

Fabrication of composite film comprising TiO₂/CdS and polyelectrolytes based on ionic attraction

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Abstract

Composite film comprising TiO₂/CdS nanoparticles and polyelectrolytes was fabricated based on electrostatic interaction. By utilizing cationic TiO₂ and anionic CdS colloids, we realized the assembly of dissimilar nanoparticles. The alternating assembly film of TiO₂/CdS and polyelectrolytes was further characterized by several methods including UV–Vis spectroscopy and transmission electron microscopy (TEM). Most importantly, surface photovoltage (SPV) measurements showed that interesting photoelectron energy conversion occurred in the TiO₂/CdS composite film. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: TiO₂/CdS composite nanoparticles; Alternating assembly; Surface photovoltage response; Charge separation

1. Introduction

Recently, the study of interparticle electron transfer between dissimilar semiconductor particles has received increasing investigations [1–6]. Combining two semiconductor particles offers an opportunity to sensitize a semiconductor material having a large bandgap and energetically low-lying conduction band by another one having a small bandgap and energetically high-lying conduction band [1–4]. Charge injection from one semiconductor into another can lead to efficient and longer charge separation, which are anticipated to have potential applications in photocatalysis and solar energy conversion [4–6].

Therefore, organizing such kind of materials into layered structure provides a possibility to fabricate a new kind of molecular or supramolecular devices. Several different strategies for fabrication of nanoparticle composite films have been reported, including Langmuir–Blodgett (LB) technique and self-assembly method [7–10]. Self-assembly based on electrostatic interaction is a rapid and experimen-

tally very simple way to produce complex layered structures. Over the past few years, many nanoparticles (such as PbI₂, TiO₂, Au, and CdS) were assembled successfully into layered systems using this method [8,9,11–14].

Here, composite film comprising TiO₂/CdS nanoparticles and polyelectrolytes was fabricated based on ionic attraction. By utilizing cationic TiO₂ and anionic CdS colloids, we realized the assembly of dissimilar nanoparticles via the special affinity between the dangling carboxylate groups and TiO₂. The alternating assembly film of TiO₂/CdS and polyelectrolytes was monitored by UV–Vis spectroscopy. The microstructure of the composite film was characterized using transmission electron microscopy (TEM). The photoelectron energy conversion in the composite film was studied successfully using surface photovoltage spectroscopy.

2. Experimental

Titanium tetrachloride, cadmium chloride, mercaptoacetic acid, and sodium sulfide were all of the highest quality of those commercially available. Poly(styrene-4-sulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA) were purchased from Aldrich.

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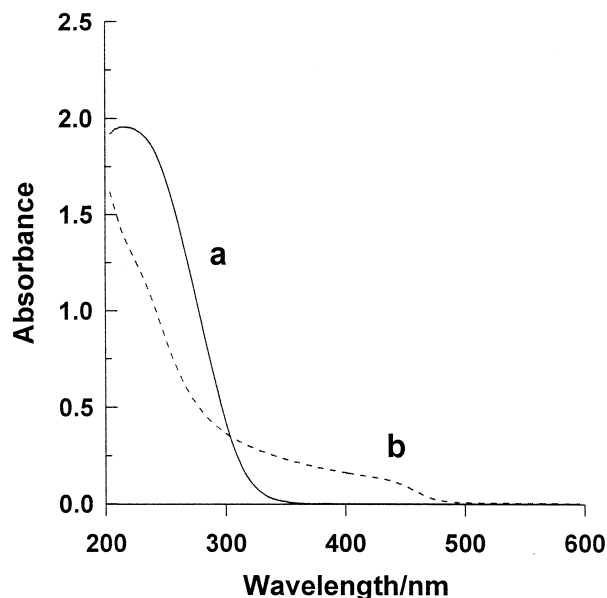


Fig. 1. UV-Vis absorption spectra of (a) TiO_2 and (b) CdS colloidal solution.

The cationic TiO_2 colloidal solution was prepared by the forced hydrolysis technique according to earlier published procedures [15]. A stable CdS colloid was prepared upon the addition of mercaptoacetic acid as a stabilizer [16]. The pH of the resulting CdS colloid solution was adjusted to 2.8–3.0 using HCl.

Multilayer films comprising $(\text{TiO}_2/\text{CdS})$ and (PDDA/PSS) have been fabricated by alternating deposition process. The first step was to modify the corresponding substrate to create a charged surface according to the literature [17]. The resulting charged substrate was first dipped into TiO_2 colloidal solution for 40 min to adsorb one layer of TiO_2 nanoparticles. After being washed with deionized water and dried, the slide was transferred to the acidic CdS colloidal solution for another 40 min in order to adsorb one layer of CdS nanoparticles. After the TiO_2/CdS adsorption, the slide was immersed to the solution containing PDDA for 30 min, and then transferred into a solution containing PSS (0.5 g/l, pH ~ 4) for another 30 min to get another negatively charged surface. The substrate was dipped into TiO_2 and then CdS again to adsorb the TiO_2/CdS . Multilayer films could be prepared through repeating the above four steps.

UV-Vis spectra were obtained using a Shimadzu 3100 UV-Vis-near-IR recording spectrophotometer. Transmission electron micrographs were taken on a Hitachi-8100 electron microscope operating at 200 kV. Surface photovoltage (SPV) measurements were carried out with a solid-junction photovoltaic cell indium tin oxide (ITO)/sample/ITO using a light source monochromator lock-in detection technique [18]. Electric field-modulated surface photovoltage spectroscopy (EFM-SPS) is a technique that combines the field effect principle with SPS.

The external electric field (EEF) was applied to two sides of the sample and regarded as positive when the side under illumination was connected to a positive electrode.

3. Results and discussion

The absorption spectrum of TiO_2 colloidal solution (Fig. 1a) exhibited typical features below 350 nm, details of which could be found elsewhere [5]. Fig. 1b showed the UV-Vis spectrum of CdS colloidal solutions. The absorption edge of the CdS was observed at about 475 nm, shifting about 30 nm with respect to bulk CdS, which illustrated that the presence of mercaptoacetic acid during the colloid preparation led to formation of very small CdS particles. The absorption spectrum of the CdS nanoparticles corresponds to particles with an average diameter of approximately 4 nm, which can be calculated by the estimation of effective bandgap (E_g) from $(\sigma h\nu)^2 = B(h\nu - E_g)$, where σ is the effective absorption coefficient and B is a constant [17].

It has shown that carboxyl groups strongly bind to the surface of TiO_2 in recent years [4,19]. The adsorption of mercaptoacetic acid onto the surface of TiO_2 through its carboxyl groups has already been proved using Fourier transform infrared (FTIR) spectra in earlier studies [17]. Therefore, it should be possible to transfer the mercaptoacetic acid-modified CdS nanoparticles to the surface covered with TiO_2 via the special affinity between the dangling carboxylate groups and TiO_2 . UV-Vis spectra were used to monitor the assembly of repeating TiO_2 and CdS units (Fig. 2). The spontaneous assembly of the cationic TiO_2 nanoparticles onto the anionic polyelec-

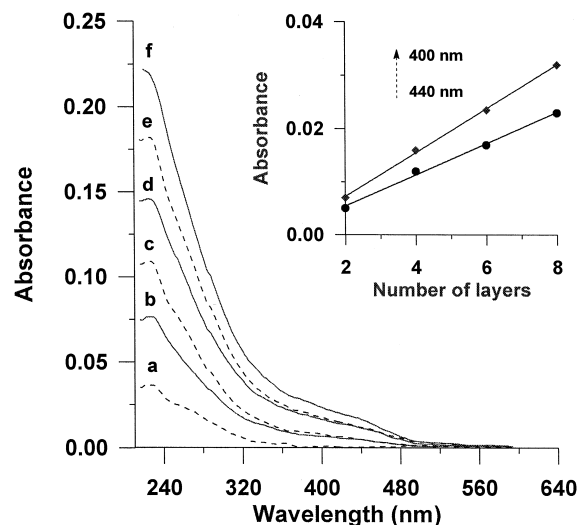


Fig. 2. UV-Vis absorption spectra of alternating film deposition of $\{(\text{PDDA}/\text{PSS})/(\text{TiO}_2/\text{CdS})\} * n$ with different numbers of layers on a quartz slide. From the lower to the upper curves, the numbers of TiO_2 layers are a, c, e, while the numbers of CdS are b, d, f. Inset: the relationship of absorbance at 400, and 440 nm vs. the number of CdS layers.

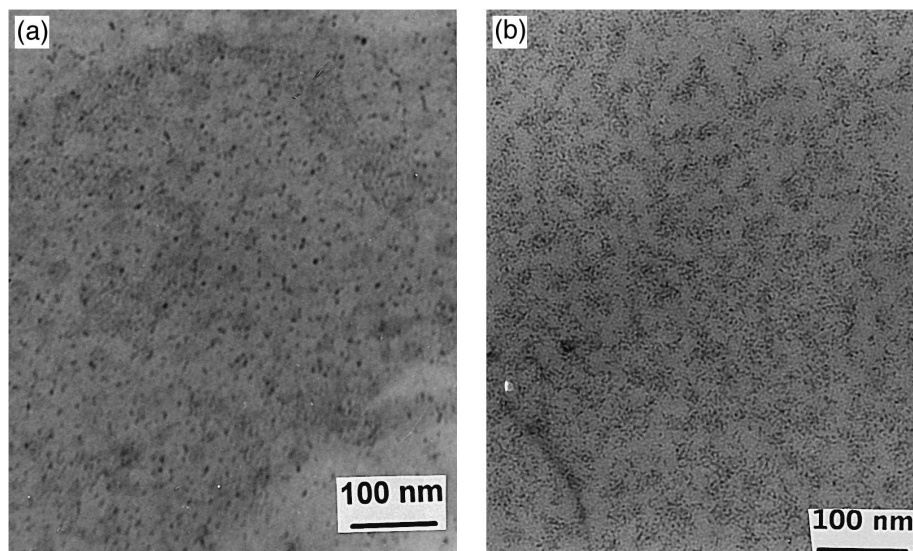


Fig. 3. Transmission electron micrographs of (a) S/(PDDA/PSS)/TiO₂, (b) S/(PDDA/PSS)/(TiO₂/CdS).

trolyte (PSS) was based on the ionic attraction developed between the oppositely charged species [14]. From curve *a*, the obvious absorption below 350 nm illustrated that TiO₂ nanoparticles were adsorbed onto the ionic substrate. By comparing curve *a* with *b*, it was found that the obvious absorption emerged around 480 nm when CdS nanoparticles were adsorbed onto the film, an effect contributed by CdS particles. With increasing TiO₂ units, there was an obvious increase of the absorbance below the 350 nm, and no obvious change was found at longer wavelength. On the other hand, the absorbance around 480 nm increased with increasing CdS units. Furthermore, the absorbance at longer wavelength was found to increase linearly with increasing CdS units. These indicated that TiO₂/CdS and polyelectrolytes can be deposited alternately onto multilayers.

The development of the composite film was studied by transmission electron micrographs. From Fig. 3, we found that TiO₂ particles in the layer of S/(PDDA/PSS)/TiO₂ were well dispersed in large area, while the particles in the layer of S/(PDDA/PSS)/(TiO₂/CdS) were close-packed with a high surface coverage. The TiO₂ particles in the first layer had an average size of 8.0 nm with a standard deviation of $\pm 20\%$. Whereas, the particles in the second layer showed relatively small sizes, with an average size of 3.8 nm (the standard deviation was found about $\pm 10\%$), which were supposed to be CdS particles.

Fig. 4 showed the surface photovoltage spectroscopy (SPS) of {(PDDA/PSS)/(TiO₂/CdS)}*4 composite films. The SPV effect, which is produced by a change in the surface potential caused by illumination, has successfully been applied to the investigation of electron process in semiconductors. It is considered as a simple and precise method for understanding interfacial electron transfer in semiconductors [18,20]. From curve *a*, it was found that the photovoltage response in the composite film appeared

below 500 nm, which was red-shifted slightly than that of the absorption edge of CdS nanoparticles (Fig. 2). The photovoltage response of the composite film became stronger when an EEF was applied. In contrast, if a negative EEF were used, the response would be inverted. The above phenomena could be explained by the SPV mechanism and the structure of the composite film. In SPS experiments, the SPV (i.e., the illumination-induced change in surface potential) is monitored as a function of photon energy. The formation of the SPV requires both photogeneration and separation of charge carriers. The former requires semiconductors with a suitable bandgap, while the latter requires the electron-hole pairs be separated and transported efficiently under a strong built-in electric field. In our case, the CdS/TiO₂ nanoparticles were sandwiched

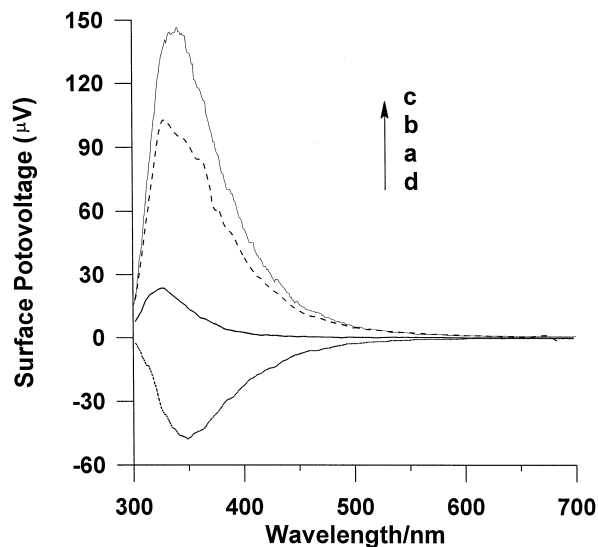


Fig. 4. Surface photovoltage spectra of ITO electrodes modified with {(PDDA/PSS)/(TiO₂/CdS)}*4 multilayer film under different external electric fields: (a) 0 V, (b) +1 V, (c) +1.5 V, and (d) -1.0 V.

between the polyelectrolyte layers, which acted as a barrier for both the set-up of an efficient electric field and the transportation of the charge carriers. On one hand, direct connection of CdS and TiO₂ nanoparticles provided a chance for photogeneration and efficient separation of charge carrier. On the other hand, a suitable EEF could not only function as a built-in field, but was meant as an additional energy source that could help the carriers go beyond the polymer-caused potential barriers. Therefore, an enhancement photovoltage response appeared under the EEF.

4. Conclusion

Polyelectrolyte/(TiO₂/CdS) nanoparticles composite film was fabricated based on electrostatic interaction. SPV measurements illustrated successfully the process of photogeneration and efficient separation of charge carrier in the composite film. By taking advantage of the self-assembly, the present method would offer a way for fabricating polymer/semiconductor composite film with precise control of layer composition and thickness as light-converting electrode for the basic research.

Acknowledgements

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