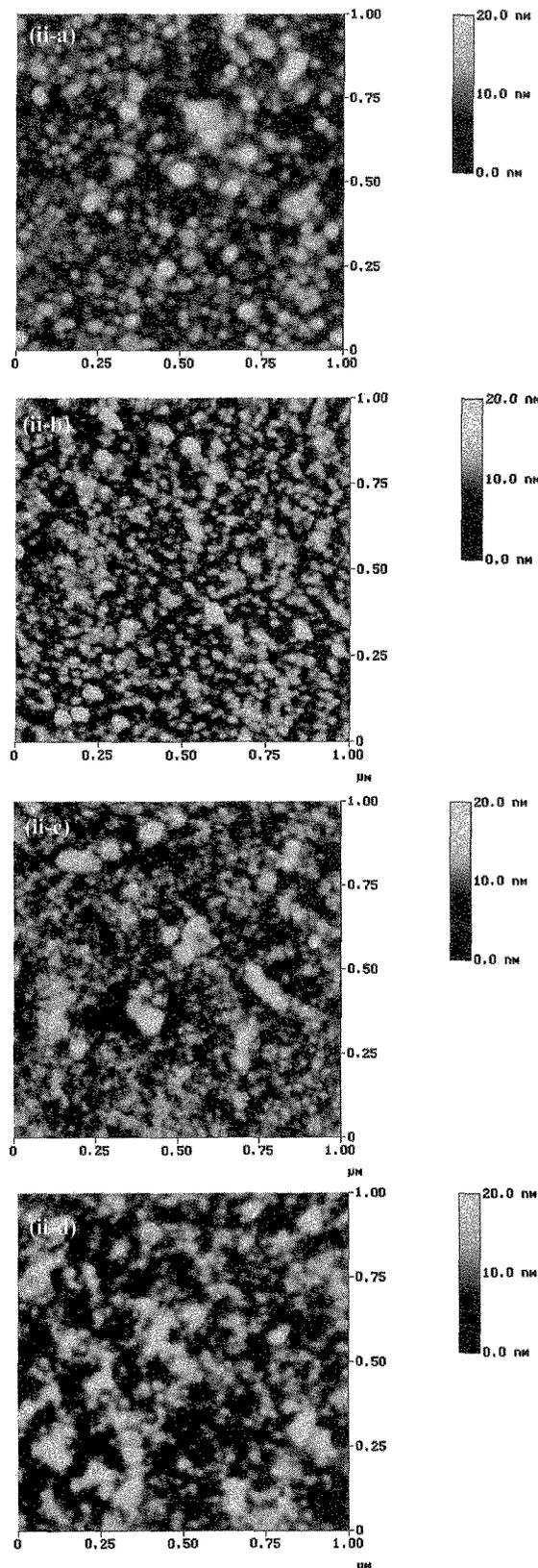

Fig. 5: AFM images of (PDDA/carboxylate-modified Ag nano particles)$_{20}$ thin film:(ii)

by the groups on the surface between carboxylate-modified Ag nano particles when the

immersion time in Ag solution was long [17]. RMS value, described as root-mean-square, was 3.650 nm (ii-a) and 4.950 nm (ii-d), respectively. It was found that the (PDDA/ carboxylate-modified Ag nano particles)$_{20}$ thin film was nearly flat by RMS value. When the immersion time in Ag solution was too long, Ag nano particles tend to be self assembled with the condition of island growth of nano particles. As the result of their agglomeration, it is seems that island growth of Ag nano particles was observed.

In Fig. 6, frequency shift of (PDDA/carboxylate-modified Ag nano particles)$_{20}$ thin films is shown. From Fig. 6, as the immersion time in Ag solution was long, the frequency shift of thin film was large. Frequency shift of (ii-b) and (ii-c) at 20 bilayers is almost equal. But, in Fig. 3, the peak intensity of (ii-c) was larger than (ii-b). From the results of AFM, compared with (ii-b), Ag nano particles in (ii-c) film were agglomerated. Therefore, it seems that though frequency shift of (ii-b) was nearly equal to (ii-c) at 20 bilayers in Fig. 6, the peak intensity was large by agglomeration of Ag nano particles in Fig. 3. The linearities of in the growth of (ii-a) and (ii-b) were better than (ii-c) and (ii-d). In the results of (ii-c) and (ii-d), when the number of bilayers was 13, frequency shift was almost saturated. This result shows the adsorption of nano particles was saturated. From these results, it seems that when the immersion time was long, the surface charge was not uniform by the agglomeration of Ag nano particles by island growth. Therefore, the adsorption of PDDA decreased. As the result, the surface charge was not change, and the next layer was not adsorbed. Therefore, it is seems that the adsorption was almost saturated. From the results of Fig. 5 and Fig. 6, it is cleared that Ag nano particles in the film fabricated with the condition of (ii-b) were most uniformly distributed in the film.
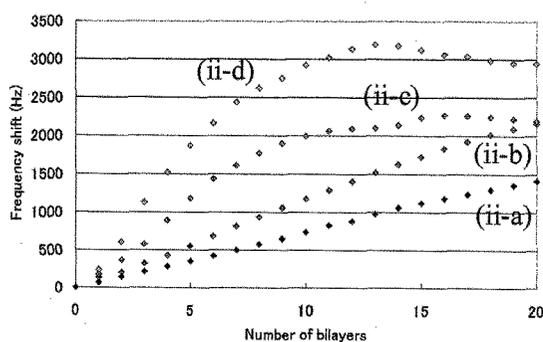
Fig. 6: Characteristics of (PDDA/carboxylate-modified Ag nano particles)$_{20}$ thin film growth by quarts crystal microbalance

In Fig. 7, Cross-sectional TEM image of (PDDA/ carboxylate-modified Ag nano particles)$_{20}$ thin film fabricated with the condition of (ii-b) is shown. It revealed that Ag nano particles were deposited flatly on polystyrene substrate.
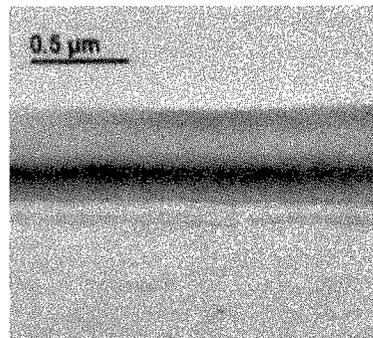
Fig. 7: Cross-sectional TEM image of (PDDA/ carboxylate-modified Ag nano patricles)$_{20}$ thin film:(ii-b)

4. CONCLUSIONS

By using layer-by-layer sequential adsorption method, polymer/metal nano particles hybrid thin film was fabricated. Carboxylate-modified Ag nano particles were uniformly distributed in the thin film. But, when immersion time in carboxylate-modified Ag solution was longer, the agglomeration was generated, and red shift and broadening of the adsorption band were comfirmed. Also, because of island growth of nano particles, it was difficult for PDDA to be deposited. As the result, it was thought that the adsorption was saturated.

5. REFERENCE

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