

Fabrication and Spectroscopic Properties of Hybrid Nanoassemblies Consisting of Metal Nanoparticles and Polymer Nanosheets

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The paper describes a versatile method for fabricating hybrid nanoassemblies of metal nanoparticles and polymer nanosheets and their spectroscopic properties. We prepared cationic polymer nanosheets by the Langmuir-Blodgett technique. The polymer nanosheets can immobilize metal nanoparticles by immersion in an aqueous solution containing metal nanoparticles. Both gold and silver nanoparticles form a monolayer on the polymer nanosheets. The driving force is based on the electrostatic interaction between positively charged polymer nanosheets and negatively charged metal nanoparticles. The amount of immobilized metal nanoparticles strongly depends on the cationic comonomer contents. Spectroscopic properties were also investigated in terms of hybrid nanoassembly structure.

Key words: nanoparticle, polymer, Langmuir-Blodgett, surface plasmon

1. INTRODUCTION

Metal nanoparticle attracts attention due to its unique features; quantum size effect, localized surface plasmon, and effective catalysis, etc [1, 2]. For instance, gold nanoparticles are expected as a high sensitive biosensor due to strong surface plasmon absorption bands [3]. To extend these fascinating aspects to further device application, a key issue is immobilization of metal nanoparticle on solid substrates. Immobilization of gold nanoparticle requires not only surface chemistry but also smooth and well defined surface at the nanometer precision. To meet these requirements, immobilization of metal nanoparticles with organic ultrathin films has been extensively investigated such as self-assembled monolayers [4], layer-by-layer film [5], and Langmuir-Blodgett (LB) film [6]. We have investigated gold nanoparticle ordering with polymer LB films [7]. The cationic polymer nanosheets fabricated by the LB technique [8] can immobilize metal nanoparticle through electrostatic interaction, resulting in the uniformly distributed metal nanoparticle monolayer formation. Besides, we can construct multilayer building blocks comprised of metal nanoparticle monolayer and polymer nanosheets. Patterned polymer nanosheets can be also obtained by photopatterning process. Therefore metal nanoparticles can be selectively immobilized on patterned polymer nanosheets. In this paper, we present preparation of hybrid nanoassemblies consisting of metal nanoparticles and polymer nanosheets. Noble metal gold and silver nanoparticles were utilized to make two-dimensional metal nanoparticle arrays. The spectroscopic properties of the hybrid nanoassemblies are discussed in terms of surface plasmon bands.

2. EXPERIMENTAL

2.1 Materials

N-Dodecylacrylamide (DDA) was synthesized according to a published process [9]. 4-Vinylpyridine

(VPy) was purchased (Aldrich) and vacuum-distilled before use. HAuCl_4 , AgNO_3 , and trisodium citrate dihydrate were purchased and used without further purification. Amphiphilic copolymers, poly(*N*-dodecyl acrylamide-*co*-4-vinylpyridine)s (p(DDA/VPy)s) with different VPy contents were prepared in toluene by radical copolymerization method. The contents of the comonomer VPy used in this study were 5.9, 11, and 29 mol%, determined by UV spectroscopy. Copolymers (p(DDA/DADOO)s, Fig. 1) were synthesized according to the literature [10]. The contents of the comonomer *N*-2-(2-(2-aminoethoxy)ethoxy)ethylacrylamide (DADOO) contents were determined by ^1H NMR. Monodispersed

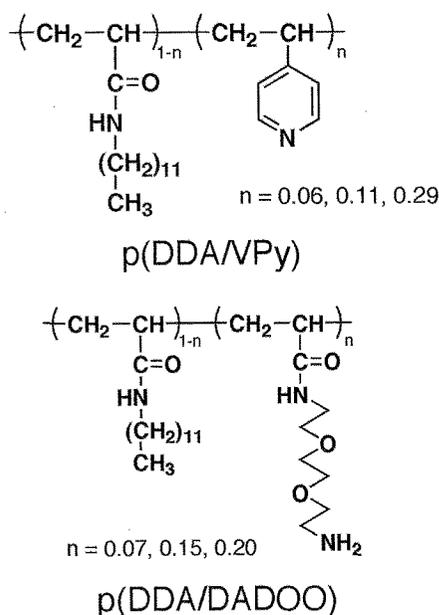


Fig. 1. Chemical structure of p(DDA/VPy) and p(DDA/DADOO).

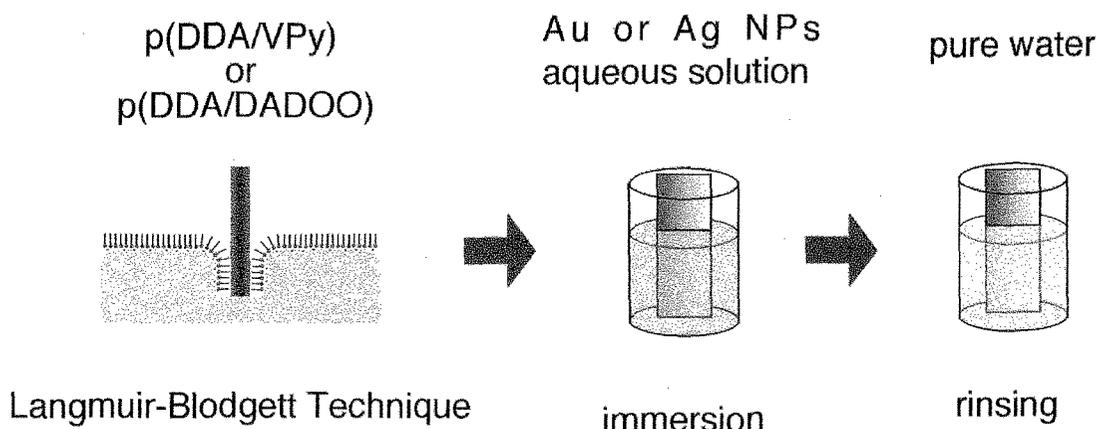


Fig. 2 Preparation of hybrid nanoassemblies with metal nanoparticle and polymer nanosheets.

gold nanoparticles were prepared by reduction of HAuCl_4 by trisodium citrate dihydrate in an aqueous solution under reflux [11]. Silver nanoparticles were synthesized from AgNO_3 and trisodium citrate dihydrate in a similar manner. The diameter determined by SEM observation was *ca.* 30 nm for gold nanoparticles and *ca.* 80 nm for silver nanoparticles.

2.2 Preparation of hybrid nanoassemblies

Glass slides and silicon wafers were cleaned with sonication and the surface was made hydrophobic before use. The experimental procedure for immobilizing the metal nanoparticles has been reported elsewhere [8]. Briefly, the cationic polymer nanosheets were transferred on solid supports by the Langmuir-Blodgett technique. Two-layer p(DDA/VPy) or p(DDA/DADOO) LB films were transferred on solid supports keeping surface pressure and temperature at 30 mN/m and 15.0 °C. The substrate was immersed in an aqueous solution of metal nanoparticles at pH = 6.0 and then rinsed in distilled water. The process was repeated to achieve the desired number of layers.

2.3 Measurements

UV-Vis absorption spectra measurements were carried out with a UV-Vis spectrophotometer (U-3000, Hitachi Co., Ltd). SEM images were taken by using a FE-SEM (JSM-7400F, JEOL) for gold nanoparticles and a high resolution SEM (S900, Hitachi) for silver nanoparticles. All the measurements were carried out under room temperature unless otherwise indicated.

3. RESULTS AND DISCUSSION

3.1 Metal nanoparticle immobilization

As described in previous papers [8,10], both copolymers of p(DDA/VPy) and p(DDA/DADOO) form highly oriented and well ordered monolayers at the air/water interface. The transfer ratios of the monolayers were almost unity for both up and down strokes. The thickness of the transferred monolayer determined by X-ray diffraction and SPR measurement was 1.7 nm for p(DDA/VPy) and 1.9 nm for p(DDA/DADOO).

As for metal nanoparticle synthesis, we obtained relatively monodispersed gold nanoparticles. In the case

of silver nanoparticles, however, the size and shape were in polydisperse state, so we centrifuged silver nanoparticle aqueous solution several times. The citrate anion ($(\text{COO}^-)_3$) acts as reductant and stabilizer. The metal nanoparticles are protected by the citrate anions of the surfactant. Gold and silver nanoparticles can be immobilized onto the polymer nanosheets by immersion method. As an advantage of polymer nanosheets, both metal nanoparticles were uniformly immobilized onto the cationic polymer nanosheets. Interestingly, the amount of the immobilized gold nanoparticles strongly depends on VPy contents. The surface charge density can be controlled by varying the VPy contents. The nanoparticles take a monolayer formation due to electrostatic repulsion among the nanoparticles. It took more than six hours to reach the saturation of metal nanoparticle immobilization on polymer nanosheets. The gold nanoparticle cannot be immobilized on p(DDA/VPy) nanosheets, when the p(DDA/VPy) nanosheets are coated with five-layer nanosheets of *N*-dodecyl acrylamide homopolymer (pDDA) nanosheets. These results give the evidence that the driving force of

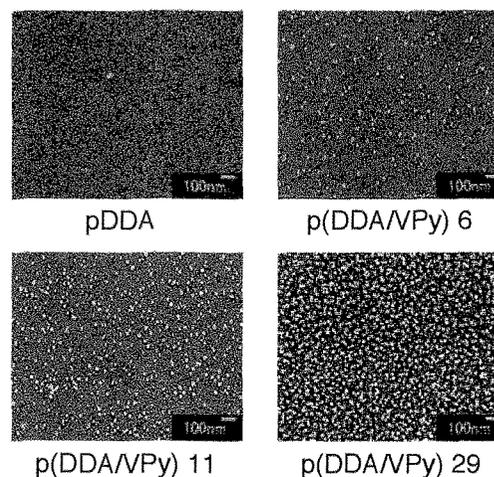


Fig. 3. SEM images of immobilized gold nanoparticles on p(DDA/VPy) nanosheets.

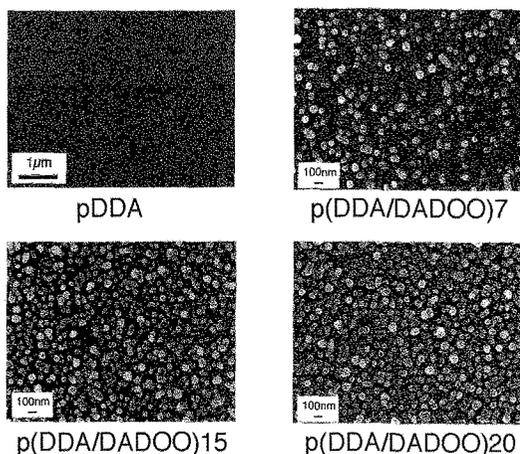


Fig. 4. SEM images of immobilized silver nanoparticles onto p(DDA/DADOO)s.

the nanoparticle immobilization is based on electrostatic interaction. The surface coverage of the gold nanoparticle on the p(DDA/VPy)29 nanosheets was estimated to be *ca.* 40 %. The surface density of VPy groups in two-layer p(DDA/VPy)29 nanosheets is calculated to be 2.64 nm^{-2} . This implies that the ratio of gold nanoparticle and VPy group in the hybrid nanoassemblies is $\sim 1 : 650$.

In the case of silver nanoparticles, it was difficult to immobilize them on p(DDA/VPy) nanosheets. Ionic strength and pH value may be possible factors to be considered, and the detailed work is now in progress. Anyway, this is the reason why we utilize p(DDA/DADOO) nanosheets as a template. Fig. 4 shows SEM images of silver nanoparticle arrays immobilization on two-layer p(DDA/DADOO) nanosheets. As similar to the gold nanoparticle immobilization, the silver nanoparticles can be randomly distributed on p(DDA/DADOO) nanosheets. The amount of the silver nanoparticles immobilized on the p(DDA/DADOO) nanosheet increased as the DADOO contents increased. In other words, the amount of the silver nanoparticle can be also tuned by changing DADOO contents.

3.2 Spectroscopic properties of hybrid nanoassemblies

Fig. 5 shows absorption spectra of gold nanoparticles immobilized on two-layer p(DDA/VPy) LB films with different VPy contents. Interestingly the shape of the absorption spectra changed drastically as the VPy contents were increased. The absorption band around 530 nm is assigned to the surface plasmon band due to the collective oscillation of the conduction band electrons at the surface of nanoparticles. New absorption band appears at the longer wavelength region as the VPy contents were increased. The band corresponds to the near-field interaction of several gold nanoparticles in the 2D gold nanoparticle array; they interact electromagnetically through a dipole coupling mechanism. This broadens and red-shifts the surface plasmon band [12,13]. No significant red shift of the broad band (600 nm) was observed as a function of VPy contents. There are a lot of dipole oscillation modes with the polarization of the exciting electromagnetic field.

The variety of different geometrical arrangements causes band broadening. In other words, the absorption band at longer wavelength region may contain a lot of oscillation mode, leading to the broad absorption band. In the case of p(DDA/VPy)29 nanosheets, the surface density of immobilized gold nanoparticle was determined to be $5.8 \times 10^{-4} \text{ nm}^{-2}$. Assuming that the gold nanoparticles are randomly distributed in the 2D field, the averaged center-to-center distance between adjacent gold nanoparticles can be estimated to be 47 nm. Since the size of gold nanoparticle is 30 nm in diameter, the end-to-end interparticle separation distance is 17 nm. It is likely that the coupling of the surface plasmon among the adjacent nanoparticles occurs in the intralayer system.

The interparticle coupling is more significant in gold nanoparticle monolayer multilayers (Fig. 5). Even in the bilayer system, a new broad absorption band around 680 nm clearly appeared. The distance between the gold nanoparticle arrays is 3.4 nm, because the thickness of the p(DDA/VPy) monolayer is 1.7 nm. Comparing the result with the intralayer gold nanoparticle ordering,

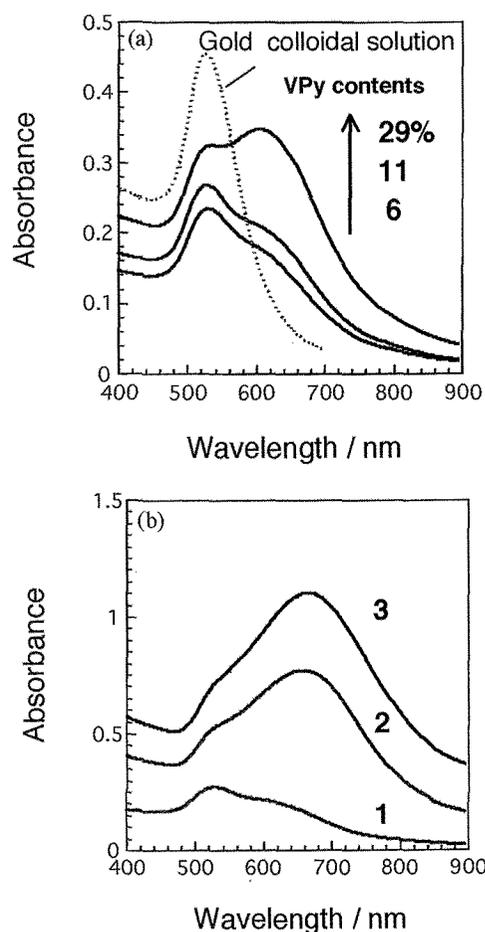


Fig. 5. Optical absorption spectra for immobilized gold nanoparticle on p(DDA/VPy) nanosheets. (a) p(DDA/VPy)/Au₁ bilayer and (b) p(DDA/VPy)11/Au_n bilayers as a function of the deposition cycle number. The number of the deposition cycles *n* are given as the trace number.

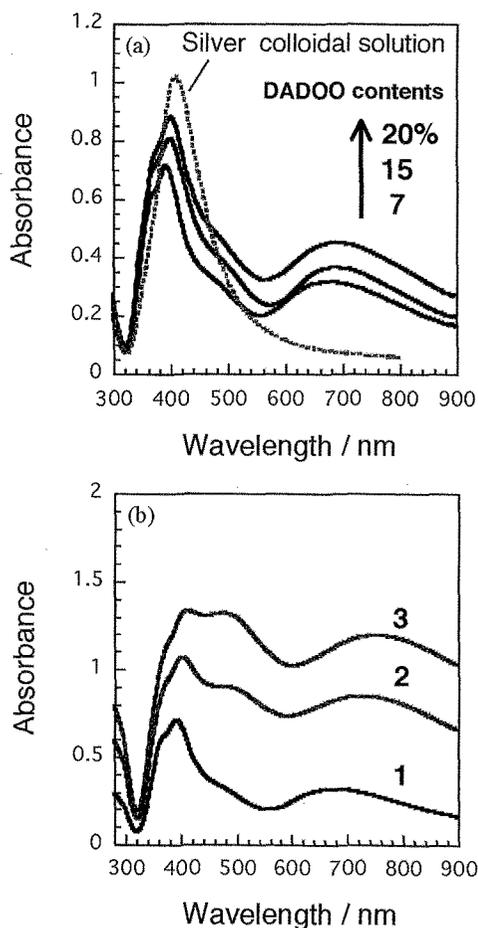


Fig. 6. Optical absorption spectra for immobilized silver nanoparticle on p(DDA/DADOO) nanosheets: (a) (p(DDA/DADOO)/Ag)₁ bilayer as a function of DADOO contents and (b) sequentially deposited (p(DDA/DADOO)₁₅/Ag)_n bilayers. n = 1–3.

gold nanoparticles become much closer to each other, leading to the broad absorption bands around 700 nm.

In the case of silver nanoparticles, the tendency is almost the same (Fig. 6). Most significant difference is the peak position. At 400 nm is the absorption band due to surface plasmon resonance for silver nanoparticles. As similar to the gold nanoparticle immobilization, broad absorption bands appear at longer wavelength region. From these results, it can be concluded that the metal nanoparticle position can be controlled at the nanometer scale because the functional groups are distributed uniformly in the polymer nanosheets. The detailed analysis for the immobilization mechanism is now in progress.

4. CONCLUSION

We demonstrated that two-dimensional ordering of noble metal nanoparticles on a solid support was controlled by polymer nanosheets fabricated by the Langmuir-Blodgett technique. Negatively charged metal nanoparticles can be immobilized on the cationic polymer nanosheets through electrostatic interaction. The nanoparticles on the polymer nanosheets were in a highly distributed monolayer state. The amount of the

immobilized metal nanoparticle can be tuned by changing the cationic comonomer contents. This implies that the separation distance among nanoparticles is controlled by polymer nanosheets. Since the LB technique can control the separation distance at the nanometer scale parallel to the surface normal, the immobilization of the metal nanoparticles can be tailored by both intralayer and interlayer arrangements. Therefore the strength of nanoparticles through-space coupling can be tuned by the variation of the spacing between the nanoparticle layers. Polymer nanosheets can open up new approach to assemble hybrid building blocks.

Acknowledgment

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (Fundamental Science and Technology of Photofunctional Interfaces, No. 417). We thank Mr. Y. Hayakawa and Mr. E. Aoyagi, Tohoku University, for the FE-SEM measurements. We also thank Prof. H. Nakanishi and Dr. A. Masuhara, IMRAM, Tohoku University, for the use of SEM. M. Mitsuishi would like to thank Hosokawa Powder Technology Foundation for financial support.

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(Received December 23, 2004; Accepted April 13, 2005)