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Multilayer ultrathin films of molecular titania nanosheets showing highly efficient UV-light absorption

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Titania nanosheet crystallites have been self-assembled layer-by-layer with poly(dimethyldiallyl ammonium chloride) onto substrates to produce ultrathin nanostructured films which exhibit highly efficient optical absorption with a sharp peak at 266 nm.

In the past decade, titania thin films have attracted tremendous attention for their optical and photochemical applications, *e.g.* UV-light shielding, solar energy conversion and detoxification of pollutants.[1] For these applications, it is of great importance to fabricate titania thin films with a well controlled nanostructure. Among a range of film growth strategies, the Langmuir–Blodgett technique and self-assembly procedure *via* sequential adsorption[2] are the most feasible and widely applicable to tailor stable and high-quality films on a nanometer-scale range. Recently these approaches have been applied for the synthesis of multilayer titania films by several groups.[3–6] These preparations incorporated titania particles of several nm in size as a film component. Hence, the resulting multilayer films were composed of alternating layers of two-dimensionally packed nanoparticles and organic substances as a binder. The titania nanoparticles were synthesized by hydrolyzing an appropriate Ti salt. It is sometimes difficult to prepare extremely small sized particles in high quality, particularly in terms of crystallinity, uniform shape and size, which is essential for fabrication of well organized films.

Recently we have demonstrated that colloidal titania nanosheets of composition $Ti_{1-\delta}O_2$ ($\delta \approx 0.09$) can be derived by completely delaminating a layered titanate.[7] The obtained semiconductor crystallite, as the elementary fragment of the layered crystals prepared at a high temperature, is characterized by its very high two-dimensionality, with a thickness of molecular dimension as well as high crystallinity, which leads to novel physicochemical properties which are distinct from those of titania nanoparticles.[8] These features of the nanosheet crystallites may have some advantages to better control nanostructures in the layering process and some enhanced physical properties may be expected for resulting multilayer assemblies in comparison with films composed of nanoparticles. Here, we report the layer-by-layer construction of a well organized multilayer system of titania semiconductor nanosheets and organic polymers, which efficiently absorb UV light with a wavelength below 300 nm.

The titania nanosheet crystallites, $Ti_{1-\delta}O_2$ ($\delta \approx 0.09$), were obtained by chemically delaminating a protonic titanate of γ-FeOOH type layered structure, $H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot H_2O$ ($\square$ = vacancy),[9] into its colloidal single layers upon action of an aqueous solution of tetrabutylammonium hydroxide (TBAOH).[7] The multilayer films were prepared by repeating the following adsorption procedures for the desired number of cycles.

Each cycle involves the immersion of a substrate such as Si wafer or quartz glass into the colloidal suspension of the titania nanosheets for 20 min, rinsing with Milli-Q filtered water (>17 MΩ cm^{-1}), and then dipping in an aqueous solution of poly(dimethyldiallyl ammonium chloride) (PDDA) for 20 min, and finally washing with water. A polycation such as PDDA was employed as a counterpart for the self-assembly process because the titania nanosheets are negatively charged. The substrates were cleaned prior to the film deposition by a method described in the literature[10] and then primed with poly(ethylenimine), PEI, to introduce positive charge onto their surface. The concentration of the titania suspension and the PDDA solution were 0.08 and 20 g dm^{-3}, respectively. The pH values of both were adjusted to *ca.* 9 by adding an appropriate amount of HCl or TBAOH. The PDDA was added as a 0.5 mol dm^{-3} NaCl solution.

Consecutive adsorption procedures as described above yielded visibly transparent thin films, the growth process of which was followed by several characterization techniques. UV–VIS absorption spectra show progressive enhancement as a function of the layer pair number (Fig. 1). The spectral profile with a pronounced peak at 266 nm is characteristic of titania nanosheets in aqueous suspension.[8] The polycations, PDDA and PEI, do not show substantial absorption in the energy region shown. Consequently, the nearly linear growth of the absorption peak indicates that an approximately equal amount of $Ti_{1-\delta}O_2$ was deposited for each adsorption procedure. The modest increase in background at a wavelength of >300 nm may arise from light scattering by the nanosheet crystallites oriented parallel to the substrate surface with lateral sizes in the submicro- to micro-meter range.

X-Ray diffraction patterns (Fig. 2) illustrate the evolution of a Bragg peak suggesting a periodicity of 1.4 nm. This diffraction peak is attributable to a so-called superlattice reflection of the inorganic/organic repeating nanostructure. The nanosheet crystallite $Ti_{1-\delta}O_2$ has an atomic architecture of γ-FeOOH type in which TiO_6 octahedra at two different levels along the sheet normal are connected with each other *via* edge-sharing to produce the two-dimensional sheet.[8] Its thickness is

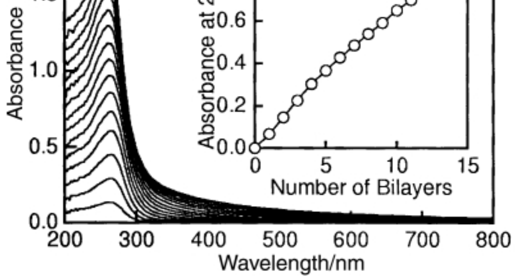

Fig. 1. UV–VIS absorption spectra of $Ti_{1-\delta}O_2$/PDDA multilayer films grown on SiO_2 glass; 0.5 × the observed absorbance at 266 nm is plotted in the inset taking into account the presence of the film on both sides of the substrate.

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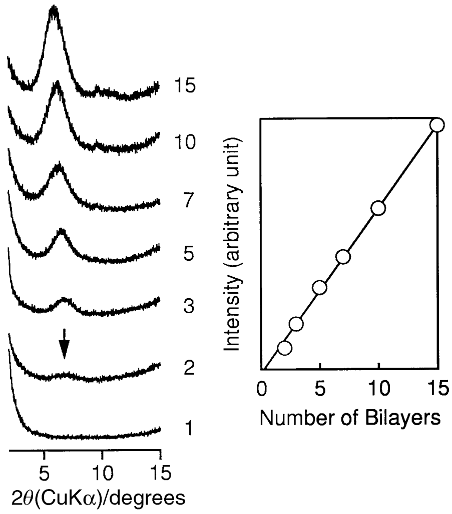

Fig. 2. X-Ray diffraction patterns of $Ti_{1-\delta}O_2$/PDDA films on SiO_2 glass with the number of layer pairs indicated.

estimated to be 0.75 nm taking into account the outermost edges of surface oxygen atoms. Accordingly, the thickness for the PDDA layer should be 0.65 nm. This dimension is reasonable for the PDDA molecular structure at the salt concentration under which the film was grown.

The intensity of the basal diffraction series for a system of N parallel nanosheets can be calculated using eqn. (1):[11]

$$I(0k0)=\frac{1}{N}\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}F^2(0k0)\frac{\sin^2(\pi Nk)}{\sin^2(\pi k)} \qquad (1)$$

where the second, third and fourth terms are the Lorentz-polarization factor, structure factor and interference function, respectively. Since the latter term is proportional to N^2 at $k = \pm 1, 2, 3$, the $0k0$ peak intensity is linearly dependent on N. This was experimentally observed as shown in inset, suggesting successful construction of the multilayer film.

The diffraction peak was detectable even for the two-unit system, *i.e.* PEI/$Ti_{1-\delta}O_2$/PDDA/$Ti_{1-\delta}O_2$. The well ordered nature of this multilayer system is principally explained by the fact that the interpenetration of inorganic and organic components is strongly reduced owing to the two-dimensional architecture of the rigid inorganic nanosheets. This is in sharp contrast to other multilayer films composed of organic polymers where neighboring layers intermingle considerably.[2]

The ultrathin titania films obtained in this study have a molecularly ordered array of the components. The film architecture is based on platelets rather than particles as found for titania films reported previously.[3–6] The multilayer repeat dimension of 1.4 nm is finer than for such previously reported films (> 3 nm).

The optical properties are also noteworthy, particularly in terms of sharp and highly efficient absorption in the UV region (< 300 nm). The sharp absorption edge, which is significantly blue-shifted relative to bulk TiO_2, may be associated with exciton confinement in the two-dimensional semiconductor crystallites which are of sub-nm thickness.[8] Theoretical calculations predict very small values, 0.3–1.9 nm, for the Bohr radius of the first exciton in TiO_2, or the threshold at which quantum size effects manifest themselves.[12,13] On the basis of the experimental data, Serpone *et al.*[14] have claimed that the exciton radius is < 1 nm. Titania nanoparticles reported so far are mostly larger in size than this size-quantization threshold. On the other hand, the nanosheet thickness is small enough to expect carrier confinement. To our knowledge, a dimension as small as 0.75 nm (the nanosheet thickness) has not previously been reported for titania systems.

The absorption efficiency was several times higher than for films incorporated with titania nanoparticles.[3–6] The optical density at a wavelength of 266 nm was 0.065 for one titania-nanosheet layer (inset in Fig. 1). Comparable data for multilayer films with titania nanoparticles and amino acid capped particles are reported to be 0.016 ± 0.008 (at 190 nm) and 0.017 (232 nm), respectively.[4,6] Note that the optical density for the nanosheet system was higher despite its smaller thickness of the titania layer (0.75 nm) in comparison with those of nanoparticles (2.3–3 nm). Although there are several factors to be considered for the origin of this intense absorption, we speculate that the size effect on oscillator strength is a likely explanation. Its significant enhancement with decreasing the size of semiconductor nanocrystallites has been theoretically predicted and has been experimentally observed for CdS nanoclusters.[15] The findings here strongly suggest promising potential of the present system for its use as photovoltanic, photochromic and catalytic devices and sensors.

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