Fabrication of Carbon Doped TiO₂ Nanotubes via In-situ Anodization of Ti-foil in Acidic Medium

Asma M. Milad, Mohammad B. Kassim, Wan R. Daud

Abstract—Highly ordered TiO₂ nanotube (TNT) arrays were fabricated onto a pre-treated titanium foil by anodic oxidation with a voltage of 20V in phosphoric acid/sodium fluoride electrolyte. A pretreatment of titanium foil involved washing with acetone, isopropanol, ethanol and deionized water. Carbon doped TiO₂ nanotubes (C-TNT) was fabricated ‘in-situ’ with the same method in the presence of polyvinyl alcohol and urea as carbon sources. The affects of polyvinyl alcohol concentration and oxidation time on the composition, morphology and structure of the C-TN were studied by FE-SEM, EDX and XRD techniques. FESEM images of the nanotubes showed uniform arrays of C-TNTs. The density and microstructures of the nanotubes were greatly affected by the content of PVA. The introduction of the polyvinyl alcohol into the electrolyte increases the amount of C content inside TiO₂ nanotube arrays uniformly. The influence of carbon content on the photo-current of TiO₂ nanotube were controlled by regulating the electrolyzing conditions such as anodization time and electrolyte composition.

This present work investigates the possibility to dope TiO₂ nanotube arrays with carbon via ‘In-situ’ anodization of Ti foil in acidic electrolyte with variable amounts of carbon dopant sourced from polyvinyl alcohol (PVA) at various duration of anodization and studies their influence to pore morphology, thickness and the elemental compositions of nanotubes films grown on titanium. As far as we know that no one has done the carbon dope by in-situ anodization technique. We also investigate the affects of carbon dopant on the photocurrent of carbon doped TiO₂ nanotube (C-TNT). The carbon doped and non-doped TiO₂ nanotube (TNT) arrays were characterized with FE-SEM, EDX, and XRD techniques. In addition, the preliminary results of their photoactivity were also reported.

II. EXPERIMENTAL WORK

A. Preparation of C doped TiO₂ Nanotubular Arrays
Titanium (99.99% purity, Aldrich) foils (1.0 × 1.0 cm) of 0.1 mm thickness were cleaned by sonicating them in acetone, iso-propanol and ethanol successively, followed by rinsing with deionized water and finally dried with nitrogen gas prior to the electrochemical treatments. The preparation of titania nanotube was similar to previously reported method with a little modification [22]. The TiO₂ and C-TiO₂ NT arrays were grown by anodization of cleaned Ti foils in acidic electrolyte containing 0.5M ortho-phosphoric acid (H₃PO₄, 85% in water, A & R marketing, UK), 0.14M sodium fluoride (NaF, 99.5%,
The working electrodes TiO$_2$ and C-Pt plate (counter electrode) and a saturated calomel electrode conducted in a standard three-electrode configuration with a Bruker D8 Advance spectrometer. A high potential ramped from the Open Circuit Potential (OCP) to 20 V in 1 V s$^{-1}$ was applied using DC power supply (Agilent, E3631A) with stirring for 45 minute. The anodized samples were rinsed with deionized water and dried in a N$_2$ stream at 100 °C for 12 hr. The anodized C-TNT arrays were annealed to form an anatase crystal structure using a muffle furnace (PyroTherm Furnace, EUROTHERM 91e) at 500 °C for 3 hours in purified air with 5 °C/min of heating rate.

**B. Characterizations of C doped TiO$_2$ Nanotubular Arrays**

The morphology of the C-TNT arrays were characterized by field emission scanning electron microscope FESEM (ZEISS, SUPRA 55VD) and the elemental contents was determined by energy-dispersive X-ray analyses (OXFORD Instruments, INCA) at 40V using Cu K$_\alpha$ radiation ($\lambda$=1.5418 Å). The crystallinity of the treated samples was established from the XRD spectra collected using Cu K$_\alpha$1 radiation on a Bruker D8 Advance spectrometer.

**C. Photoelectrochemical Measurement**

The photoelectrochemical measurement (PEC) was conducted in a standard three-electrode configuration with a Pt plate (counter electrode) and a saturated calomel electrode (reference electrode). The working electrodes TiO$_2$ and C-TiO$_2$ NTs have an active area of 0.6 cm$^2$. The electrochemical cell was equipped with a quartz glass window. A 450W Xenon lamp was used as the light source. The preparation of TiO$_2$ and C-TiO$_2$ NTs samples for PEC analysis has been described in earlier publication [23]. The electrolyte (1M KOH) was purged with a nitrogen gas for 30 minutes before the tests and the scan rate was set at 50 mVs$^{-1}$. The potential and photocurrent produced by the TiO$_2$ and C-TiO$_2$ NTs were recorded using an Ametek Versastat4 potentiostat to establish the I-V profiles.

**III. RESULTS AND DISCUSSION**

The current density transient was recorded during the anodic oxidation process (see fig 1). All anodization potentials were ramped from OCP to anodization voltage (20V) with a sweep rate of 1 V/s in ortho-phosphoric acid/NaF electrolyte with different percentage of polyvinyl alcohol (PVA) for 45 min. The initial exponential current decays refer to high-field TiO$_2$ formation, which is about 50 nm thick [24]. The mechanism of the C-TiO$_2$ NT formation are expected to be similar to previous reports [25]. From Fig 1, the current transients’ exhibits in all electrolytes, different behaviours with current densities vary with different electrolytes. In the case of increasing PVA percentage, the current density decays were decreasing slowly and smoothly. The highest current density during the anodization was exhibited by 0 and 0.5 wt % PVA in ortho-phosphoric acid/NaF electrolyte. This suggested that the PVA content in the electrolyte was affected reversibly by the flow of anodized current density. It was found that the samples, which were anodized with different amount of PVA in the electrolytes, needed a certain period of time until their nanotube structures become self-organized, in other words until the anodization attained a steady state situation.

A field emission scanning electron microscope was used to characterize the morphologies and micro-structure of the samples. Fig 2 showed a cross-sectional and bottom view, Fig. 3 showed the surface and EDX results of the samples anodized at 20 V with different percentages of PVA in ortho-phosphoric acid/NaF medium for 30, 45 and 60 minutes.
Fig. 3 Surface view and elemental compositions of C-TiO\textsubscript{2} nanotube array prepared by anodization in phosphoric acid/NaF electrolyte at 20V with different amounts of PVA content (a) 0 wt (b) 0.5 wt% (c) 1.0 wt% and (d) 1.5 wt% of PVA.

From these figures, we can conclude that the ‘in-situ’ anodization technique was able to produce a self-ordered nanotubular structure in the presence of PVA. The C-TNT arrays appeared clean compared to specimen without PVA. The lengths of C-TNT were approximately 0.320 to 0.471 µm. The diameter ranges from 96 to 165 nm for samples which were anodized in ortho-phosphoric acid/NaF electrolyte with different amounts of PVA. The EDX results showed all C-TNTs contains Ti, O and C elements (fig. 4 (a), (b) and (c)). The C content increases upon introduction of PVA. It was observed that a longer anodization time increases the C content much further.

Fig. 5 and 6 showed the affects of PVA content and anodization time on diameter and length of C-TNT arrays. The diameter of C-TNTs and the length decreases with increase in anodization time. On other hand, the affects of PVA content on the morphology and microstructure was not straight forward and difficult to understand.

Fig. 4 FESEM micrographs showing the surface morphology and elemental compositions of C-TiO\textsubscript{2} nanotube array prepared by anodization in the phosphoric acid/NaF electrolyte containing 1.0 wt% PVA at different time; (a) 30 min, (b) 45 min and (c) 60 min.

Fig. 5 The effects of PVA content on C-TNT arrays diameter and length for samples anodized in ortho-phosphoric acid/NaF electrolyte at 20V.

Fig. 6 The effects of anodization time on C-TNT arrays diameter and Length for samples anodized in ortho-phosphoric acid/NaF electrolyte with 1 wt% of PVA at 20V.
B. X-Ray Diffraction Analysis

The degree of crystallinity and crystal phases of the C-doped TiO\textsubscript{2} nanotube were determined by examining the X-ray diffraction (XRD) diffractogrammes at a scanning rate of 0.025°/min from 20° to 80°. The samples were annealed at temperature 500 °C. A closer examination of the XRD diffractogram revealed that all three phases namely anatase, rutile and titanium were observed at various angles with Ti peaks were due to the substrate. All samples were exhibited high degree of crystallinity with preference for a Rutile phase at low PVA content. However, at higher PVA content the anatase phase became more prevailed due to its stability. It is worth to note that the crystalline phase was affected by the PVA content during the anodization process as shown in Fig. 7.

Fig. 7 XRD diffraction C-TNTs arrays anodized with different wt% of PVA in Phosphoric acid/NaF electrolyte (a) Ti foil, (b) 0 wt%, (c) 0.5 wt%, (d) 1.0 wt% and (e) 1.5 wt% PVA.

C. Photoelectrochemical Analysis

The comparisons of the photocurrent density vs. applied potential curves of the TiO\textsubscript{2} and C-TiO\textsubscript{2} photoanode in the dark and under Xenon illumination showed in Fig. 8. The observed dark current densities were found to be negligible (approach to zero). The photocurrent densities of C-TiO\textsubscript{2} photoanode are varied by PVA content in the electrolyte. This indicates that the C-doped TiO\textsubscript{2} photoanodes produced have the potential to increase the visible light photosresponse (fig. 8 f). However, the current density of all sample with PVA increase rapidly, except for sample with 1.0 wt % PVA. (Fig. 8f) the photocurrent increases slowly with bias potential zero until the voltage reached 0.1V vs. SCE, then the current decreases rapidly. The best photocurrent response was recorded by photoanode with 1.0wt % PVA and 30 min anodization period.

IV. CONCLUSION

A highly ordered carbon-doped titania nanotube arrays was successfully fabricated from Ti foil by adding different amounts of polyvinyl alcohol (PVA) as carbon source to the anodization electrolyte ( 0.5M ortho-phosphoric acid and 0.14 M sodium fluoride, NaF) at 20 V. The anodized samples were annealed at 500 °C in purified air for 3 hours. A C dopant sourced from different amounts of PVA was incorporated into the titania nanotube during the anodization process. The diameter (96 to 165 nm) and length (0.320 to 0.471 µm) of the C-TNTs were influenced by PVA content and anodization time. The best photocurrent density was recorded for C-TNTs with 1.0 wt% PVA with anodization period of 30 min in phosphoric acid/NaF electrolyte with Xenon light illumination.

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