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Assembly of alternating TiO_2/CdS nanoparticle composite films

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A composite film comprising TiO_2 and CdS nanoparticles was fabricated based on an alternating deposition method; this was confirmed by UV–VIS spectroscopy, TEM, and photocurrent measurements.

Recently, the organization of semiconductor nanoparticles into layered structures has received increasing attention.[1,2] Several different strategies for the fabrication of nanoparticle composite films have been reported, including Langmuir–Blodgett (LB), self-assembly and casting techniques. Self-assembly is a rapid and experimentally very simple way to produce complex layered structures with precise control of layer composition and thickness. Over the past few years, many nanoparticles (such as PbI_2, TiO_2, CdS, and Au) have been assembled successfully into layered systems using the self-assembly method.[3,4]

'Coupled' nanoparticles consist of semiconductor particles having a large bandgap and an energetically low-lying conduction band, combined with particles having a small bandgap and an energetically high-lying conduction band.[5,6] Charge injection from one semiconductor into another can lead to efficient and longer charge separation by minimizing the unwanted electron–hole recombination pathway. Therefore 'coupled' type nanoparticles are anticipated to have potential applications in photocatalysis and solar energy conversion. Here, by utilizing TiO_2 and CdS colloids, we demonstrate the formation of a composite film comprising different nanoparticles based on an alternating deposition method. UV–VIS spectra illustrated that TiO_2 and CdS nanoparticles can be deposited uniformly onto multilayers. Photoelectrochemical measurements demonstrated that effective charge separation occurred in the nanocomposite film.

The cationic TiO_2 colloidal solution was prepared by the forced hydrolysis technique.[6] A stable CdS colloid was prepared upon the addition of mercaptoacetic acid as a stabilizing agent.[7] The carboxylic groups from the mercaptoacetic acid modified on the surface of the particles resulted in anionic CdS particle surfaces. In a typical preparation of acidic CdS colloid, a 100 ml solution of 1.0×10^{-3} mol l^{-1} $CdCl_2$ and 2.0×10^{-3} mol l^{-1} mercaptoacetic acid was prepared, Na_2S (10 ml, 1.0×10^{-3} mol l^{-1}) was then injected under vigorous stirring. The pH of the resulting yellow colloid was adjusted to 3.0 by dropwise addition of 0.01 mol dm^{-3} HCl.

Multilayer ultrathin films comprising TiO_2 and CdS have been fabricated by an alternating deposition process (Fig. 1). The first step is to modify the corresponding substrate to create a charged surface according to the literature.[8] The resulting charged substrate was first dipped into a TiO_2 colloidal solution for 40 min to absorb one layer of TiO_2 nanoparticles. After washing with deionized water and drying, the slide was transferred to the acidic CdS colloidal solution for another 40 min in order to adsorb one layer of CdS nanoparticles. The multilayer films were obtained through repeating the above procedure using the TiO_2 and CdS colloidal solutions.

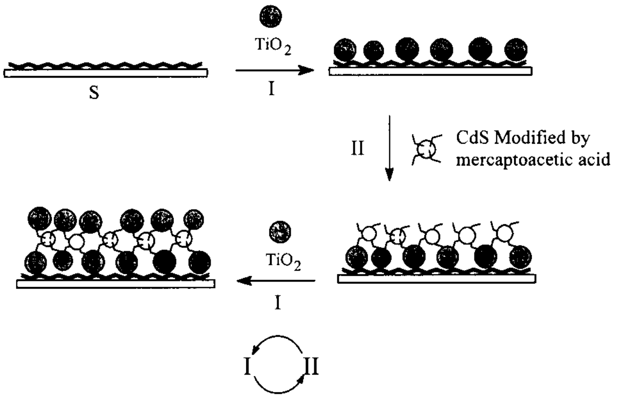

Fig. 1 Schematic drawing for the build-up of an alternating film of TiO_2/CdS. S is the abbreviation for surface charged substrate. Procedures I and II represent the adsorption of TiO_2 and CdS nanoparticles.

Since the isoelectric point of titanium dioxide is at pH = 5–7, the surface of TiO_2 particles will therefore carry net positive charges at $pH < 4$. Therefore we envisaged the substitution of TiO_2 particles for polycationic compounds. Here we first obtained a TiO_2 monolayer covered substrate based on electrostatic interaction, after which the substrate was dipped into CdS colloid stabilized by mercaptoacetic acid. It is well known that carboxyl groups bind strongly to the surface of TiO_2.[6] Therefore, it is possible to transfer the mercaptocarboxylic acid stabilized CdS nanoparticles to the surface of the TiO_2 monolayer, and a heteromultilayer would be fabricated by repeating the TiO_2 and CdS units.

UV–VIS spectra, obtained using a Shimadzu 3100 UV–VIS–NIR recording spectrophotometer, were used to monitor the self-assembly of the repeating TiO_2 and CdS units (see Fig. 2). The absorption spectra of CdS and TiO_2 nanoparticles exhibit typical features around 450 nm and below 350 nm respectively, details of which can be found elsewhere.[7,9] The spontaneous assembly of the cationic TiO_2 nanoparticles onto the anionic polyelectrolyte (PSS) is based on the ionic attraction developed between the oppositely charged species.[10] From curve 1, the obvious absorption below 350 nm illustrated that TiO_2 nanoparticles were absorbed onto the ionic substrate. By comparing curve 1 with curve 2, it was found that an obvious absorption emerged around 450 nm when the CdS nanoparticles were adsorbed onto the film, an effect caused by CdS particles. With increasing the number of TiO_2 units, there is an obvious increase of the absorption below 350 nm, which decreases only slightly at longer wavelengths owing to slight desorption. Furthermore, the absorbance around 450 nm was found to increase linearly with increasing numbers of CdS units. Another linear relationship between the absorbance at 250 nm for TiO_2 and the number of layers of TiO_2 deposited also appears, if the absorbance at 250 nm for CdS is omitted. These indicate that both TiO_2 and CdS can be deposited uniformly onto multilayers. However, the development of the

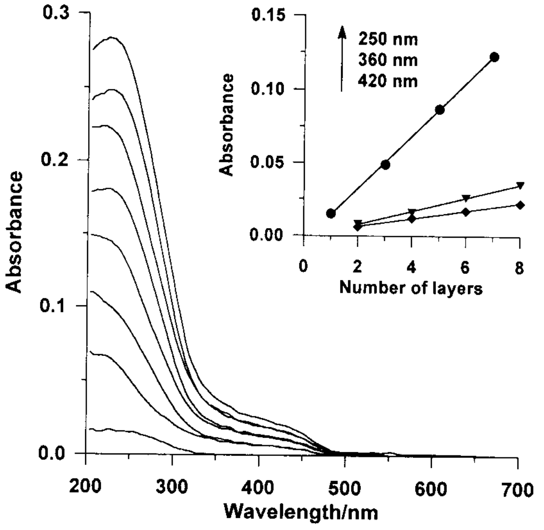

Fig. 2 UV–VIS absorption spectra of alternating film deposition of TiO_2/CdS with different numbers of layers on a quartz slide. From the lower to the upper curves, the number of TiO_2 and CdS layers is 1, 3, 5, 7 and 2, 4, 6, 8 respectively. Inset: the relationship of absorbance at 420 and 360 nm *vs.* the number of CdS layers, and 250 nm *vs.* the number of TiO_2 (the absorbance at 250 nm for CdS was omitted).

alternating TiO_2/CdS component structure is shown in a very idealized manner in Fig. 1. From the transmission electron micrographs, we found TiO_2 particles in the first layer (S/TiO_2) were well dispersed over a large area, the particles in the second layer (S/TiO_2/CdS) were close-packed with a high surface coverage, while the images of the multilayer (the third layer) showed obvious spherical agglomerates. Although the absorption kinetics experiments illustrated a rapid adsorption process, 40 min immersions still result in well packed TiO_2/CdS alternating assemblies according to TEM measurements.

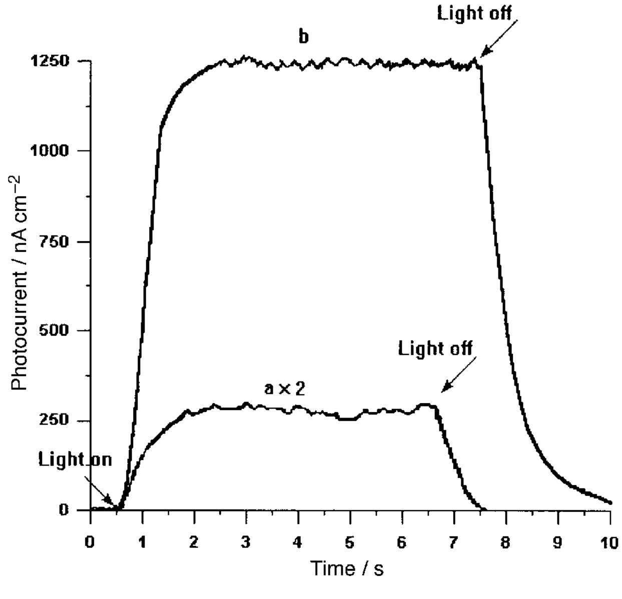

Fig. 3 Photocurrent response of ITO electrodes modified with nanoparticle multilayers: (a) 15 layers of TiO_2/PSS, (b) 15 layers of TiO_2/CdS

Fig. 3 shows the photocurrent response for a 15-layer TiO_2/CdS composite film and a TiO_2/PSS composite film modified on ITO electrodes. Photocurrents were measured by illuminating the self-assembled, film-carrying ITO electrode by a defocused light (300 W xenon lamp). The photocurrent was registered at potentiostatic conditions, $\Delta V = 0.6$ V (Ag/AgCl standard). The standard electrolyte consisted of 0.4 mol l^{-1} Na_2S and 0.1 mol l^{-1} Na_2SO_3. Comparison of curves b and a shows that the intensity of the former sample was enhanced significantly relative to that of the latter, which indicates that efficient charge transfer occurred in the composite films. In addition, the photovoltage of TiO_2/CdS composite films with 83 mW cm^{-2} in standard electrolyte *versus* the Ag/AgCl rest potential was −50.8 mV. CdS has a small bandgap and an energetically high-lying conduction band, while TiO_2 has a large bandgap and an energetically low-lying conduction band. Under irradiation, electrons generated in the CdS layers would transfer to the conduction band of TiO_2. On the other hand, holes remain in CdS. It was found that the photocurrent response was greater when a sulfide electrolyte which consists of a redox couple such as S^{2-}/SO_3^{2-} was selected instead of Na_2SO_4. From earlier studies of Q-particle-sensitized nanoporous electrodes,[5] we therefore considered that holes but not electrons would react with the electrolyte when the electrolyte consists of the redox couple, which would reduce the electron losses in the TiO_2 layers after the charge separation and thus lead to a greater photocurrent response.

In conclusion, a new kind of TiO_2/CdS alternating film comprising different nanoparticles was fabricated based on an alternating deposition method. UV–VIS spectra illustrated that TiO_2 and CdS could be deposited uniformly onto multilayers. Significant enhancement was found in the photocurrent response of a TiO_2/CdS composite film modified ITO electrode compared with a TiO_2/PSS composite film modified ITO electrode, indicating that efficient charge transfer occurred in the former system.

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