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Synthesis and electrophoretic deposition of hydrothermally synthesized multilayer TiO_2 nanotubes on conductive filters

Ali Can Zaman [a], Cem B. Üstündağ [a,b], Figen Kaya [a], Cengiz Kaya [a,*]

[a] Department of Metallurgical and Materials Engineering, Yildiz Technical University, Davutpasa Campus, Esenler, Istanbul, Turkey
[b] Vocational School, Department of Ceramics, Yildiz Technical University, Maslak Campus, Maslak, İstanbul, Turkey

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ABSTRACT

TiO_2 nanotubes were synthesized by the decomposition of titanium isopropoxide in water and the calcination at 450 °C for 2 h to form TiO_2 nanoparticles. The synthesized TiO_2 in anatase form nanoparticles were processed hydrothermally in 10 M NaOH solution at 130 °C for 24 h to obtain multilayer TiO_2 nanotubes. TEM analysis revealed that the diameters of the tubes were around 10 nm and they are in the length of 100 nm. Subsequently, colloidal suspensions containing 1% wt. Of TiO2 nanotubes were prepared with TEA and butanol and electrophoretic deposition (EPD) experiments were conducted in order to obtain coatings on Ni and carbon filters using a deposition time of 10 min. and an applied voltage of 65 V. It is also shown that multilayer TiO_2 nanotubes having outer diameter around 10 nm and inner diameters of 4.3 nm can be produced using the described technique. EPD is also shown to be an effective technique to coat three dimensional components, such as Ni and C filters for various applications including water and air purification systems.

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1. Introduction

Since the size, morphology and the state of the crystalline phase determines the performance of nanostructured TiO_2 [1], obtaining appropriate materials is crutial for the corresponding applications.

The high surface area to volume ration of TiO_2 nanotubes makes them suitable candidates for the applications utilizing photocatalysis [2]. There are several methods for preparation of TiO_2 nanotubes, such as depositon with templates [3] and anodic oxidation of titanium [4]. But Kasuga pioneered the hydrothermal synthesis, as a simple and promising method of synthesizing TiOx nanostructures exhibiting high aspect ratio [5].

TiO_2 coatings on filters can be used to remove persistent organic compounds and microorganisms in water and in air as well. TiO_2 coatings can be obtained by various techniques such as plasma chemical vapor deposition [6], microwave activated chemical bath deposition [7], plasma spray [8] and EPD [9–11]. EPD is a relatively easy suitable technique for the preparation of uniform coatings on wide range of shapes or porous structures [9]. In addition the depositon thickness can be controlled easily [9].

In this study, multilayer TiO_2 nanotubes are first synthesized by hydrothermall processing and then the nanotubes were deposited electrophoretically on Ni and carbon substrates. It is shown that multilayer TiO_2 nanotubes having outer diameter around 10 nm and inner diameters of 4.3 nm are successfully produced using the described technique.

2. Experimental

The experimental details are shown in Fig. 1. Titanium tetraisopropoxide (TTIP) to 2-propanol and water volume ratios were kept to be 10 ml, 20 ml and 400 ml, respectively. The pH of the water was adjusted at 1.5 before the dropwise addition of TTIP and 2-propanol mixture. After 24 h of mixing the colloidal suspensions were ready to use. The colloidal suspensions of the TiO_2 nanotubes were prepared using butanol media and triethanolamine (TEA) as a dispersant. The solids-loading was adjusted to be ~1% wt. of the solution. After that 3 h of ball milling and ultrasonication were implemented to each suspension. The deposition cell consists of two counter electrodes positioned ~20 mm away from nickel and carbon filters. Deposition time of the substrates was 10 min. under the potential of 65 V. Coated samples were dried and sintered at 400 °C for 2 h.

TEM observations were used to investigate the size and shape of the elongated products obtained by hydrothermal synthesis. TEM samples were prepared using carbon coated cupper grids 3 mm in diameter. Fort the TEM sample preparation a 0.1 wt.% suspension was prepared and the grid was immersed in the suspension to make sure that there are enough particles left on the grid for observations. SEM investigations were performed on gold coated samples to observe the obtained coatings on porous substrates.

3. Results and discussion

Fig. 2. illustrates TEM images of hydrothermally synthesized TiO_2 nanotubes. It is clearly shown that a nanotube having outer diameter around 11 nm and inner diameter of 4.3 nm (Fig. 2a). Fig. 2b illustrates

* Corresponding author. Tel.: +90 2123834713; fax: +90 2123834665.
E-mail address: cngzky@yahoo.co.uk (C. Kaya).

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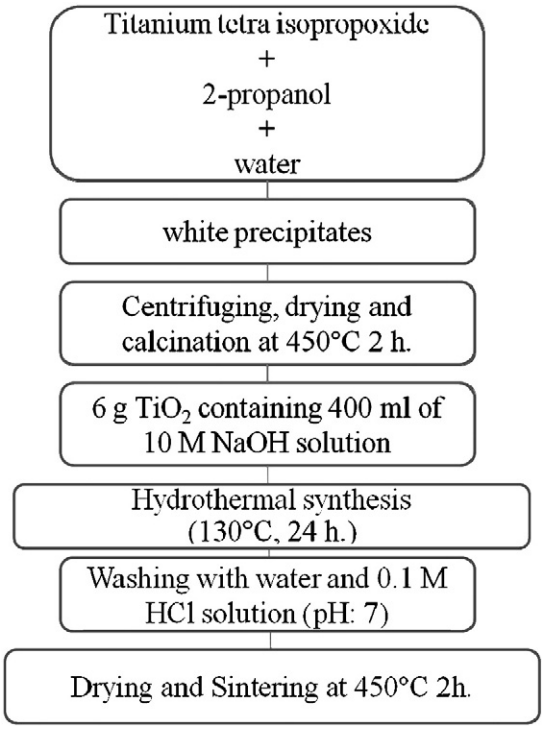


Fig. 1. The experimental details conducted for the preparation of the TiO_2 nanotubes.



Fig. 3. Images of TiO_2 suspensions; the stable TiO_2 nanotube suspension prepared with TEA addition (a) and the unstable suspension of TiO_2 without addition of TEA (b).

higher magnification TEM image of a nanotube, revealing that nanotubes have multiple shells, consists of several layers/sidewalls. Number of the sidewalls of the nanotube is not constant and there is a difference in the opposing sides of the nanotube changing from 5 to 6. The interlayer spacing between the layers was measured to be 0.4 nm. The length of the nanotubes is in the range of 100 nm (see Fig. 2c). Cross-sectional view of nanotubes shows that nanotubes can have 3 and 4 cylinders, as shown in Fig. 2d. In terms of the formation mechanism of

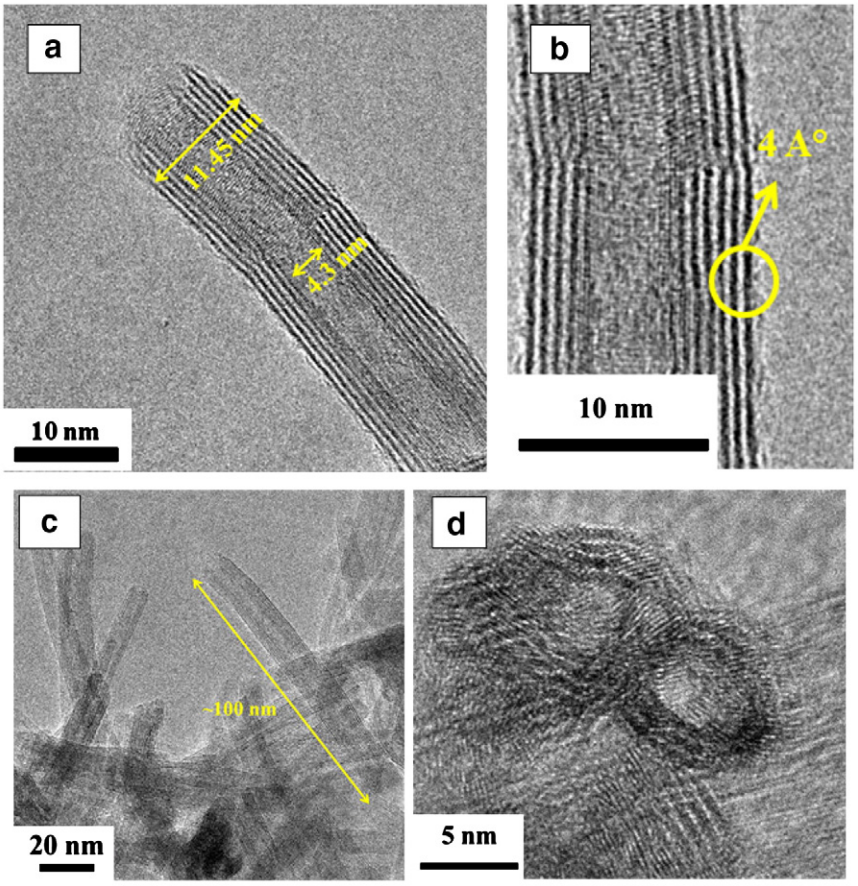


Fig. 2. TEM images of multilayer TiO_2 nanotubes; low (a) and high (b) magnifications and the general microstructure (c) of the tubes and cross-sectional view of two nearby nanotubes (d).

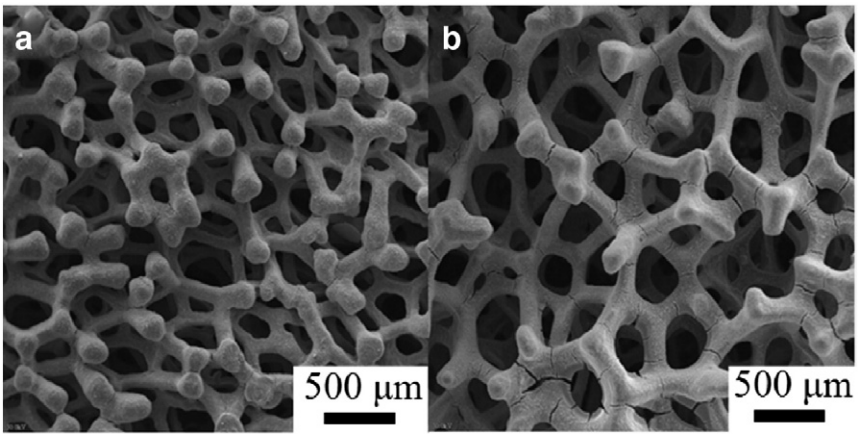


Fig. 4. The SEM images of coated nickel (a) and carbon (b) filters by means of EPD (sintered at 400 °C for 2 h.).

nanotubes, the TEM results shown in Fig. 2 were reviewed as wrapping of separate layers, therefore nanotubes show different number of shells at different sides.

Fig. 3a and b show the suspensions of TiO_2 without and with the addition of TEA, respectively. Stability of the suspensions was considerably increased with addition of TEA, as shown in Fig. 3a while without TEA addition, it is not possible to obtain stable colloidal suspension of TiO_2 nanotubes and this is due to lack of sufficient charges on nanotubes.

Fig. 4. shows SEM images of TiO_2 nanotube coatings on Ni (Fig. 4a) and carbon (Fig. 4b) filters after sintering at 400 °C for 2 h. Uniformity of the coating throughout the filters reflects the stability of the suspensions used. No cracks were determined on the Ni coatings (see Fig. 4a) while some cracks are seen on the carbon filters (see Fig. 4b). Occurence of cracks on carbon filters may be due to the absorbance of the solvents leading to rapid drying and consequently resulting in the formation of cracks.

4. Conclusions

TiO_2 nanotubes were synthesized from TiO_2 nanoparticles by means of hydrothermal synthesis under alkaline conditions (130 °C, 24 h.). Outer and inner diameters of nanotubes were determined to be 10 nm and 4.3 nm and the lengths are approximately 100 nm. Stable suspensions of TiO_2 nanotubes were prepared via butanol and triethanolamine to coat Ni and carbon based filters using electrophoretic deposition. SEM images revealed that the coatings (sintered at 400 °C for 2 h.) on Ni and carbon filters are uniform. There is a tendency to form cracks on C coatings and this may be attributed to the high solvent absorption capability of the carbon filters which leads to cracking. It is shown in the present work that TiO2 nanotubes can easily be synthesized by hydrothermal processing and electrophoretic deposition is an effective way of coating three dimensional Ni and C filters in a short time. The obtained coated filters may find application in water or air purification systems.

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