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Short communication

Effect of ethylene glycol concentration on the morphology and catalytic properties of TiO_2 nanotubes

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ABSTRACT

Effect of ethylene glycol (EG) concentration on the micromorphology and photocatalytic property of TiO_2 nanotubes was investigated. When EG concentration is varied from 10% to 90%, Ti foil was first oxidized to form a multiporous structure, and the nanotube structure was observed at EG concentration of 70%. Increasing the EG concentration further resulted in more regular and longer TiO_2 nanotube arrays with smaller diameters. The photocatalysis experiments showed that the nanotube structure was beneficial for the photocatalytic degradation of Rhodamine B; however, TiO_2 nanotubes with smaller diameters displayed decreased catalytic activity.

1. Introduction

In recent years, titanium dioxide (TiO_2) materials have received increasing attention due to their non-toxic and anti-corrosion nature, high stability, and excellent photocatalytic properties [1–3]. Particularly, TiO_2 nanomaterials characterized by specific micromorphologies with outstanding optical and chemical properties are widely used in self-cleaning applications [4], for solar water splitting [5], and in biomedical implant devices [6].

Self-organized TiO_2 nanotube layers (TiO_2 NTbs), which are electrochemically grown on the surface of Ti substrates and characterized by vertically aligned tube-like arrays, have garnered increasing interest. Compared to the compact TiO_2 nanoparticle layers, the TiO_2 NTbs showed higher photocatalysis efficiency by providing a shorter diffusion path, which facilitated the fast separation of light-generated electron-hole pairs [2]. The doping of the TiO_2 NTbs was also investigated to enhance their photocatalytic efficiency. M. M. Momeni and co-works reported a series of doped TiO_2 NTbs, including Au/TiO_2-WO_3 [7], Cu/TiO_2-WO_3 [8], Cr-TiO_2 [9], *etc.* These results have shed new light on the preparation of high-efficiency photocatalysts at low cost. Nevertheless, to fully understand the effect of the physicochemical properties of pure TiO_2 NTbs on their photocatalytic efficiency remains important for designing of high-efficiency photocatalysts.

Recently, self-organized TiO_2 NTbs have been successfully prepared by electrochemical anodization oxidation under well-defined anodizing conditions [10–13], *i.e.* a specific electrolyte composition, anodization voltage, anodization temperature, and anodization time. Sergiu P. Albu and co-workers have contributed to the development of tailored anodizing approaches, enabling the growth of aligned nanotube layers with tube lengths ranging from several hundreds of nanometers to several hundreds of micrometers [14]. During the anodization process, the fluoride ions contained in the electrolyte have been considered the most important factor determining the growth of TiO_2 NTbs. Several researchers have shown that the fluorinion concentration not only controls the growth speed of TiO_2 NTbs, but also influences the tube length and diameter of the TiO_2 NTbs [15–18]. In our previous report, we demonstrated the influence of fluorinion concentration on the microstructure of TiO_2 NTbs and their relevant photocatalytic performances [19]. We found that regular TiO_2 NTbs can be generated when the fluorinion concentration reached 50 mM or above. Longer TiO_2 NTbs are beneficial for UV light absorption, enabling the generation of more electron-hole pairs. However, the integrity of TiO_2 NTbs also affects the photocatalytic performance because the defects in TiO_2 NTbs can act as recombination centers for the electron-hole pairs. The introduction of a highly viscous organic solvent, such as ethylene glycol (EG) and propanetriol, was beneficial for achieving TiO_2 NTbs with smooth homogenous walls and high aspect ratios [20,21]. However, the effects of EG concentration on the micromorphology of TiO_2 NTbs and their corresponding photocatalytic properties have not yet been studied.

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In this study, we systematically investigate the influence of EG concentration on the physicochemical properties of TiO_2 NTbs prepared by anodization oxidation. The corresponding photocatalytic performances are further investigated by photo-decolorization of an organic dye. The significant effect of EG concentration on the formation of TiO_2 NTbs will be demonstrated and the relevance between their micromorphology and photocatalytic performances will be presented.

2. Experimental

2.1. Preparation of TiO_2 nanomaterials

The TiO_2 nanomaterials were prepared by a standard electrochemical anodization process, as illustrated elsewhere [19]. The detailed procedure has been described in the supporting information. The electrolyte composed of EG and deionized water was used during the process. The volume concentrations of EG used were 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%. In addition, 0.15 mol/L of NH_4F and 0.11 mol/L of citric acid were dissolved in the electrolyte. All chemicals were of analytical reagent grade.

2.2. Physicochemical properties characterization

Top-view and side-view images were obtained using a scanning electron microscope (SEM, ZEISS, ΣIGMA HD/VP). The high-resolution images of a single TiO_2 nanotube were obtained using transmission electron microscopy (TEM, jem-2100). The crystalline phase of the TiO_2 nanomaterials was identified using X-ray diffraction studies (XRD, D/max-2200PC, Rigaku). The micromorphology and surface roughness of TiO_2 NTbs were analyzed by atomic force microscopy (AFM, Park XE-100). An X-ray photoelectron spectrometer (XPS, AXIS Ultra, Kratos) was used to investigate the chemical composition of the TiO_2 NTbs. The binding energies of the obtained XPS spectra were calibrated based on the deviation of adventitious carbon (284.8 eV). The light absorption ability of the samples was investigated by UV–vis diffuse-reflectance spectroscopy (DRS, Shimadzu UV-2450).

2.3. Photocatalytic performance characterization

The photocatalytic performances of the TiO_2 nanomaterials were characterized in terms of the photo-decolorization of Rhodamine B (RhB) under irradiation by a high-pressure mercury vapor lamp (250 W). The detailed experimental procedure has been described in the supporting information.

3. Results and discussion

3.1. Micromorphology of the as-prepared TiO_2 nanomaterials

In order to elucidate the effect of EG concentration on the formation of TiO_2 NTbs, the top-view images of all the samples were obtained (Figs. 1 and S1 in supporting information). At very low EG concentrations (10%, Fig. S1a), a multi-porous structured layer was etched out on the Ti foil surface after anodization at 50 V for 2 h. With increasing EG concentration (20–60%, Figs. 1a and S1b–e), the size of the pores in the layer increased and the multiporous layer became less compact. When the EG concentration increased to 70%, a small amount of irregular nanotubes with non-uniform tube diameters appeared in the nanoporous oxide layer (Fig. S1f). Upon further increasing the EG concentration to 80%, the nanoporous layer disappeared and packed TiO_2 NTbs were formed with an average tube diameter of 127 nm (Fig. S1g). When the EG concentration reached 90% (Fig. 1b), the average diameter of the obtained TiO_2 NTbs array decreased to ~103 nm. The representative elemental energy-dispersive X-ray (EDX) mapping and EDX spectra of samples (Figs. S2–S4) showed that both nanoporous structured TiO_2 and the TiO_2 NTbs were mainly composed of the elements Ti and O, with trace amounts of N, F, and C.

To investigate the influence of EG concentration on the thickness of the oxide layers, side-view SEM images of the oxide layers prepared at different EG concentrations were obtained (Fig. S5a–i). The thickness of the oxide layer as the function of EG concentration is shown in Fig. S6. At lower EG concentrations (Fig. S5a–f), the thickness of the nanoporous structured oxide layer was limited to ~600 nm. When few TiO_2 NTbs originated from the nanoporous layer (70%, Fig. S5g), the thickness increased to 883 nm. When packed TiO_2 NTbs appeared at the EG concentration of 80%, the tube length increased sharply to 2.3 μm (Fig. S5h). Further increase in the EG concentration to 90% was accompanied by the tube length increasing to ~4.2 μm (Fig. S5i and j). Thus, we can conclude that higher EG concentrations facilitated the formation of TiO_2 NTbs. It has been shown that the thickness of the oxide layers is essentially the result of a steady-state situation between the electrochemical formation of TiO_2 at the Ti foil surface and the chemical dissolution of the thus-formed TiO_2 by fluorides in the electrolyte [22,23]. The addition of optimized EG concentration could decrease the dielectric constant and diffusivity of the electrolytes, which restricts the chemical etching of the as-formed oxide layer, leading to the formation of tube-like TiO_2 [24]. The top-surface morphology and roughness of TiO_2 NTbs (90%) were further investigated using AFM (Fig. S7). The roughness of the TiO_2 NTbs surface was 141.5 nm, which indicates an uneven tube height. The high-magnification top-view and side-view SEM images (Fig. S8) of selected samples demonstrated that many defects occurred on the nanoporous structured TiO_2 oxide layer. On the other hand, the formation of the tube-like structure diminished the defects and resulted in a smoother tube surface.

To clearly observe the inner and outer surfaces of the as-formed TiO_2 NTbs, the TEM images of the samples prepared at EG concentrations of 80% and 90% were obtained (Fig. 2a and b, respectively). Interestingly, the tube wall of the TiO_2 NTbs prepared at EG concentration of 80% was contorted with varying thickness (~32 nm in average), while the TiO_2 NTbs formed at EG concentration of 90% possessed straighter and smoother tube surface with an average tube wall thickness of 24 nm.

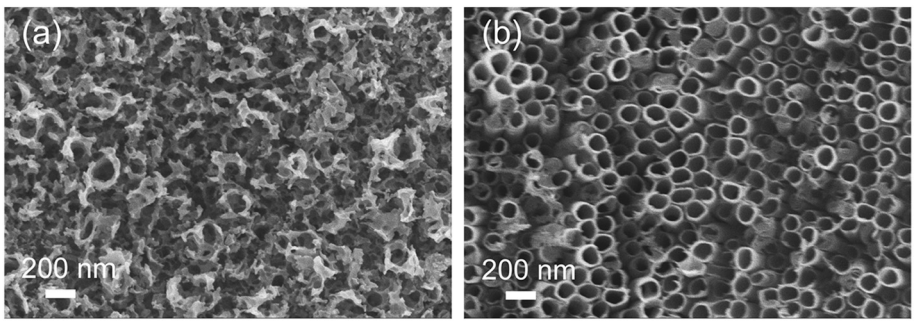

Fig. 1. The representative top-view SEM images of the oxide layers on Ti foil surface prepared at EG concentration of 50% (a) and 90% (b), respectively.