Multilayer Hybrid Films of Titania Semiconductor Nanosheet and Silver Metal Fabricated via Layer-by-Layer Self-Assembly and Subsequent UV Irradiation

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Received October 16, 2005. Revised Manuscript Received December 2, 2005

Interesting multilayered nanostructures of molecular-scale alternating titania nanosheet and silver metal have been successfully fabricated by combined use of a layer-by-layer route and an in situ room-temperature ultraviolet irradiation technique with a titania nanosheet and a polyethylenimine−Ag^+ (PEI−Ag^+) complex as the electrostatic building blocks. The consecutive buildup of the PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_{n-1}$ film was monitored by UV−vis absorption spectroscopy. The nearly linear increase in absorbance as a function of the sequential assembly number for the multilayer film indicates that almost same amount of materials was deposited in each dipping cycle. The tunable repeating ordered structure of titania nanosheet−silver multilayer films can be obtained by varying the concentration ratio of Ag^+ to the repeating unit of PEI, essential for meeting the demands on the diverse application of the multilayer films.

Introduction

Self-assembly of the semiconductor and metal in the nanoscale range into ultrathin mono- or multilayered structures is important for many applications, including nonlinear optics, microelectronics, and chemical sensors. Semiconductor−metal heterostructures with a tunable composition have been demonstrated to facilitate charge rectification, beneficial for the improvement of photoelectrochemical performance and optical properties of the nanostructure.[1] Rao and coworkers reported superlatticelike arrays of semiconductor and metal nanoparticles with dithiols as cross-linkers.[2] Several research groups have considerably contributed to the synthesis of core−shell-type semiconductor−metal nanocomposites, fabricated by the growth of metallic monolayers on highly monodispersed semiconductor nanocrystallites, or conversely, semiconductor monolayers on metal nanocrystallites.[3] However, as the architecture of functional nanoscale building blocks and their assembled interfaces play a crucial role in the construction of electronic and photonic devices,[4] exploration of highly controlled two-dimensional semiconductor−metal heterostructures still remains a challenge.

Recently, unilamellar inorganic nanosheets, which are usually produced via exfoliation of related bulk layered compounds, have received growing attention as building blocks for the layer-by-layer (LBL) films.[5] The advantages of this technique are, on one hand, that the continuous inorganic nanosheets effectively prevent the interpenetration of adjacent anion and cation layers and, on the other hand, that inorganic compounds, compared to the organic linkers, represent a wide variety of aspects of materials science and physics in areas that include optical, electronic, electrochemical, magnetic, catalytic, and chemical/biological applications. Recent reports on functional oxide nanosheets, for example, $Ti_{1-\delta}O_2$, MnO_2, and Nb_6O_{17},[6−8] have further stimulated the interest on this fascinating class of nanoscale materials. A variety of nanostructured hybrid systems have been fabricated using these nanosheets as building blocks.[9] However, to the best of our knowledge, there is no report on the fabrication of self-assembled LBL multilayers of the semiconductor nanosheet−metal nanocomposite system.

In this paper, we report on the fabrication of well-defined multilayer assemblies composed of titania nanosheet and

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10.1021/cm052284y CCC: $33.50

silver metal via LBL deposition and subsequent UV irradiation. Here, we use a negatively charged titania nanosheet of composition $Ti_{0.91}O_2^{-0.36}$ and a positively charged silver-coordinated−polyethylenimine (PEI) complex as the electrostatic building blocks. The highly crystalline titania nanosheet is of extremely high two-dimensional anisotropy with lateral dimensions of 0.1−1 μm and a thickness of ∼0.75 nm.[6] PEI is a well-known polyelectrolyte binder for LBL self-assembly. The organic ligands of amine or imine groups have strong chelating capability toward transition metal ions. In the present case, by making use of the effective chelating capability of PEI to Ag^+, the PEI−Ag^+ coordination compound was applied as a positively charged component. The titania nanosheet and the PEI−Ag^+ complex were sequentially adsorbed onto a substrate. The resulting nanostructured films were exposed to UV light, leading to the in situ photoreduction of the Ag(I) ion into Ag metal.

Experimental Section

Chemical Reagents. All chemical reagents were of reagent grade and used as received without further purification. A 50 wt % aqueous solution of PEI ($M_w = \sim 7.5 \times 10^5$) was provided by Aldrich Chemical Co. All water used throughout the experiments was purified to a resistivity of greater than 17 MΩ cm by passing through a Millipore Milli-Q membrane filtration system. A colloidal suspension of exfoliated titania nanosheets was synthesized by delaminating a layered protonic titanate, $H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$ (□: vacancy), with the γ-FeOOH structure into single layers, according to the procedure described previously.[6] Briefly, an intimate stoichiometric mixture of Cs_2CO_3 and TiO_2 was heated at 800 °C for 20 h to produce a precursor cesium titanate, $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ (□: vacancy), followed by treatment with 1 mol dm^{-3} HCl solution at room temperature, forming $H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$. The resulting acid-exchanged product was filtered, washed with water, and air-dried. The as-produced protonic titanate (typically, 1 g) was shaken vigorously in 250 cm^3 of 0.017 mol dm^{-3} tetrabutylammonium hydroxide solution at ambient temperature for 10 days. This procedure yielded a stable colloidal suspension of a unilamellar nanocrystalline titiania nanosheet of $Ti_{1-\delta}O_2$ ($\delta \sim 0.09$).

Fabrication Procedure of the Multilayer Assemblies of Alternating Titania Nanosheet−Silver. The detailed fabrication procedure of the multilayer assemblies of alternating titania nanosheet−silver via combination of the LBL route and in situ room-temperature UV irradiation technique is outlined below. A surface-cleaned quartz glass substrate was modified by being treated with a protonic PEI aqueous solution of 2.5 g dm^{-3} at pH = 9.0−9.1 for 20 min to introduce positive charge to the substrate surface, followed by thorough washing with water (step 1). Note that diluted HNO_3 solution was used to adjust the pH values of all the solutions in the present work. Then, the protonic-PEI treated substrate was immersed in a colloidal suspension of the negatively charged titania nanosheets (the suspension of titania nanosheet of concentration of 0.08 g dm^{-3} was used throughout the experiments) at pH = 9.0−9.1 for another 20 min, followed by careful washing with water (step 2). The substrate was then immersed in the PEI−Ag^+ complex solution for 20 min and rinsed with water, producing the first self-assembly of the titania nanosheet/PEI−Ag^+ complex (step 3). For the typical preparation of the PEI−Ag^+ complex aqueous solution of a 1:6 concentration ratio of Ag^+ to the repeating unit of PEI, 50 cm^3 of 0.02 mol dm^{-3} $AgNO_3$ solution was slowly added into 50 cm^3 of 5.0 g dm^{-3} PEI solution at pH = 9.0−9.1 under stirring. The mixture solution was then stirred for 1 h, driving completion of the coordination reaction. Generally, as one Ag^+ ion can coordinate with two amino groups, it is believed that all of the Ag^+ ions can be changed into the coordinating form with PEI. The PEI−Ag^+ complex-deposited substrate was immersed in the colloidal suspension of titania nanosheets again for 20 min and then rinsed with water (step 4). Steps 3 and 4 were repeated alternately several times. Thus, a transparent colorless multilayer film composed of *n* layer pairs, PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_{n-1}$, was achieved without visible defect. Finally, the resulting multilayer thin film was exposed to UV light for 24 h (step 5), during which the Ag(I) component was photoreduced into Ag metal, forming Ag nanoparticles between the titania nanosheet galleries. As PEI is photosensitive to decomposition, especially with the photocatalytic properties of the titania nanosheet, the polyelectrolyte linker of the multilayer film was photolysized to NH_4^+ under the UV irradiation, acting as counterions for the negatively charged titania nanosheets.[9c] This photo-producing residue of PEI has been demonstrated to have little influence on the electrochemical and photoelectrochemical properties of the titania multilayer film.[10] By further varying concentration ratio of Ag^+ to the repeating unit of PEI, the multilayer assemblies of alternating titania nanosheet−silver with a tunable repeating distance can be obtained. A UV lamp (UVF-204S San-ei Electric Co. Ltd) was used for irradiation of the films. Samples were placed at ∼10 cm from the light source.

Characterizations. UV−vis absorption spectra were recorded on a Hitachi U-4000 spectrophotometer equipped with an integrating sphere detection system for the multilayer films on quartz glass substrates. High-resolution X-ray photoelectron spectra (XPS) were collected at a takeoff angle of 45° using a Physical Electronics XPS-5700 spectrometer with an Al Kα X-ray line (1486.6 eV) and the 0.8 mm diameter probing size. The vacuum inside the spectrometer during analysis was $\sim 10^{-7}$ Pa. X-ray diffraction (XRD) data were collected using a Rigaku Rint 2000S powder diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 0.154\,05$ nm).

Results and Discussion

The consecutive buildup of the PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_{n-1}$ film was monitored by UV−vis absorption spectroscopy. Figure 1 (solid curves) shows UV−vis absorption spectra of the PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_{n-1}$ films fabricated with the titania nanosheet and the PEI−Ag^+ complex with a 1:6 concentration ratio of Ag^+ to the repeating unit of PEI [hereafter the sample was denoted as (PEI/Ag/6:1)$_{n-1}$]. The pronounced peak at 265 nm can be assigned to characteristic absorption of the titania nanosheet, because there is no absorption for the PEI−Ag^+ complex in the UV−vis wavelength range. The nearly linear increase in absorbance as a function of the sequential assembly number for the multilayer film, as shown in the inset (labled as ⊗), indicates that almost the same amount of the deposited materials was deposited in each dipping cycle. The modest increase in the background at a wavelength of >300 nm can be attributed to light scattering by the nanosheet crystallites oriented parallel to the substrate surface with lateral sizes in the submicro- to micrometer range. Further results show that the PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_{n-1}$ multilayer films can be successfully fabricated with the wide range of concentration ratios of Ag^+ to the repeating unit of PEI. The inset in

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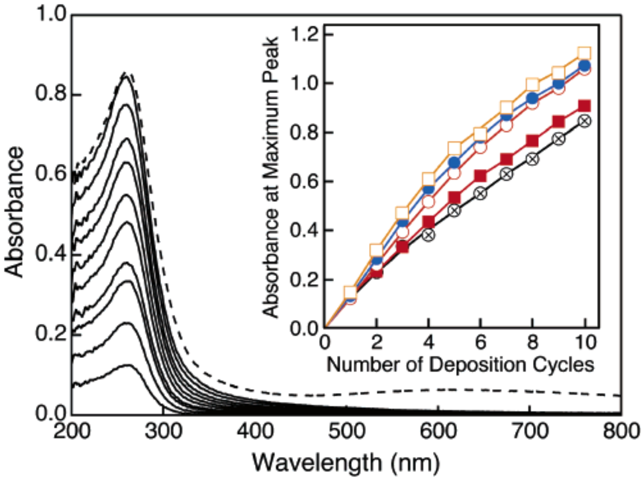

Figure 1. UV−vis absorption spectra in the buildup process of the PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_{n-1}$ multilayer film (solid curves) and its UV-treated product (dashed curve) with a PEI−Ag^+ complex of a 1:6 concentration ratio of Ag^+ to the repeating unit of PEI. The inset is the peak-top absorbance of as-prepared PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_9$ multilayer film as a function of deposition cycles fabricated with the titania nanosheet and the PEI−Ag^+ complex of various concentration ratios of Ag^+ to the repeating unit of PEI: ⊗ for 1:6, ■ for 1:18, ○ for 1:60, ● for 1:180, and □ for 1:600.

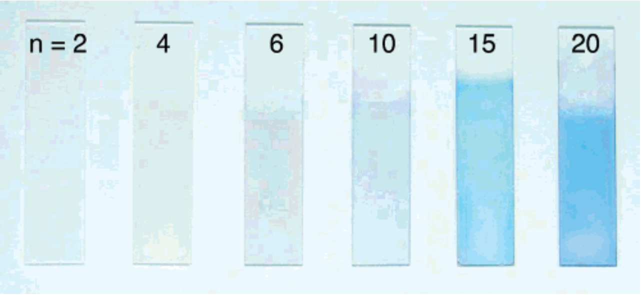

Figure 2. Photograph of color transition of the UV-treated (PEI/Ag/6:1)$_{n-1}$ multilayer films.

Figure 1 presents the peak-top absorbance of the as-prepared PEI/$Ti_{1-\delta}O_2$/(PEI−Ag^+/$Ti_{1-\delta}O_2$)$_9$ multilayer film as a function of deposition cycles fabricated with titania nanosheet and the PEI−Ag^+ complex of various concentration ratios of Ag^+ to the repeating unit of PEI. It can be seen that the peak-top absorbances in all curves exhibit the nearly linear increase with deposition cycles. With decrease of the concentration ratio of Ag^+ to the repeating unit of PEI in the PEI−Ag^+ complexes, the deposited amount of the titania nanosheet in each cycle increased. As the formation of the PEI−Ag^+ complex can be considered a process in which Ag^+ substitutes for H^+ of the protonic PEI to coordinate with PEI, it may be deducible that the protonic PEI is more favorable for the deposition of the titania nanosheet in the buildup process of the multilayer film compared to the PEI−Ag^+ complex. This conclusion may be motivating information for investigation of the mechanism of the present LBL self-assembly of the titania nanosheets and the PEI−Ag^+ complex.

Figure 2 shows a photograph of color transition of the UV irradiation-treated (PEI/Ag/6:1)$_{n-1}$ film with increase of the deposition layers. It can be seen that after the UV irradiation treatment, the colorless film gradually turned to bluish gray with increase of the deposition layers, indicating the photoreduction transformation of Ag(I) to Ag element in the multilayer film. It is likely that this reduction reaction was accelerated by the titania nanosheet which shows high photocatalytic activities.[9c] The corresponding UV−vis absorption spectrum of the (PEI/Ag/6:1)$_9$ multilayer film is presented as a dashed trace in Figure 1. The UV irradiation brought about the evolution of a broad peak, centered at about 620 nm and extending to the near-infrared range. As the UV irradiation induces no change of the UV−vis absorption spectrum of the titania nanosheet under the present experimental condition, it is reasonable that the peak can be attributed to the surface plasmon resonance (SPR) of Ag element from the photoreduction of Ag(I). Compared to widely reported typical silver spherical nanoparticles with the UV−vis absorption peak at around 400 nm, it is obvious that the Ag formed between titania galleries exhibits a large red shift. The red shift of the SPR band of the present Ag component may be due to high refractive index of $Ti_{1-\delta}O_2$ nanosheets as the surrounding medium and the interaction of Ag component in the same titania gallery and among neighboring ones.

High-resolution XPS analysis was used for further characterization of the fabricated UV-treated (PEI/Ag/6:1)$_9$. As shown in Figure 3a, the $2p_{3/2}$ and $2p_{1/2}$ core levels of Ti that occurred at 458.1 ± 0.2 and 463.8 ± 0.2 eV, respectively, agree well with the binding energies for TiO_2 in the literature and indicate the successful adsorption of titania nanosheets. The absence of energy deviations suggests that charging of the samples could be ignored. The O 1s peak was also detected at a binding energy of 529.6 ± 0.2 eV (Figure 3b), which is characteristic of O bound to Ti.[11] Figure 3c shows the high-resolution XPS spectrum of Ag in the multilayer film. The peaks at 366.9 ± 0.2 eV and 373.0 ± 0.2 eV are assigned to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. The narrow widths of the peaks suggest that the Ag component is situated in a similar condition throughout the film. The XPS peaks of the Ag in the film are shifted toward lower energies compared to those of the bulk. Such a shift may be due to the influence of the surface oxygen component of the titania nanosheet on arrangement of the outer-layer electrons of the Ag.[12−14] It has been demonstrated that NH_4^+ and NO_3^- are the most usual final products in the photocatalytic degradation of amines.[15] In the case of the titania nanosheet as a building block for the multilayer films, the formation of NH_4^+ was preferred, as cationic species are required to maintain the total charge neutrality of the system for the negatively charged nanosheet.[9d,e] The resolved XPS peak of

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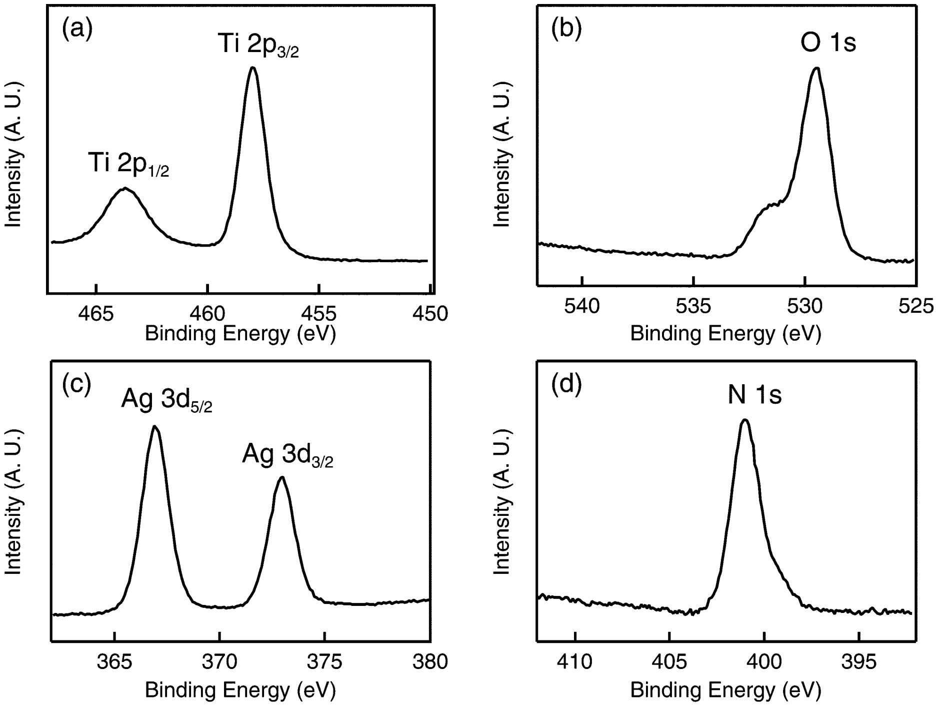

Figure 3. High-resolution XPS data of the UV-treated (PEI/Ag/6:1)$_9$ multilayer film: (a) Ti 2p, (b) O 1s, (c) Ag 3d, and (d) N 1s.

the binding energy assigned to the N 1s component of NH$_4^+$ was detected at 401.1 ± 0.2 eV as shown in Figure 3d, being consistent with FT-IR data. Absence of NO$_3^-$ at a higher binding energy of 406−408 eV supports the preferred formation of the NH$_4^+$.

The structural order in the multilayer film was confirmed by XRD. Figure 4a shows the XRD pattern of the UV-treated (PEI/Ag/6:1)$_9$. Two diffraction peaks were observed at $2\theta = 5.2$ and 10.4°, which can be indexed as 010 and 020 basal reflections of the nanostructure, respectively.[6] The titania nanosheet and Ag metal alternate in a parallel arrangement, having a repeating distance of about 1.7 nm. When this pattern was compared with that for the as-prepared film before UV irradiation (Figure 4f), a negligible change in peak location was found, except for some broadening upon irradiation. In contrast, in a control test, UV irradiation of the PEI/Ti$_{1-\delta}$O$_2$ multilayer film without Ag decreased its basal spacing from 1.7 to 0.9 nm, which is compatible with our previous study.[9c] Consequently, the thickness of the Ag metal in the nanosheet galleries is deduced to be ~0.8 nm. The produced Ag atoms into the Ag may prop open the gallery space, compensating for the decrease of basal space due to the photodecomposition of PEI under UV irradiation.

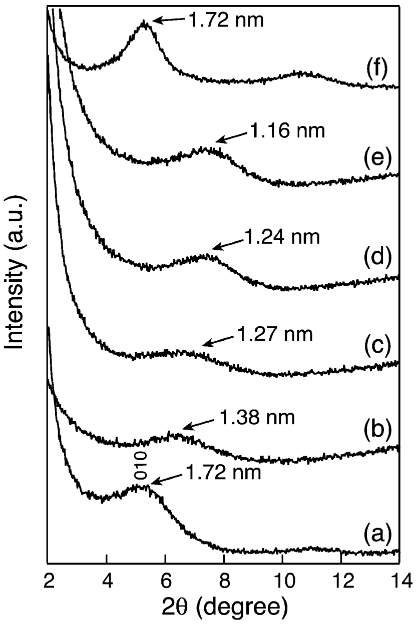

Figure 4. XRD patterns of the titania nanosheet/Ag multilayer films constructed with the titania nanosheet and the PEI−Ag$^+$ complex of various concentration ratios of Ag$^+$ to the repeating unit of PEI: (a) 1:6, (b) 1:18, (c) 1:60, (d) 1:180, and (e) 1:600. The pattern (f) is for the as-prepared (PEI/Ag/6:1)$_9$ multilayer film.

It is known that well-defined ordered solids fabricated from tailored nanocrystalline building blocks provide opportunities for optimizing properties of materials and offer possibilities for observing interesting and potentially useful new collective physical phenomena.[16] The tunable repeating space in the solid is a key determinant of the magnetic, optical, and electronic properties of nanocomposite materials. In the present case, the repeating spacing in the titania nanosheet/Ag multilayer films can also be controlled by adjusting the concentration ratio of Ag$^+$ to the repeating unit of PEI. Figure 4b−e shows the XRD patterns of the photoirradiated (titania nanosheet/Ag)$_{10}$ films fabricated with the PEI−Ag$^+$ complex of various concentration ratios of Ag$^+$ to the repeating unit of PEI. It can be seen that all of the products exhibit a typical 010 basal reflection, showing a lamellar structure. The repeating spacing, as noted in the figure, decreased gradually with decreasing the concentration ratio of Ag$^+$ to the repeating unit of PEI from 1.38 nm for 1:18 to 1.16 nm for 1:600. Thus, the repeating spacing of the multilayer films can be varied continuously in the present semiconductor−metal system.

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Finally, it is interesting to discuss the architecture of the Ag formed in the multilayer film. Recently, Walter[17] and Shirai et al.[18] reported the preparation and structure of extremely thin Pd and Pt nanosheets by reducing palladium or platinum chloride−graphite intercalation compounds in a hydrogen atmosphere, using the two-dimensionally limited space of graphite galleries; the two-dimensional growth was permitted for metal particles by the steric hindrance. Similarly, it is expected that the Ag atoms in the present film produced via UV irradiation may grow preferentially along the lateral direction of the $Ti_{1-\delta}O_2$ galleries into two-dimensional Ag morphology with an extremely small thickness. As it is well-known that spherical Ag nanoparticles with a diameter smaller than 2 nm do not display a distinct absorption band, the absorption band of the Ag nanoparticles in the multilayer film shown in the Figure 1 may also originate from the longitudinal mode of the proposed two-dimensional anisotropic Ag nanoparticle, which also partially contributed to the red shift of the absorption band. The two-dimensional growth of Ag nanolayers in the nanosheet galleries needs further confirmation.

Conclusions

We have fabricated novel self-assembled multilayers of molecular-scale alternating titania nanosheet−silver via combination of the LBL route and an in situ room-temperature UV irradiation technique. The UV−vis absorption spectroscopy demonstrates that the titania nanosheet and the PEI−Ag^+ complex can be successfully utilized as building blocks for consecutive construction for the self-assembled multilayer film in the wide range of concentration ratios of Ag^+ to the repeating unit of PEI. The multilayer repeating spacing in the titania nanosheet/Ag films can be controlled by simply varying the concentration ratio of Ag^+ to the repeating unit of PEI. The potential application of the unique electronic behavior of the ultrathin titania semiconductor nanosheets connecting with silver metal is currently being studied.

Acknowledgment. This work has been supported by CREST of JST (Japan Science and Technology Agency).

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