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Electrophoretic deposition and optical property of titania nanotubes films

Ning Wang, Hong Lin, Jianbao Li *, Xiaozhan Yang, Bo Chi

State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

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Abstract

In this paper, titania nanotubes (TNTs) films have been fabricated successfully by electrophoretic deposition (EPD) on Nesa glass. EPD is performed in non-aqueous TNTs suspension with 0.2 wt.% polyvinyl butyral (PVB) as a dispersant. The influence of the pH value on the zeta potential and the viscosity of the suspension was investigated by a zeta potential measurement and a viscometer. Scanning electronic microscope (SEM) micrographs indicate that the microstructures of the films are greatly affected by the applied electric field. It has been found that the optimal deposition condition is the pH value of ~5 and the applied electric field of 10 V/cm. In addition, the optical property of TNTs films deposited at 10 V/cm for 2 min is also studied in detail.

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Keywords: Electrophoretic deposition; Titania; Nanotubes; Optical property

1. Introduction

Titania is an exceptional material and has many important applications in areas such as environmental purification, photocatalyst, gas sensors, and high efficient solar cell [1–4]. In recent years, titania nanotubes (TNTs) are of particular interest, since they have large surface area and particular tubular structure, moreover, their potential breakthrough in high efficient dye-sensitized solar cells would come true [5–7].

Electrophoretic deposition (EPD) is an effective method to fabricate thin and thick coatings on conductive substrates. EPD is a process whereby charged particles in an aqueous or non-aqueous suspension are deposited onto a shaped electrode with opposite charge under the action of an applied electric field. It can offer rigid control of film thickness, uniformity and deposition rate. It is especially attractive owing to its low cost of equipment and starting materials. Due to its advantages, EPD has been widely investigated in areas such as structural and functional coatings, as well as forming of superconductors, laminar composites and fuel cells [8].

Despite the large amount of reports on EPD in the literature for various materials, the investigation on the application of this technique to the fabrication of TNTs films hasn't been found up to the present.

The objectives of the present work are to search for the optimal EPD condition of TNTs suspension and to prepare TNTs films with homogeneous porous structure and controllable thickness.

2. Experimental details

All chemicals are analytical grade and used without further purification. The powders used in the present work are TNTs powders synthesized by ion exchange approach and all nanotubes are open-ended with 3~5 nm in inner diameter, 8~12 nm in outside diameter and 200~400 nm in length [9]. TNTs powders (0.5 g), ethyl alcohol (30 ml) as a solvent, and polyvinyl butyral (PVB, 0.066 g, average molecular weight (M_w): 19,000) as a dispersant, were put into a 50 ml beaker. Nitric acid (0.1 M) was used to adjust the pH value of the suspension. Uniform and stable suspension was obtained by ultrasonic treatment (~10 min) and continually stirring (~5 min).

Nesa glass substrates (SnO_2:F~10 Ω/□, Nippon Ashahi glass Co. Ltd., Japan) was used as a substrate. Prior to deposition, the substrate was thoroughly cleaned by ultrasonic in acetone, ethyl alcohol and distilled water successively. EPD was carried out at different DC electric fields by setting the

* Corresponding author.
E-mail address: wangn02@mails.tsinghua.edu.cn (J. Li).

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cathode potential at an interval of 1 V in the range from 10 to 30 V versus a stainless steel electrode and the distance between two electrodes was about 1 cm. After EPD process, the substrate was carefully pulled upwards from the EPD tank to avoid any adverse influence of drag force between the suspension and the surface of deposited wet film. The samples were dried slowly to prevent them from cracking and then annealed at 350∼550 °C for 1 h.

In order to study the dispersion of the TNTs suspensions with 0.2 wt.% PVB as a dispersant, the zeta potential (ζ) and the viscosity of the suspension at different pH were measured using a zeta potential measurement (LeZa-600, Otsuka Electronics Co. Ltd., Japan) and an R-type rotational viscometer (RC-500, Toki Sangyo Co. Ltd., Japan) at a shear rate of 100 s^{-1}, respectively.

The micrographs of as-deposited samples were observed by using a scanning electronic microscope (SEM, S-4100, Hitachi Co. Ltd., Japan). The ultraviolet and visible transmittance spectra of titania nanotubes films annealed at different temperatures were measured by a UV-Vis recording spectrophotometer (UV-Vis 2100S, Shimadzu Co. Ltd., Japan).

3. Results and discussion

3.1. The dispersion of TNTs suspension

Fig. 1 shows the zeta potential value as a function of the pH value of the TNTs suspension in ethanol. Generally speaking, high absolute zeta potential value indicates a high degree of particle dispersion in the suspension, thus high absolute zeta potential value is mostly desired for the forming of a uniform and steady suspension. It can be seen from Fig. 1 that the isoelectric point (IEP) of the TNTs suspension is at pH=5.3, where there is no excess surface charge and the zeta potential value is almost zero. The electrostatic interaction is minimum at this point, the suspension is most unstable and the particles tend to agglomerate due to the action of Van Der Waals attractive force [10]. The suspension has relatively high positive charge at pH=2. The positive charge decreases up to the IEP and then becomes a negative charge with the further increase of the pH value.

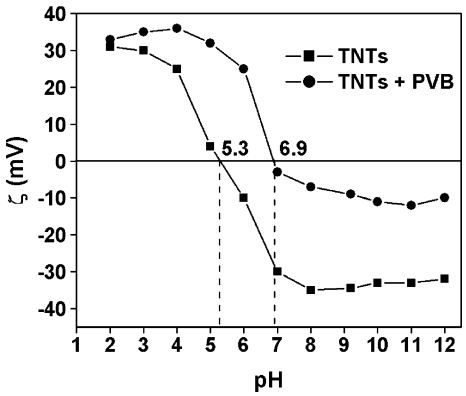

Fig. 1. The zeta potential value vs. the pH value of the TNTs suspension without PVB and containing 0.2 wt.% PVB as a dispersant.

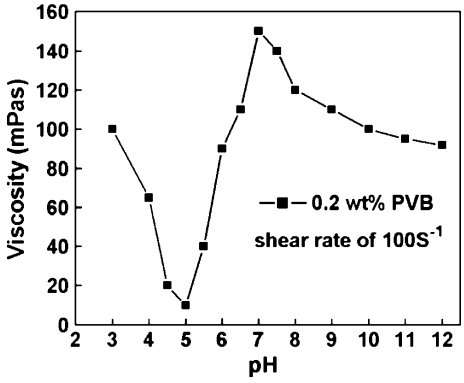

Fig. 2. The viscosity vs. the pH value of the TNTs suspension with PVB contents of 0.2 wt.% versus the pH value at a shear rate of 100 s^{-1}.

To modify the positively charged TNTs, polyvinyl butyral (PVB) with the content of 0.2 wt.% is used as a dispersant. Fig. 1 also shows that PVB addition gives higher positive charge to the surface of TNTs in the pH range of 2∼6. Then, the surface charge rapidly changes to negative after pH>6. Here, the IEP shifts from pH=5.3 to pH=6.9, which mainly derives from that PVB with aldehyde groups (−COH) adsorbs H^+ ions in the suspension and becomes charged positively. After the surface of TNTs absorbs positive charged PVB molecules and becomes more repulsive, uniform and dispersed suspension forms by the large repulsive force between positive charged particles. Hence, PVB is an effective dispersant to modify TNTs and the surface-modified TNTs with PVB could be deposited easily on the cathode at pH=2∼6 under a dc electric field.

Fig. 2 shows the viscosity of the TNTs suspension with PVB contents of 0.2 wt.% versus the pH value at a shear rate of 100 s^{-1}. With the increase of the pH value, the viscosity of the suspensions sharply decreases (pH<5). At pH ∼5, the viscosity remains at a very low level, which is indicative of good dispersion of the suspension. However, the viscosity increases rapidly at pH>5 that arises from that the repulsive force between particles increases when the pH value is apart from the IEP. At pH ∼7, the suspension has the maximum viscosity which indicates a high degree of particle flocculation in the colloid, which is properly consistent with the result of the zeta potential shown in Fig. 1. At basic pH area, a decrease of viscosity is observed, which is also mainly due to that the repulsive force between particles increases when the pH value is apart from the IEP.

Stable suspensions with the lower viscosity values and higher absolute zeta potentials are considered to be very suitable for EPD. Hence, the pH value of the TNTs suspension with PVB contents of 0.2 wt.% was adjusted to ∼5 in the following EPD experiments.

3.2. Electrophoretic deposition behavior of TNTs suspension

Fig. 3 shows the change in the deposit weight of TNTs films against the deposition time at different applied electric fields during EPD. As known, the deposition rate is dependent on the deposition time and the applied electric field [11]. As seen from Fig. 3, the amount of deposit increases with deposition time