Molecular Self-Assembly of TiO₂/Polymer Nanocomposite Films

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Multilayer ultrathin films composed of titanium dioxide nanosized particles and ionic polystyrene molecules have been fabricated on single-crystal silicon, quartz, and glass substrates by a novel molecular self-assembly process. X-ray photoelectron spectroscopy (XPS) indicates that the formed cationic TiO₂ particles adsorb only on negatively charged and not on positively charged surfaces. Contact angle measurements demonstrate that the water contact angle oscillates regularly in accordance with which molecules form the outermost layer of the films. A molecular-level ordered transparent film, up to 120 layers (60 bilayers) in thickness, has been obtained and characterized by UV−vis spectroscopy. It is also demonstrated that film transmission in the UV light range decreases progressively with an increasing number of the bilayers and negligible attenuation in the visible range.

Introduction

Thin films of titanium dioxide have many useful optical, electrical, and chemical properties such as very high refractive index (2.57 at 550 nm for anatase crystal and 2.74 for rutile crystal), excellent transmittance of visible light,[1] very high relative dielectric constant ϵ_r (170 parallel to the optic axis, [001]; 89 perpendicular to the optic axis, i.e., parallel to [100]),[2] and excellent photocatalytic ability to break down organisms and bacteria under even indoor room lighting conditions.[3] Nanosized titanium dioxide particles are technologically important in many applications because of their high surface area per unit volume, which greatly increases their activity as a catalyst and sensitivity as a sensor, and unusual and interesting physicochemical and nonlinear optical properties.[4,5] Optically transparent thin films of nanometer-scale TiO₂ would be of additional interest for possible applications including ultraviolet filters for optics and packaging materials, nonlinear optics, membranes for nanofiltration, antireflective coatings, n-type semiconductor and dielectric layers, O₂ and NO₂ sensors, and coatings to maintain an organic- and bacteria-free environment.[6]

Several different strategies for fabrication of TiO₂ thin films have been reported, including sol−gel synthesis,[7] vacuum vaporization,[8] sputtering,[9] metal organic chemical vapor deposition (MOCVD),[10] chemical vapor deposition (CVD),[11] the Langmuir−Blodgett (LB) method,[12] and self-assembly monolayer adsorption on −SO₃-functionalized surfaces.[13] But there are some inherent limitations associated with these methods, some of which include limited film area or thickness, mechanical instability, high temperature and solvent involvement, film nonuniformity, costly fabrication, and complex process control. Owing to these limitations, the full range of exploitation of the potential offered by TiO₂ materials and thin films is strongly limited.

In this paper, we describe a method for the stepwise construction of molecular-level ordered TiO₂/poly(sodium 4-styrenesolfonate) (PSS) nanocomposite films by a layer-by-layer self-assembly process.[14] It will be demonstrated that this new process can be successfully carried out with ultrathin (∼1 nm) layers of polymer and inorganic TiO₂ (∼3 nm) molecules. Since the isoelectric point of titanium dioxide, based on various data,[15]

corresponding to pH = 4.5−6.8 and their particle size and surface charges are extremely sensitive to processing variables such as concentration, pH, temperature, the abilities of stabilizers, and nature of the anion,[13] the preparation of highly charged nanosized particles that maintain stability over periods of months is very difficult. In our approach, a key feature is to prepare and maintain highly charged and nanosized TiO₂ particles that are stabilized over long periods of time. Up to 120 layers (60 bilayers) of molecular-level ordered, transparent films have been prepared and characterized by UV−vis spectroscopy, contact angle, and X-ray photoelectron spectroscopy measurements.

Experimental Procedure

Poly(sodium 4-styrenesolfonate) (M_w = 70 000) (PSS), poly(allylamine hydrochloride) (M_w = 50 000−65 000) (PAH), and TiCl₄ (99.99%) were obtained from Aldrich, and *N*-2-(2-aminoethyl)-3-aminopropyltrimethoxysilane (94%) (APS) was purchased from Hüls America, Inc.

Solutions containing PSS were prepared by dissolving 120 mg of the polymer in 60 mL Milli-Q water and then acidified with 60 mL of HCl in order to set the same pH as that of the polycation solution. The solutions were then filtered through a 0.45 μm filter.

In a typical preparation of cationic TiO₂ complex, reagent grade TiCl₄ was slowly added dropwise to a flask containing 6 M aqueous HCl under vigorous stirring to make the resulting solution 0.5 M in TiCl₄. The immediate formation of a transparent colloidal dispersion was observed after aging at 80 °C for 4 h, and these solutions were observed to be stable for at least 6 months. The particle size in the dispersion ranges from 2 to 4 nm and the average size was 3 nm as revealed by TEM micrographs.

The ultrapure water used for all experiments and for all cleaning steps was obtained from a Barnstead Nanopure III system. The resistivity was about 18 MΩ/cm. The pH of the rinsing water was adjusted with HCl to be the same as those of the polycation and polyanion solutions.

The substrates of quartz, p-111 single-crystal silicon, and glass used for the deposition were cleaned with "piranha solution", a 30:70 mixture of 30% hydrogen peroxide (H₂O₂) and concentrated sulfuric acid (H₂SO₄) at 80 °C for 1 h followed by extensive rinsing with Milli-Q water, a final rinsing with

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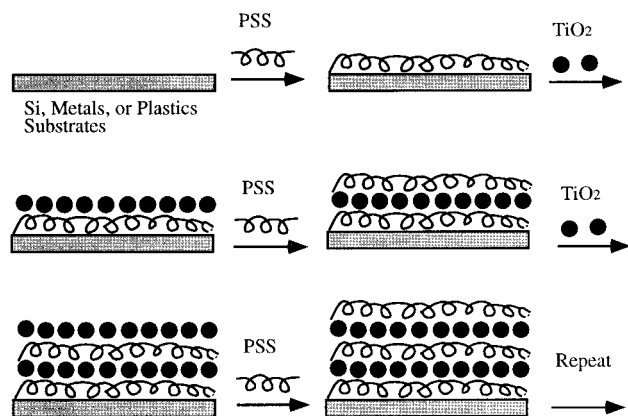
Figure 1. Procedures for fabrication of ultrathin multilayer TiO_2/polymer films.

absolute ethanol, and drying in an oven. The substrates thus cleaned were dipped in a solution of 5% APS in pure toluene for 15 h. Afterward, the substrates were ultrasonically agitated for 30 min each in toluene, methanol/toluene (1:1), and methanol. Finally, they were extensively rinsed with Milli-Q water to remove residual APS and dried. Such an APS-modified surface is positively charged.

The fabrication of TiO_2/polymer multilayer films was carried out as follows (Figure 1). An APS-modified substrate with a surface area of 7 cm^2 was immersed in the anionic solution of PSS for 10 min, then rinsed extensively with water and blown dry with nitrogen gas. Subsequently, the slide was dipped into the cationic solution of TiO_2 for 15 min followed by extensive washing with water and drying with nitrogen gas. Thus, by repetition of this simple two-step process in a cyclic fashion, the layer-by-layer self-assembly consecutive layers of TiO_2 nanoparticles and layers of polymer into multilayer films were obtained.

X-ray photoelectron spectroscopy (XPS) is an ideal instrument for the surface analysis of chemical change as a result of adsorption of polymer and TiO_2 molecules because of its high sensitivity and nondestructive nature. XPS analysis was performed using a Perkin-Elmer PHI 5400 spectrometer with a Mg K (1253.6 eV) achromatic X-ray source operated at 15 KeV and an emission current of 20 mA. The vacuum inside the analysis chamber was maintained at $< 2 \times 10^{-7}$ Torr during the analysis. Samples with a dimension of 1 cm $\times$ 1 cm were mounted on the sample holder with double-sided tape. Analyses were obtained for the center area of 2 $\times$ 2 mm^2. All samples used for XPS measurements were single-crystal silicon substrates and were analyzed at ambient temperature.

UV−vis spectroscopy (Hitachi U-2000) was used to monitor the layer-by-layer deposition process. The regular increase (decrease) in the absorption (transmittance) spectra is due to the layer-by-layer deposition process. Consecutively alternating multilayer assemblies were also characterized by advancing contact angle measurements on a Rame Hart 100-00 115 contact angle goniometer. A water drop of 5 μL was delivered from the tip of a syringe and carefully placed on the film surface with a smooth vertical motion. Contact angles were determined within 1 min of applying the drops to the film. The tangent to the drop at its intersection with the surface from the right and left sides was estimated visually. All the reported values are the average of at least eight measurements taken on both sides of at least four drops.

Results and Discussion

To integrate polymer and TiO_2 particles into ultrathin multilayer films by the layer-by-layer self-assembly process,

(a)

(b)
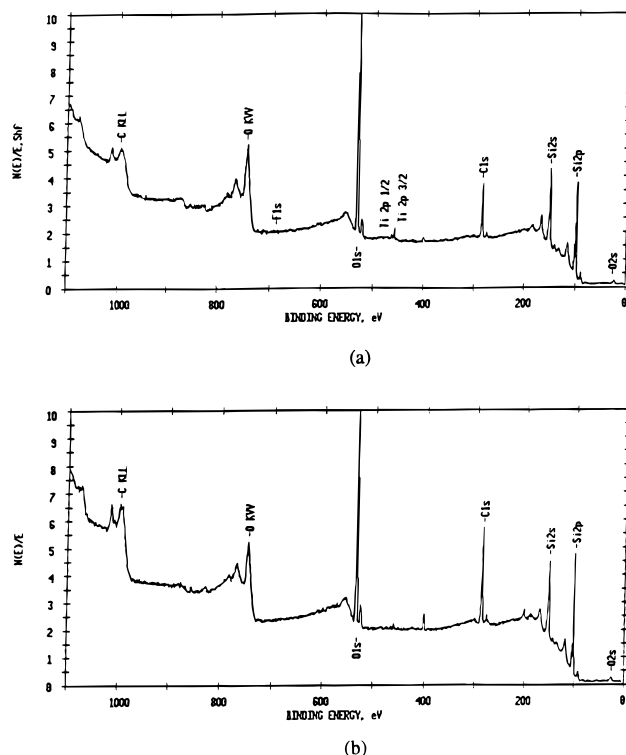
Figure 2. (a) Survey scan XPS spectrum of cationic TiO_2 particles adsorbed on negatively charged PSS/APS-modified single-crystal silicon substrate. (b) Survey scan XPS spectrum of cationic TiO_2 particles adsorbed on positively charged APS monolayer-modified single-crystal silicon substrate.

the basic requirement is to synthesize stable, nanosized ionic TiO_2 complexes. Titanium aqueous solution chemistry is complicated and marked by the formation of various complexes that are very sensitive to a number of processing variables such as the water/$TiCl_4$ ratio, pH, the reaction temperature, the stabilizer, and the nature of the anion.[13,16,17] It is commonly agreed that the preparation of titanium dioxide colloidal dispersions consisting of particles of narrow size distribution is possible at very low pH in which the hydroxylation and hydrolysis occur at a reasonable rate. At a high pH value, these processes occur too fast to yield particles of uniform size. Thus, the preparation of TiO_2 colloids is usually carried out in highly acidic solutions at elevated temperature.[13,17,18]

To make transparent films consisting of TiO_2 particles, it is imperative to minimize light scattering by controlling the particle size. Cationic nanosized TiO_2 complexes with a narrow particle size distribution were obtained when highly acidic titanium tetrachloride solutions were aged at elevated temperature for 4 h. Figure 2a shows the XPS survey spectrum from TiO_2 thin films deposited on a surface of anionic PSS polyelectrolyte for 20 min at room temperature. A clear Ti signal is present at 458.6 eV ($2p_{3/2}$) and a relatively small peak at 464.5 ($2p_{1/2}$), which agree with reference values for bulk TiO_2.[19] Whereas when the APS (positively charged) modified silicon substrate was immersed in the titanium dioxide colloid solution for 15 min, there is no obvious adsorption of Ti as shown by XPS in Figure 2b because of an electrostatic repulsion between these two cationic species. Although the thickness of the APS monolayer is only 9 Å, it can effectively prevent the adsorption of titanium dioxide with the same charge sign, which indicates that the prepared cationic TiO_2 complexes have sufficient surface charge to ensure the requisite strong electrostatic interaction. To investigate the quality of the charge-maintaining ability of TiO_2 colloids for the multilayer deposition, a positively charged

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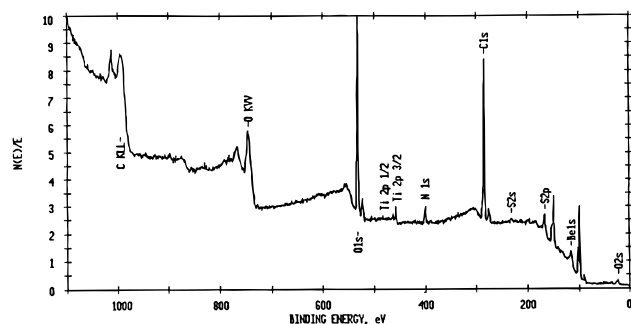
Figure 3. Survey scan XPS spectrum of positively charged PAH monolayer atop two bilayers of TiO₂/PSS on single-crystal silicon substrate.

PAH layer on top of 2 bilayers of PSS/TiO₂ was formed and characterized by XPS as displayed in Figure 3. Strong N (1s, 401.9 eV) and Ti ($2p_{3/2}$, 458.6 eV; $2p_{1/2}$, 464.5 eV) are exhibited, indicating that the alternating deposition of cationic TiO₂ and anionic PSS results in the formation of a multilayer film. Note that the intensities of the photopeaks of Si 2s, and Si 2p decrease significantly as the multilayer films cover the silicon surface. The TiO₂ particle size is estimated to be less than 5 nm, since the detectable depth of XPS is in the range 5−8 nm, which is consistent with the results of the average particle size estimated to be 3 nm by TEM micrographs.

The spontaneous, layer-by-layer self-assembly of the cationic TiO₂ nanoparticles between the anionic polyelectrolyte (PSS) layers is based on the ionic attraction developed between the oppositely charged species, which promotes strong interlayer adhesion and a uniform and linear multilayer deposition process. The key to a regular multilayer buildup is the reversal of the surface charge in each adsorbed layer as shown in Figure 1. Since titanium possesses a high complex-forming ability, the acid used as a stabilizer should be strong enough to guarantee the requisite positive charge on the particles, and the processing variables should be adjusted to ensure only cationic, rather than neutral and negative titanium oxide, complexes coexist. For the latter systems in which the cationic, neutral, and anionic as well as anionic PSS layers form a compositionally uniform bilayer structure, one would expect the contact angle to be essentially independent of which layer is outermost[20] and the buildup of multilayer films would be terminated. Alternately, if most complexes formed in the solution are positively charged and the interlayer interpenetration is limited, one would expect the wettability of the film surface to be determined by the structure of the outermost layer,[21] and the multilayer TiO₂/PSS nanocomposite film should be built-up. Figure 4 shows that for the TiO₂/PSS system, water contact angles are determined by the outermost layer. The water contact angle for the APS-modified surface is 18°, corresponding to the APS monolayer formed on the substrate. Anionic PSS adsorbs on this surface and increases the contact angle to 37°. The increased contact angle is attributable to the adsorption of PSS with polar head groups attached to the positively charged surface with the nonpolar hydrocarbon chains oriented upward toward the bulk portion of the droplet. When TiO₂ complexes adsorb on the PSS surface, the contact angle decreases to around 22° because of the hydrophilic property of titanium oxide complexes. It can be seen that the average water contact angle oscillates according to which ions form the outermost layer with the alternation of TiO₂ and PSS and remains about the same even after 26 layers (13 bilayers) were deposited onto the positively charged surface (APS-modified silica surface). This clearly demonstrates that the consecutive adsorption of anionic PSS and cationic TiO₂ is
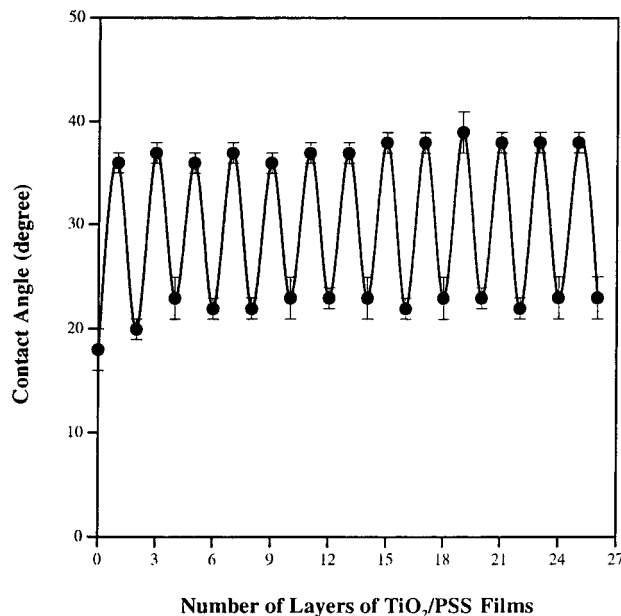

Figure 4. Advancing contact angles of TiO₂/PSS multilayer films as a function of the number of layers deposited on a positively charged (APS) surface.
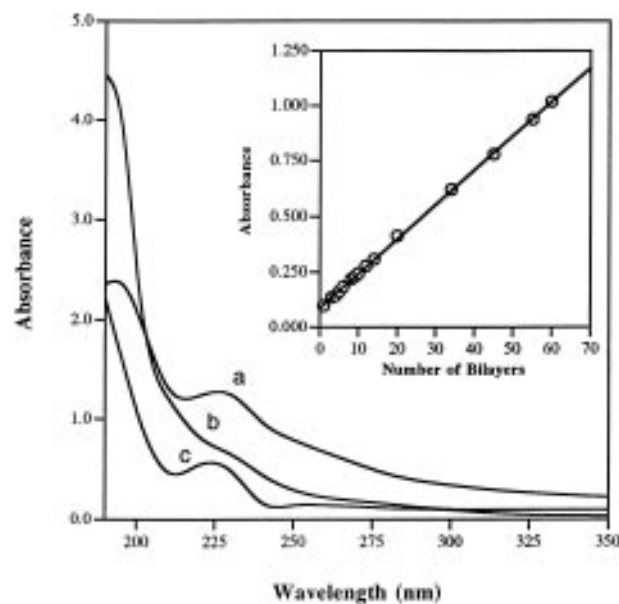
Figure 5. Optical absorption spectra: (a) thin film of TiO₂/PSS on quartz; (b) TiO₂ colloids in water; (c) polystyrene (PSS) solution in water. The inset shows the linear relationship between absorbance at 190 nm and number of bilayers of TiO₂/PSS deposited.

stepwise and that the deposition process is very consistent from layer to layer and highly reproducible.

Optical UV−vis spectroscopy was also used to characterize the growth of the multilayer structure in the amount of material deposited per layer. Optical absorbance spectra following the deposition process and growth of the TiO₂/PSS multilayer films, up to 60 bilayers on an APS-modified quartz slide, are shown in Figure 5. For comparison, the optical absorbance spectra of aqueous solutions of PSS and TiO₂ nanoparticle dispersions are also shown in Figure 5. It can be seen that the absorbance spectra of the TiO₂/PSS multilayer films are the spectra overlap of the individual PSS and TiO₂ layers and are retained in the same fashion as more layers are built up. Two absorption bands are observed at 194 and 228 nm. No shift in maximum absorption and light scattering is observed as the number of the multilayer thin film layers increases, which means that there
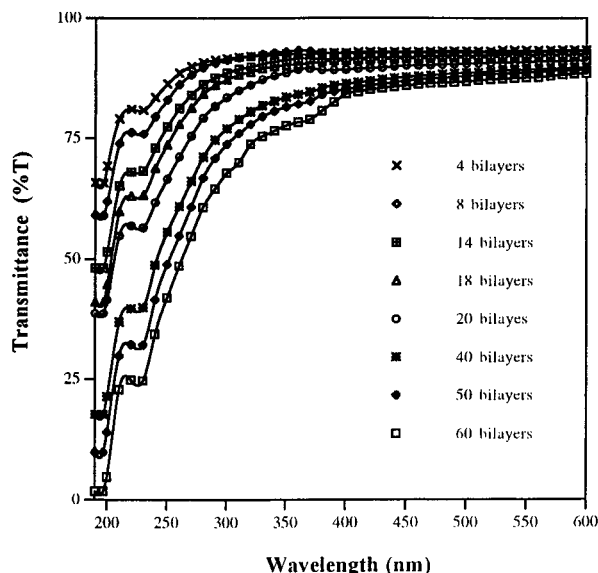
Figure 6. UV−vis transmittance versus wavelength of TiO$_2$/PSS films on quartz.

is no molecular aggregation between adjacent layers, and the domain size of TiO$_2$ particles remains small, at most less than 13 nm based on an estimation from Raleigh scattering. It can be seen that a linear deposition pattern of a 60-bilayer film is observed with respect to the number of bilayers of films, yielding an average optical density of 0.016 ± 0.008 (at 190 nm) per bilayer. The linear nature of the plot suggests that each layer adsorbed contributes an equal amount of material to the thin film. As seen in this figure, the consecutive adsorption of layers is stepwise and the deposition process is linear and consistent from layer to layer.

Measurement of the spectral transmission of the film versus wavelength is shown in Figure 6. As expected, the transmission in the UV light range decreases progressively with an increasing number of bilayers, while only small changes occur in the visible region. It can be seen that transmission drops from 66% for a 4-bilayer film coating to 9.7% for a 60-bilayer film coating at 190 nm. Based on our previous work with other PSS-based bilayer systems, the thickness contributed per bilayer by the PSS, as determined by spectral ellipsometry measurements, is 0.6 nm, and the average TiO$_2$ particle size is 3 nm, so the thickness of one bilayer of TiO$_2$/PSS film is estimated to be about 3.6 nm. It thus can be estimated that the total thickness of 60 bilayers of a TiO$_2$/PSS film is about 216 nm.

The general preparative method described in this paper offers a potentially powerful strategy for fabricating ordered conjugated polymer/TiO$_2$ (for example, nanosized p−n, p−n−p, n−p−n

junctions and superlattice and metal−insulator semiconductor structures) and high-performance polymer/TiO$_2$ (polyimide/TiO$_2$, polyamide/TiO$_2$) multilayer thin films with controlled thickness, functional compounds, and controlled molecular architecture on many modified substrates such as plastics, metals, and semiconductors[22−24] at room temperature and ambient conditions, which may lead to novel optical, electronic, mechanical, chemical, and electro-optical devices with low cost.

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