

Titanate nanotube thin films *via* alternate layer deposition†

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Layer-by-layer growth of titanate nanotubes on glass substrates was achieved by alternate layer deposition using an aqueous solution of colloidal titanate nanotubes and that of a polycation. Even a single layer thin film of titanate nanotube shows high photoinduced hydrophilicity.

Titanium oxide (TiO₂)-based materials are extensively studied in areas such as photocatalysis¹ and photovoltaics.² TiO₂ has a strong oxidation activity and photoinduced hydrophilicity.³ Thus, it has been applied to various industrial items that possess self-cleaning and anti-fogging properties. Recently, titanate nanotubes (TNT)⁴⁻⁶ have been intensely investigated as unique materials with one-dimensional (1D) nanostructures and high specific surface areas. However, TNT have only been studied in powder form and the thin film form has not been reported. Thin film fabrication on glass and plastic substrates is indispensable for applying TNT as photocatalysts and to other devices.

This paper reports the preparation of a stable TNT-dispersed solution and fabrication of optically transparent nanostructured TNT thin films by alternate layer deposition, which display photoinduced hydrophilic properties.

TNT were synthesized by a previously reported hydrothermal method.^{4,5} Typically, 0.96 g TiO₂ (anatase) powder with a diameter of 20 nm was added to 80 mL of 10 M NaOH aqueous solution in a 100 mL stainless Teflon-lined autoclave and heated at 120 °C for 40 h. After the reaction, a white precipitate was filtered and washed with 0.1 M HNO₃ aqueous solution and then washed with distilled water. The X-ray powder diffraction pattern was similar to that previously reported.^{4,5} Nanotubular structures with approximately a 9 nm diameter and several hundred nanometres in length were observed by SEM and TEM.

A colloidal suspension of TNT was prepared by stirring TNT powder (0.5 g) in 50 mL of 1 M HNO₃ aqueous solution for 15 h at room temperature. A gelatinous deposit was separated by centrifuging at 5000 rpm for 15 min. Then adding this to 50 mL of 0.2 M tetra(*n*-butyl)ammonium hydroxide (TBAOH) aqueous solution, which was stirred for 15 h at room temperature, resulted in a translucent solution. The zeta potential experiment indicated that the pH at the point of zero charge (pzc) of TNT was *ca.* 5.5.

Fig. 1 illustrates a transmission electron micrograph (TEM) image of TNTs in TBAOH aqueous solution and demonstrates that the nanotubular structure is maintained after treatments with acidic and basic solutions. In contrast, TNT powder could not be dispersed in TBAOH aqueous solution without an acidic treatment. Therefore, the acid treatment is indispensable for dispersing nanotubes in TBAOH solution. The acid treatment contributes to the protonation of the nanotube surface, which stabilized the nanotubes in the TBAOH aqueous solution by exchanging H⁺ for TBA⁺.

Nanostructured TNT thin films were fabricated by alternate layer deposition similar to that previously reported.⁷⁻⁹ In this case, TNTs act as negatively-charged particles and poly(ethyleneimine) (PEI) or poly(diallyldimethylammonium chloride) (PDDA) was the polycation. The TNTs were negatively charged by adjusting the TNT solution to pH 9 above the pzc. Alternate adsorption occurred

by means of the Coulombic force between TNTs and polycations. A pyrex glass substrate previously coated by dipping into an 0.2 M aqueous solution of PEI for 20 min and rinsing with ion-exchanged water was used to prepare a positively charged surface. Then the substrate was exposed to the above-mentioned TNT-TBAOH aqueous solution for 20 min, rinsed with ion-exchanged water, and immersed in an 0.2 M aqueous solution of PDDA for 20 min, and rinsed with ion-exchanged water. This process can be repeated until the desired number of TNT layers is achieved. The TNT/polymer hybrid film was abbreviated as PEI/(TNT/PDDA)_{*n*-1}/TNT film, where *n* is the number of adsorption cycles. The PEI/(TNT/PDDA)_{*n*-1}/TNT films were optically transparent up to 10 adsorption cycles.

Fig. 2 shows a tapping-mode AFM image of the film after the first deposition of TNTs (denoted PEI/TNT film) on pyrex glass. The surface was uniformly covered with monodispersed nanotubes. Height profile measurements indicated that the average height of nanotubes on the substrate was *ca.* 10 nm, which was consistent with the diameter of TNT.

UV-vis absorption spectra of PEI/(TNT/PDDA)_{*n*-1}/TNT films grown on pyrex glass show that the absorbance in the spectral range

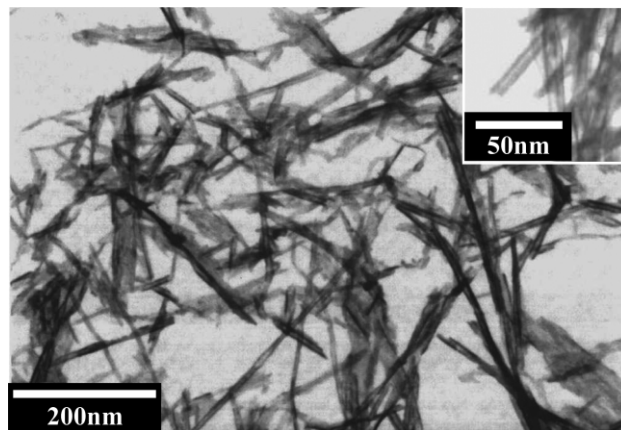


Fig. 1 TEM image of TNTs in a TBAOH aqueous solution. Inset shows higher magnification image.

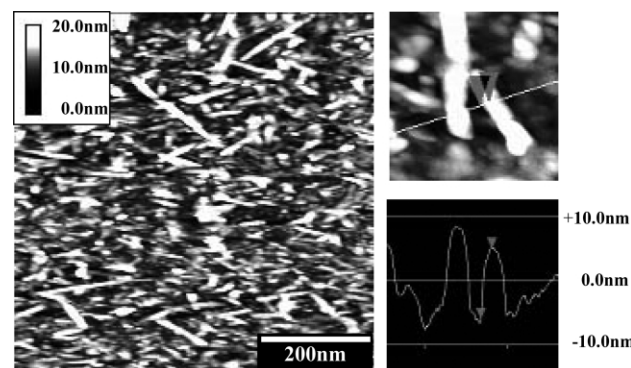


Fig. 2 AFM image of the first layer of TNTs deposited on the glass/PEI substrate.

† Electronic supplementary information (ESI) available: XRD patterns of TNT, surface and cross-sectional SEM images of thin films after 5 and 10 cycles. See <http://www.rsc.org/suppdata/cc/b3/b316924c/>

of 240–400 nm (Fig. 3) increased with the number of adsorption cycles increased. The absorbance value at 260 nm increased linearly *versus* the number of adsorption cycles (inset of Fig. 3). PEI and PDDA did not have absorption in the same spectral region.⁹ Film thicknesses after 5 cycles and 10 cycles by SEM were *ca.* 50 nm and 100 nm, respectively. Therefore, the thickness for each adsorption cycle is *ca.* 10 nm. These results suggest that the layer-by-layer growth of TNTs on the substrate was achieved by alternate adsorption with PEI and PDDA. In particular, nanotubes were deposited as a monolayer in the PEI/TNT film. We also confirmed the layer-by-layer growth of TNTs on other substrates such as a Si wafer. Hence this fabrication process of TNT thin films is expected to be applied to various substrates.

To investigate the photochemical properties of a TNT/polymer hybrid thin film, the change in water contact angle of the bilayered PEI/TNT film under UV irradiation from a 150 W Hg–Xe lamp was used to evaluate the photoinduced hydrophilic properties (Fig. 4). When initially irradiating, the contact angle decreased to nearly 0 degrees within 60 min. XPS measurements revealed that the N1s peak assigned to PEI (400 eV) became undetectable after UV irradiation for 80 min, while the N1s peak assigned to NH₄⁺ (401.5 eV) was observed after UV illumination. These results indicate that PEI is decomposed by the photocatalytic activity of TNT. NH₄⁺ was not decomposed to NO_x or NO₃⁻, which suggests that the ammonium cation stably existed on the surface of anionic TNT similar to that reported for titania nanosheets.¹⁰ Moreover, the surface morphology remained unchanged after irradiating with AFM and SEM. Therefore, UV treatment converted the PEI/TNT bilayered film to a polymer-free, monolayered TNT thin film. After the initial illumination, the substrate was stored in the dark and clean-air conditions for a month. Subsequently, the TNT thin film reproducibly demonstrated high photoinduced hydrophilicity in the second and third irradiation. In earlier literature, it has been reported that the photoinduced hydrophilic conversion of TiO₂ (anatase or rutile) thin films is associated with the surface structure.^{11,12} A similar surface reaction seems to occur on the TNT surface. At present, the thickness of TiO₂ films was several tens of nanometres to evaluate photoinduced hydrophilicity. In the present paper, it is noteworthy that the photoinduced hydrophilicity proceeds even in the monolayered TNT film. In addition,

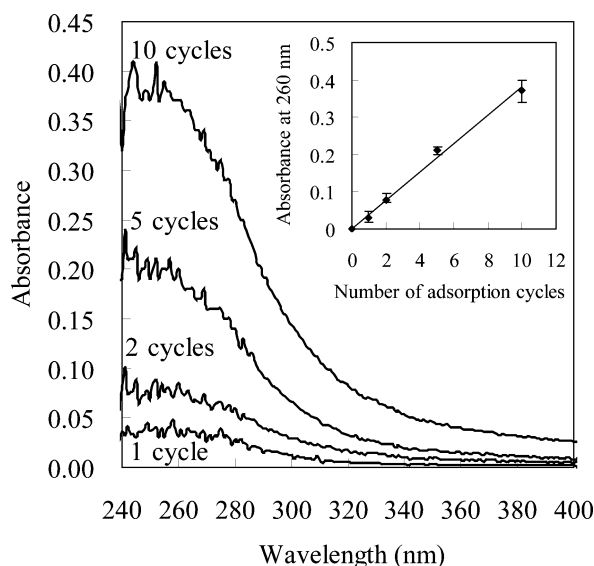


Fig. 3 UV-vis absorption spectra of PEI/(TNT/PDDA)_{n-1}/TNT film. Inset shows a plot of absorbance at 260 nm vs. number of adsorption cycles.

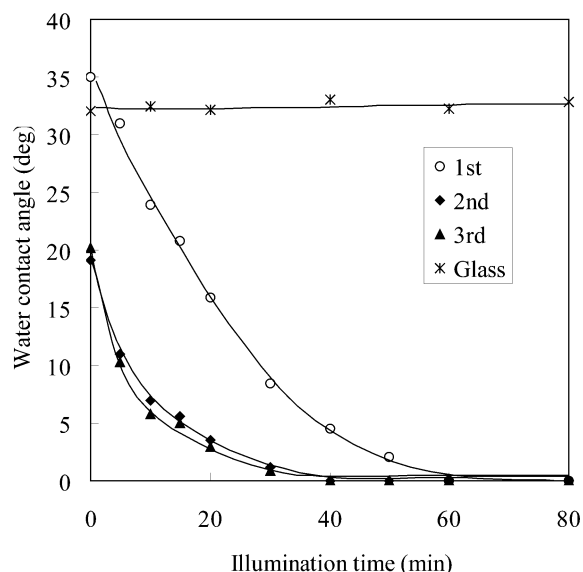


Fig. 4 The change in water contact angle of PEI/TNT thin film under UV irradiation.

photochemical reactions of multilayered TNT/polymer films were evaluated. Our XPS measurements revealed that PEI and PDDA were decomposed by UV irradiation. Then the thickness of PEI/(TNT/PDDA)_{n-1}/TNT films (*n* = 5,10) was slightly decreased ~10% after the UV irradiation, and this thickness shrinkage was due to the decomposition of polycation layers.¹⁰ Moreover, the water contact angle of polymer-free multilayered TNT films became 0 degrees under illumination.

In summary, TNT thin films can be successfully fabricated by alternate layer deposition using TNT stably dispersed in aqueous solution and cationic polymers. We demonstrated that even monolayer TNT deposition drastically changed the surface properties. This process is applicable to other types of substrate such as glass, plastics, and metals. It may be potentially applied to various industrial items such as sensors and photovoltaic devices.

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