



Electrophoretic deposition of titanate nanotube films with extremely large wetting contrast

Yuekun Lai^{a,b}, Yicong Chen^a, Yuxin Tang^b, Dangguo Gong^b, Zhong Chen^{b,*}, Changjian Lin^{a,*}

^aState Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

^bSchool of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

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ABSTRACT

A facile electrophoretic deposition (EPD) process has been developed to prepare thin films consisting of titanate nanotubes (TNTs) that were synthesized by a hydrothermal approach. Such an EPD process offers easy control in the film thickness and the adhesion to the substrate was found to be strong. The chemical composition and structure of the products have been characterized by XRD, HRTEM, and FESEM. It was found that the functionalization of TNTs plays a key role on the electrolyte stability and the formation of a uniform TNT film with good adhesion. The as-prepared TNT films show exceptional superhydrophilic behavior with ultra-fast spreading, while it converts to superhydrophobicity yet with strong adhesion after 1H,1H,2H,2H-perfluorooctyl-triethoxysilane modification. This study provides an interesting method to prepare films with extremely high wettability contrast that are useful for producing different types of functional materials.

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1. Introduction

Since Kasuga et al. reported the fabrication of protonated titanate nanotubes (TNTs) by hydrothermal process at 1998 [1], TNTs had attracted tremendous interest due to its large specific surface area, excellent ion-exchange and intercalation activities. It can be used as absorbants, deodorants, and functional nanoparticle carriers [1–5]. Moreover, TNTs can be transformed to another important material, TiO₂ in nanotubular form, which has many important applications in photocatalysis, solar cells and gas sensors [6–9]. Recently, great efforts were focused on the TNT formation mechanism, chemical compositions, and property improvement. However, the issues such as the effective preparation of uniform TNT films with controllable thickness and their wetting properties need to be further investigated [10,11].

Recently, Tian et al. [12] reported a simple hydrothermal and seeded growth process to fabricate TNT film by directly immersing Ti substrate in concentrated NaOH solution for certain time. However, this method is restricted to synthesis of titanate films on Ti substrate and the film may be exfoliated with increasing process duration. Miyauchi, Bando et al. [2,3] had further developed an alternate layer deposition technique to prepare thin TNT films.

Their method suffers from a major drawback as it could only deposit about 10 nm in each assembly step, which makes it difficult to apply in practical applications when a thick layer is needed. Electrophoretic deposition (EPD) technique is a widely used industrial process that has been applied for fast deposition of large scale field emitter film with good adhesion [13]. However, the poor dispersion of TNTs in aqueous or organic matrix greatly blocks the fabrication of uniform TNT film. Therefore, it remains so far a challenge to develop a method to effectively prepare uniform TNT film with good adhesion. The surface functionalization of TNTs may be a good alternative to solve the problem of TNT powder agglomeration. We thus expect it will be possible to fabricate uniform functional TNT film with good adhesion by EPD technique.

Here, we reported a new way to prepare highly dispersed colloidal suspension and applied it to effectively deposit uniform TNT films by a simple EPD process under ambient condition. The as-prepared TNT films show good adhesion to the substrate without annealing post-treatment. The effect of electrolyte and potential on the morphology of the as-prepared TNT film was investigated. And a formation mechanism of the TNT films is discussed. The wettability of the TNT film was also reported.

2. Experimental

The sodium titanate powders were prepared using a modified hydrothermal process similar to that described in previous report

* Corresponding authors. Tel.: +65 9137 2963; fax: +65 6790 9081 (Z. Chen), tel./fax: +86 218 9354 (C. Lin).

E-mail addresses: aszchen@ntu.edu.sg (Z. Chen), cjlin@xmu.edu.cn (C. Lin).

[1–3]. In a typical synthesis, a 0.5 g TiO_2 (anatase) powder was dissolved in 30 mL of 10 mol/L NaOH solution and then transferred into 50 mL of Teflon-lined autoclave at 130 °C for 48 h. Following that, the sodium TNT materials were treated with HNO_3 solution to form hydrogen titanate. Subsequently, 0.25 g TNT powders were vigorously stirred in 25 mL of 0.2 mol/L tetrabutylammonium hydroxide (TBAOH) aqueous solution for 24 h to obtain stable suspension. A colloidal aggregate centrifuged from the above suspension were further dispersed in 50 mL anhydrous ethanol with a pH about 9.6–10.0 for anodic EPD. A 2 cm² FTO glass (or 316L stainless steel) was acted as anode and a Pt sheet was used as the cathode. At room temperature, the optimized experimental was conducted under 30 V with a distance of 2 cm between the two electrodes.

The morphologies were observed using high-resolution transmission electron micrograph (HRTEM, Philips Tecnai F30) and field emission scanning electronic micrograph (FESEM, LEO-1530). The crystallinity was measured using an X-ray diffractometer with Cu K α radiation (XRD, Philips X'pert-PRO PW3040). The zeta potential was measured by a Zetasizer Nano ZS (Malvern Instruments, UK). The contact angles were measured at ambient temperature using an OCA 20 instrument (Dataphysics, Germany).

3. Results and discussion

Fig. 1a shows the typical HRTEM micrograph of the TNTs in TBAOH aqueous solution. Highly dispersed nanotubes of several hundred nanometers were clearly observed. Some nanosheet structures were also found due to incomplete sheet wrapping. The magnified image (Fig. 1b) shows that nanotubes have an outer and inner diameter of ~ 11 and 5 nm, and the interlayer spacing is ~ 0.78 nm. The dispersion of the two types of titanate powders (hydrogen and sodium, 10 mg/mL) in anhydrous ethanol with (A,B) and without (C,D) TBAOH is shown by the inset of Fig. 1b. The most stable and homogeneous colloidal suspension was produced by TBAOH pretreated hydrogen titanate. In contrast, the

sodium titanate powders with or without TBAOH treatment could not be well dispersed. Although the hydrogen titanate powder without TBAOH pretreatment in anhydrous ethanol was relatively stable, it could not be deposited under anodic electrophoretic deposition. We believe that, the treatment with TBAOH aqueous solution leads to homogeneous TNT colloidal suspension due to the electrostatic repulsive interaction among hydrogen titanate nanotubes via TBA cation intercalation or absorption.

Fig. 1c shows XRD patterns of the as-prepared sodium-TNTs and TBA-TNTs. It is seen that all diffraction peaks matched well the standard data for orthorhombic titanate ($\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$, JCPDS No. 47-0124). The titanate characteristic peaks at around 10° (200) and 28.5° (310) are significantly weakened and shifted to lower angles, which indicates the adsorption of TBA⁺ ions on TNT layered structures. The zeta potential experiment indicated that the pH value at the isoelectric point (IEP) of the stable TBA_nH_{2-n}-Ti₂O₅ suspension in anhydrous ethanol was at around 5.5 (Fig. 1d). Therefore, the negative charged TNTs can be deposited by anodic EPD.

Fig. 2a and b shows the typical FESEM images of as-prepared TNTs deposited by anodic EPD under 30 V for 2 min. It can be clearly observed that the negatively-charged TNTs have uniformly covered the substrate to form a compact film, indicating that the modified TNTs are effective for the anodic EPD. The inset of Fig. 2b shows that the corresponding thickness is about 450 nm. No obvious change of the surface morphology was found after by sonication for 30 min, indicating the as-prepared TNT films have strong bonding to the substrate before annealing post-treatment. It is easy to fabricate transparent or semi-transparent TNT films by adjusting the electrophoretic potential and time to control the film thickness. Moreover, the TNT films can be changed to anatase TiO_2 nanotube without obvious morphology change by annealing at or below 450 °C (Fig. 2e) or by a low temperature wet chemical process [6,14]. However, when annealed at 600 °C, phase transformation and collapse of nanotube walls have resulted in growth of

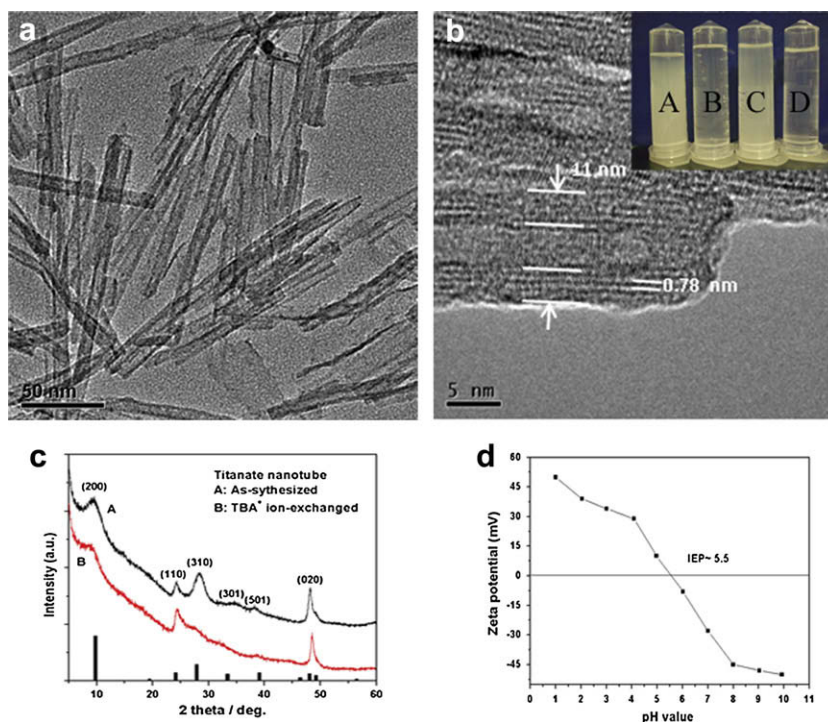


Fig. 1. (a, b) HRTEM images of TNTs in TBAOH aqueous solution; (c) XRD pattern of (A) sodium TNTs and (B) TBA-TNTs powder; (d) zeta potential of TBAOH pretreated TNT colloid in anhydrous ethanol. The inset shows the photograph of hydrogen TNT and sodium TNT powder in anhydrous ethanol solution static stored for 30 min with (A, B) and without (C, D) TBAOH pretreatment.

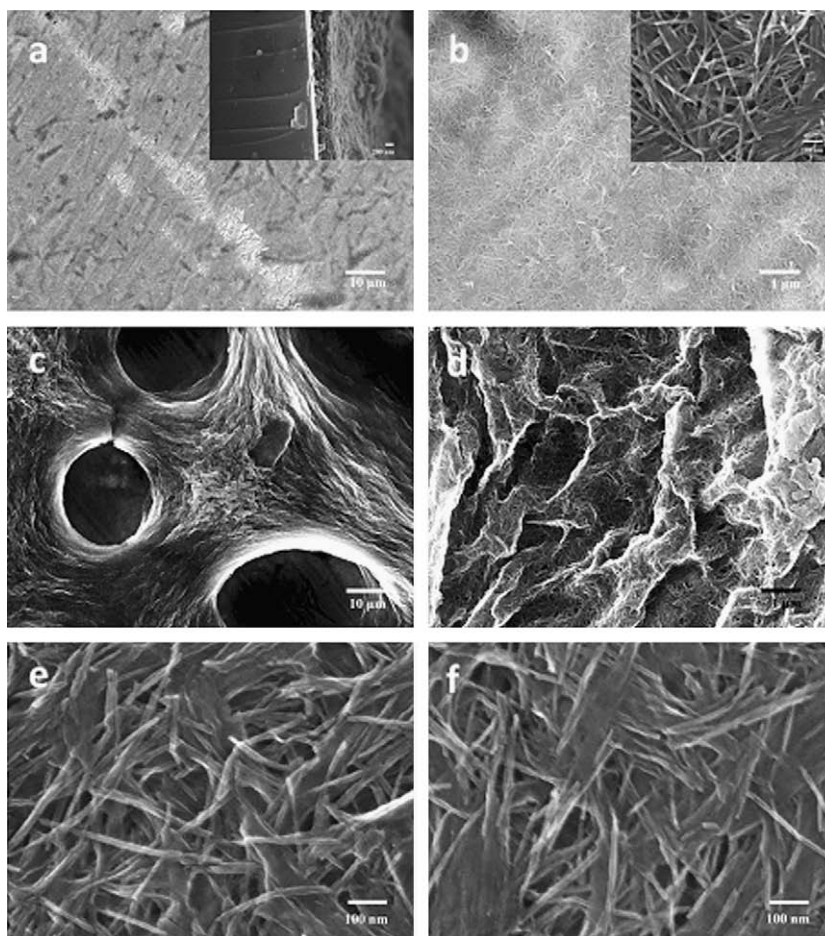


Fig. 2. FESEM images of the TNT films by EPD with 30 V for 2 min. (a, b) TNT film; (c, d) TNT film fabricated without the pretreatment of TBAOH; (e) 450 °C and (f) 600 °C annealing. The inset figures are the corresponding cross-sectional and magnified images.

anatase TiO₂ nanocrystallines and the densification of surface structures (Fig. 2f).

Fig. 2c and d shows typical FESEM images of TNT film without TBAOH pretreatment by cathodic EPD in acidic aqueous solution (pH ~ 3.0). Rough TNT film was loosely packed with many micropores and the deposition could be easily peeled off by water flushing due to the obvious agglomerate of TNTs. These micropores were formed due to the hydrogen gas evolved by the discharge of H⁺ ions. The evolved hydrogen gas accumulated on the cathode, which blocked the TNT deposition, leaving the circular pores on the surface. When the working electrode acted as anode in the negatively-charged TNT solution by adjusting the pH to ~10.0, TNTs could not be deposited successfully. The reason is that the electric field force was not able to overcome the electrostatic repulsive force resulted from the double electric layer. Therefore, the pretreatment with TBAOH solution is important for the successful deposition of high quality uniform TNTs films.

Fig. 3a shows the behavior of a water droplet on the as-prepared TNT surface. The time sequence is shown in the right down corners of the images. The water droplet quickly spread to a contact angle around 6° at 0.02 s, and completely wetted the titanate porous film within 0.16 s. This result indicates the as-prepared film deposited by EPD is superhydrophilic with ultra-fast spreading even before the UV irradiation. This may be due to the large amount of dangling bonds produced during the hydrothermal process and the effect of capillary penetration through the 2D net-like porous layered structures. Moreover, the superhydrophilic performance was stable with no obvious

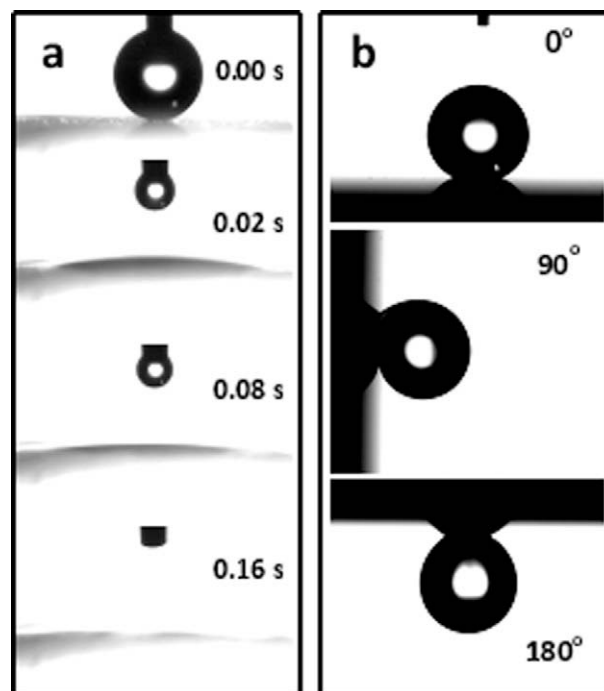


Fig. 3. Wettability of the TNT films. (a) Superhydrophilicity with ultra-fast wetting and (b) superhydrophobicity with high adhesion after PTES modification.

change for at least one month. However, the contact angle of the corresponding nanostructured film was changed greatly from nearly 0 to 152.3° (the top-right inset in Fig. 3b) after soaking in 1H,1H,2H,2H-perfluorooctyl-triethoxysilane (PTES) solution for 60 min. For comparison, the contact angle on a “flat” surface and its corresponding PTES modified sample is about ~46° and 115°, respectively. These results indicate that the porous titanate surface have an amplification effect to make hydrophilic and hydrophobic surface superhydrophilic and superhydrophobic [15,16]. The droplet behavior on such superhydrophobic TNTs film is very much different to the usual superhydrophobic surface on which water droplet can be easily rolled off with a small titling angle [17–20]. The bead was firmly adhered to the surface when the TNT sample was tilted to a vertical position, or even when turned upside down. This interesting observation shows that the PTES modified TNT films exhibited a very strongly adhesion to the substrate, while spreading was prohibited. We believe the horizontally densely packed titanate nanotubes with an average diameter of about 10 nm played a vital contribution to the unique combination of strong adhesion and virtually no spreading, presumably by generating large van der Waals attraction from the large surface area in very close contact with water [21].

4. Conclusions

In summary, we developed a TBA⁺ ion functionalization process to obtain a stable electrolyte for electrophoretic deposition of uniform TNT films in large scale. The TBA⁺ ions play a crucial role not only in the stabilization of the electrolyte, but also in the fabrication of a uniform layer of thin film with good adhesion and controllable thickness. The as-prepared TNT film shows superhydrophilic behavior with ultra-fast spreading, and it changes to superhydrophobicity with strong adhesion after the PTES modification. This study provides an interesting and useful platform for the design of functional materials and devices when extremely large wettability contrast is needed. In addition, we believe that such titanium oxide based nanostructured film can be potentially applied to ultra-fast wetting, rain harvest and microfluidic transportation.

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