



Effect of sodium carbonate as an additive on the morphology and photocatalytic activity of TiO₂ nanotubes



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ABSTRACT

The major purpose of this research is increasing the photocatalytic activity of TiO₂ nanotube arrays by doping with sodium and carbon for using in water splitting as photoanode. The synthesized TiO₂ nanotubes (TNA) were characterized using FESEM (Field Emission Scanning Electron Microscope), XRD (X-ray Diffraction), DRS (Diffraction Reflection Spectroscopy) and XPS test (X-ray Photoelectron Spectroscopy) analyses. The results of FTIR and XPS confirmed the presence of sodium and carbon in the lattice of TNA as dopants. Moreover, the DRS test showed the decrease in the band gap energy of TNA from 3.20 to ~2.88 eV; uv-visible test exhibited extension in the absorption edge of pure TiO₂ nanotubes from Uv-light (396 nm) to visible light (488 nm). In addition, the results of photoelectrochemical measurement indicated that the photocurrent density of doped TiO₂ nanotubes increased about 5 times than that of the pure compounds.

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1. Introduction

In the recent decades, the use of clean fuels such as hydrogen has drawn considerable attentions. There are many methods to produce hydrogen; one of them is chemical electrolysis of water under the sun light which is called water splitting reaction [1–3]. This nomination is due to its compatibility with environment and also its low cost [4]. In this technique a material with suitable photocatalytic activity under the sun light, is required [5,6]. In 1972, Honda and Fujishima proposed the use of TiO₂ electrode in water electrolysis process for the first time [7,8]. After that, TiO₂ as a suitable photocatalytic material has attracted many attentions, thus, different researches have been conducted to investigate the properties of TiO₂ nanotubes up to now [9,10]. Actually, among the different structures of TiO₂, the nanotube arrays which are synthesized by electrochemical method are preferred because of the long range order, high aspect ratio, large surface area [11], desirable application in solar light alteration, photoelectrochemical stability and low cost [12,13]. Furthermore, the TiO₂ nanotubes have better photocatalytic activity than their powder form [14].

The restriction of using these nanotubes in water splitting process as photoanode is their wide band gap energy (about 3.2 eV

for anatase phase and 3 eV for rutile phase). Therefore, their photocatalytic activity is only limited to UV-light region ($\lambda < 388$ nm) which involves very the TiO₂ nanotubes small part of solar spectrum of about 5% [15–18]. Despite, the major part of solar energy (approximately 45%) relates to the visible light [19,20]. In fact, by doping with nonmetal elements such as C, N, F, etc and metal elements such as Fe, Co, Ni, Cu, etc, it is possible to extent their absorption edge to the visible light with affecting their electronic structure [21–23]. Indeed, adding metal or non-metal as dopant individually, has not noticeable effect on the absorption edge and photocatalytic activity of nanotubes whilst simultaneous doping with metal and non-metal as dopants is very effective [24].

In this research, the morphology as well as the photocatalytic activity of doped TiO₂ nanotubes was investigated. Doping was performed through the adding of sodium carbonate which causes the doping with sodium as metal and carbon as non-metal. The effect of doping on the extension of absorption edge to uv-visible region was studied.

2. Experimental procedure

2.1. Anodizing process

All of the anodization experiments were carried out at room temperature in a two-electrode electrochemical cell. The initial materials were Ti foil with 99.9% purity having thickness of

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0.25 mm as anode and graphite thin film with thickness of 1 mm as cathode. Before anodizing, Ti foil was sanded with abrasive papers from 320 to 2500 and polished with solution containing Al_2O_3 particles (0.3 μm). Then, it was rinsed with acetone and ethanol (volume ratio 1:1), afterwards, it was washed with deionized water and finally dried at ambient temperature. All of the experiments were performed at the constant DC voltage of 50 V. Area ratio of anode to cathode was 1: 1 and distance between them was fixed as 3 cm. The used electrolyte includes ethylene glycol, 3 vol% of deionized water, NH_4F (0.2 M) and different concentrations of sodium carbonate as an additive (0.01, 0.02, 0.03 and 0.04 M).

2.2. Characterization of TiO_2 nanotube arrays

The structure and morphology of arrays were investigated by X-ray diffraction (XRD, STOE D-64295, $\text{Cu K}\alpha$ radiation, $\lambda = 0.15406 \text{ nm}$ at a scanning rate of $10^\circ \text{ min}^{-1}$) and Field Emission Scanning Electron Microscopy (FESEM, ZEISS –SIGMA VP Germany), equipped with EDS. The mean crystallite size of TiO_2 nanotubes was determined from the broadening of XRD lines using Williamson Hall procedure [25,26]. To correct the instrumental errors the powder diffraction pattern of an alumina sample was used [26].

To determine the band gap energy, the Diffuse Reflectance Spectra (DRS, Avaspec-2048-TEC) with Ava lamp DH-S setup and UV-vis (Varian Cary 500 UV-vis-NIR spectrophotometer) with wave length of 300–600 nm were applied. Elemental composition of TiO_2 nanotubes was evaluated by XPS (X-ray Photoelectron Spectroscopy) test.

2.3. Photoelectrochemical measurement

To study the photoelectrochemical performance of the samples, 3 standard electrodes were used where Pt is the counter electrode, Ag/AgCl is the reference electrode and TiO_2 nanotubes synthesized with different concentrations of sodium carbonate are working electrodes. Moreover, the electrolyte contained KOH (1 M) in ethyleneglycol (10%wt) solution, under the visible light irradiation

($100 \text{ mW}/\text{cm}^2$) of at 50 mV. To simulate the solar light, 150W xenon ozone-free lamp was applied.

3. Results and discussion

3.1. The morphology characterization

Fig. 1 shows the top and cross section FE-SEM images of TiO_2 nanotubes which were synthesized in the pure organic electrolyte and also in the organic electrolyte with sodium carbonate as an additive. As could be seen, after one hour of synthesizing, in the pure electrolyte, the nanotubes with length of $\sim 0.95 \mu\text{m}$ and relatively good surface order have been formed. The growth rate of nanotubes calculated by dividing the length to the synthesis time was estimated as $\sim 0.016 \mu\text{m}/\text{min}$.

The cross section image of synthesized nanotubes in the organic electrolyte containing additive indicates the formation of, smooth and highly order nanotubes with no ripple on their wall. According to the calculations, by enhancing the concentration of additive from 0.01 to 0.03 M, the growth rate of nanotubes increases from 0.23 to $0.42 \mu\text{m}/\text{min}$. Further enhance in the concentration from 0.03 to 0.04 M, results in the reduction of growth rate from 0.42 to $0.24 \mu\text{m}/\text{min}$. In addition, the walls of nanotubes which were synthesized in this concentration (0.04 M) were destroyed. Thus, it could be said that there is an optimal value for concentration of this additive in organic electrolytes which is about 0.03 M. The effect of different concentrations of sodium carbonate on the characterization of TiO_2 nanotubes has been summarized in Table 1.

It could be inferred from this Table that by increasing the concentration of this additive from 0.01 to 0.03 M, the growth rate and thickness of the nanotubes increase while the inner diameter decreases. Hence, using this additive not only has not negative effect on the tubular structure of nanotubes but also improves their morphology. By considering these results, the best concentration of sodium carbonate as an additive in organic electrolyte is 0.03 M.

Generally, the synthesis process of TiO_2 nanotubes includes two reactions: 1) electro chemical etching and (2) chemical dissolution [5] as follow:

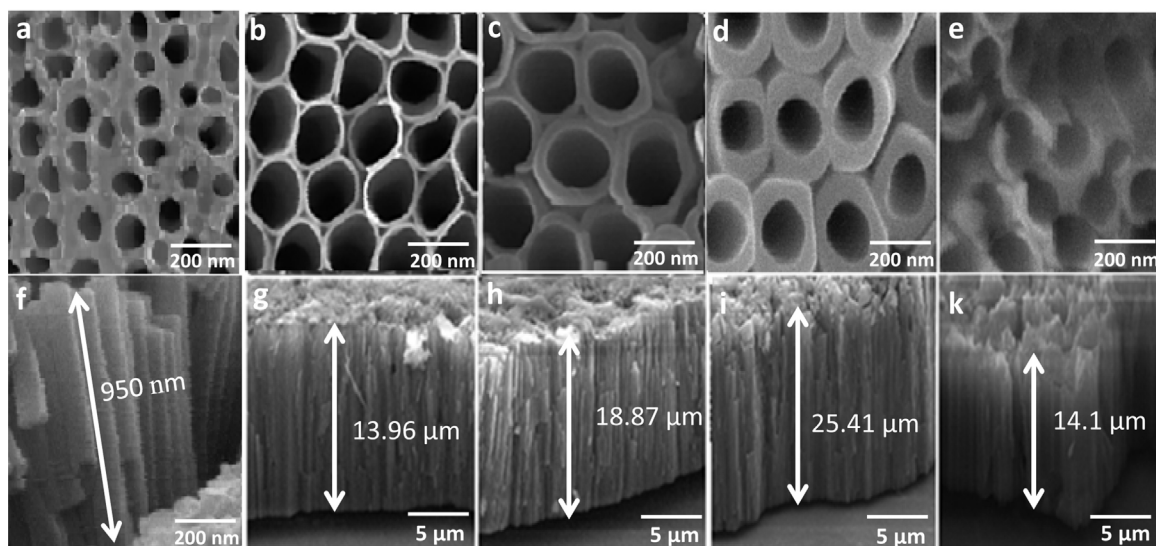
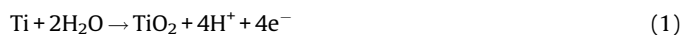


Fig. 1. Top-view FESEM images of (a) pure TiO_2 nanotubes and doped TiO_2 nanotubes derived from addition of sodium carbonate with different concentrations of (b) 0.01, (c) 0.02, (d) 0.03 and (e) 0.04 M, respectively, and (f-k) corresponding cross-section FESEM images.

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