



# Photoelectrochemical water splitting on chromium-doped titanium dioxide nanotube photoanodes prepared by single-step anodizing



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## ARTICLE INFO

### Article history:

Received 31 December 2014  
Received in revised form 16 February 2015  
Accepted 17 February 2015  
Available online 11 March 2015

### Keywords:

TiO<sub>2</sub> nanotubes  
Cr doping  
Water splitting  
Photo-electrochemical

## ABSTRACT

Cr-doped TiO<sub>2</sub> nanotubes (Cr-TiO<sub>2</sub>NTs) with different amounts of chromium were obtained directly by the electrochemical anodic oxidation of titanium foils in a single-step process using potassium chromate as the chromium source. The effects of chromium amount in anodizing solution on the morphologies, structure, photoabsorption and photoelectrochemical water splitting of the TiO<sub>2</sub> nanotube array film were investigated. Diffuse reflectance spectra showed an increase in the visible absorption relative to undoped TiO<sub>2</sub>NTs. The photoelectrochemical performance was examined under visible irradiation in 1 M NaOH electrolyte. Photo-electrochemical characterization shows that chromium doping efficiently enhances the photo-catalytic water splitting performance of Cr-doped TiO<sub>2</sub> nanotube samples. The sample (Cr-TiO<sub>2</sub>NTs-1) exhibited better photo-catalytic activity than the undoped TiO<sub>2</sub>NTs and Cr-TiO<sub>2</sub>NTs fabricated using other chromium concentrations. This can be attributed to the effective separation of photogenerated electron-hole upon the substitutional introduction of appropriate Cr amount in to the TiO<sub>2</sub> nanotube structure.

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## 1. Introduction

Direct conversion of solar energy into clean chemical fuels is one of the most important scientific challenges of 21st century. The development of an alternative energy sources to fossil fuel becomes much more important. Many scientists believe that the use of photoelectrochemical (PEC) water-splitting system is one of the most promising technologies for producing hydrogen gas to secure a clean and sustainable supply of energy [1–3]. In 1972, photochemical water splitting using titanium dioxide (TiO<sub>2</sub>) as photoelectrode was successfully reported by Fujishima and Honda [1]. Since then, TiO<sub>2</sub> has been gained much more scientific interest and extensively used as an efficient photoelectrode in PEC water splitting for H<sub>2</sub> generation because of its unique and promising functional properties, such as high photocatalytic activity, long term photo-stability, superior oxidation ability, inertness to chemical environment, as well as low cost [3–6]. TiO<sub>2</sub> is a wide band gap semiconductor with energy of 3.0–3.2 eV. However, due to its wide band gap energy, TiO<sub>2</sub> is active only under near-ultraviolet irradiation. Therefore, numerous studies have been carried out over the last 20 years to develop modified TiO<sub>2</sub> catalysts so that they are active under visible light irradiation. One of the most

studied methods is by doping the TiO<sub>2</sub> materials with metal ions or nonmetallic elements [7–20]. Among different dopant materials, doping with transitional metals is one of the most efficient methods. Recent theoretical calculations showed that 3d transition metals have good potential as a substitutional dopant for TiO<sub>2</sub> because of their ability to induce significant spin polarization and reduce the energy gap of rutile by forming intermediate bands with adequate curvatures and density of states [21–23]. Unlike defect states in the form of nearly straight horizontal lines within the energy gap, these curvy intermediate bands can act as stepping-stones to relay valence electrons to the conduction band. As a result, the optical absorption edge of TiO<sub>2</sub> is shifted into the visible or even infrared spectral range of solar irradiance [21–24]. Different methods were used to prepare chromium-doped TiO<sub>2</sub>. Cracia et al. investigated the photocatalytic properties of Cr-doped TiO<sub>2</sub> thin film prepared by ion beam-induced CVD and found that incorporation of chromium produces a progressive shift of the absorption threshold toward the visible [25]. Some reports have shown that the Cr-doped TiO<sub>2</sub> obtained by sputtering is much more efficient to induce a red shift of the absorption edge in the visible light region than that obtained by the sol-gel technique [26–29]. Fan et al. synthesized the mesoporous Cr-doped TiO<sub>2</sub> photocatalyst with worm-like channels using an evaporation-induced self-assembly approach and found that the doped chromium can significantly improve the absorption of mesoporous TiO<sub>2</sub> in the visible

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light region [30]. Hydrothermal doping method was also found an effective way to prepare chromium doped  $\text{TiO}_2$  photocatalysts and improves the photocatalytic activity [31]. Recently, Mishra et al. synthesized the low-content chromium doped titania nanotubes using electrochemical anodization of Ti–Cr alloys, but encountered difficulty in adjusting the dopant concentration [32].

In this study, at the first stage, self-ordered Cr-doped  $\text{TiO}_2$  nanotube layers with different amounts of chromium were synthesized by a single-step anodization of titanium substrate in an organic bath containing of ethylene glycol (EG)–fluoride electrolyte containing various amounts of potassium chromate. The significance of self ordered Cr-doped  $\text{TiO}_2$  nanotube layers is one-step and easy synthesis of them; achieving the optimal morphology, length, diameter, thickness and surface area of the nanotubes by controlling various parameters of anodizing such as anodizing voltage, time, electrolyte temperature, electrolyte type and concentration. Also in these layers, different amount of desired dopants were doped during synthesis of  $\text{TiO}_2$  nanotubes and this reduces the cost of prepared material. After preparation of self-ordered Cr-doped  $\text{TiO}_2$  nanotube layers, in the next step, the quantity effect of chromium in anodizing solution on the PEC water splitting performance of highly ordered Cr-doped  $\text{TiO}_2$  nanotube arrays (Cr– $\text{TiO}_2$ NTs) was investigated. The quantity of dopant introduced to a semiconductor affects many of its electrical and optical properties. Since in the in-situ anodizing method, the desired metal cation (usually as its salts) is added to the electrolyte, so, its quantity in anodizing solution should be optimized. In this work,  $\text{TiO}_2$  nanotube array films with different amounts of chromium were obtained by controlling the concentration of chromium in anodizing electrolyte. Since photocatalytic properties of Cr-doped  $\text{TiO}_2$  nanotube arrays affected by amount of chromium doped in them, so, analyzing quantity effect of chromium in anodizing solution is very important and affects their photo-electrochemical (PEC) water splitting performance. To our knowledge, the quantity effect of chromium in Cr-doped  $\text{TiO}_2$  nanotube layers for  $\text{H}_2$  generation in PEC water splitting has not been reported. The morphology and structure were characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction. Optical properties were investigated by UV–Vis diffuse reflectance spectra.

## 2. Experimental details

The Cr-doped  $\text{TiO}_2$  nanotubes films on titanium substrate were prepared directly by using an electrochemical anodic oxidation process. In a typical preparation procedure, the Ti foils (99.99% purity, thickness of 1 mm) were first mechanically polished with different emery type abrasive papers (with the following grades: 60, 80, 600, 1200 and 2500), rinsed in a bath of distilled water, and then chemically etched by immersing in a mixture of HF and  $\text{HNO}_3$  acids for 30 s. The ratio of components HF/ $\text{HNO}_3$ / $\text{H}_2\text{O}$  in the mixture was 1:4:5 in volume. The last step of pre-treatment was rinsing with distilled water. The anodization process was carried out in an electrolytic cell using a titanium foil as anode and graphite foil with about  $12 \text{ cm}^2$  geometric areas as cathode. Anodizing was performed in a solution of ethylene glycol (98 ml) containing 0.001 M ammonium fluoride and 2 ml distilled water, followed by the dissolution different concentrations of potassium chromate ( $\text{K}_2\text{CrO}_4$ ). The temperature of the electrolyte was maintained during the anodizing process at  $(25 \pm 1)^\circ\text{C}$ . Anodization was performed for 6 h at a constant potential of 60 V using a controlled DC power supply source (ADAK, PS405). A schematic representation of the anodizing setup is shown in Fig. 1. After anodizing, the as-formed samples were annealed in oxygen atmosphere at  $400^\circ\text{C}$  for 2 h ( $2^\circ\text{C}/\text{min}$ ). The concentration of potassium chromate in anodizing solution was 0, 5, 15 and 25 mM, respectively. The as prepared films were marked as  $\text{TiO}_2$ NTs, Cr– $\text{TiO}_2$ NTs-1, Cr– $\text{TiO}_2$ NTs-2 and Cr– $\text{TiO}_2$ NTs-3 corresponding to the gradually increased concentration of  $\text{K}_2\text{CrO}_4$ . Table 1 summarizes the experimental conditions for 4 different samples.

The surface morphologies of all samples were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4160, Japan) and the elemental composition was estimated by energy dispersive X-ray spectroscopy (EDX). The crystalline phases were identified by XRD (Philips XPert). UV–Vis diffuse reflectance spectra of samples were recorded using UV–Vis spectrophotometer (JASCO V-570).

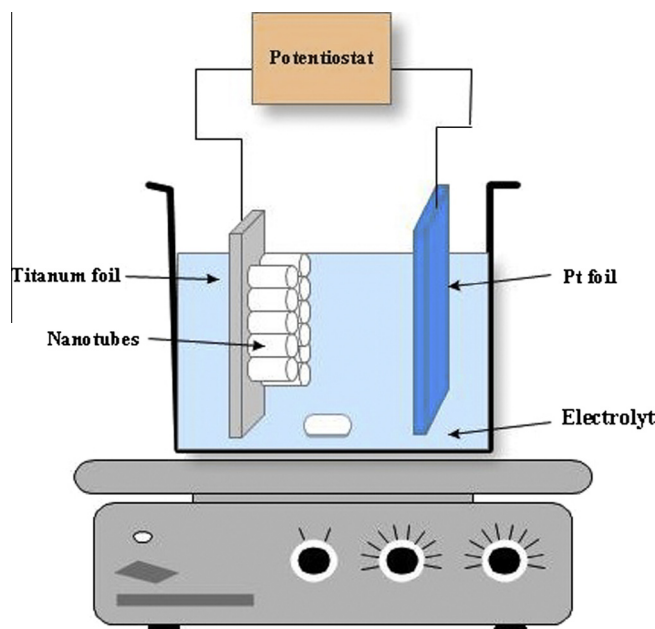


Fig. 1. Schematic representation of the anodizing setup used to fabricated Cr– $\text{TiO}_2$ NTs samples.

The photoelectrochemical measurement was performed using a Compactstat IviumStat (Model 2.175) with a three electrode configuration: a working electrode ( $\text{TiO}_2$ NTs/Ti or Cr– $\text{TiO}_2$ NTs/Ti), a platinum-wire counter electrode and an Ag/AgCl reference electrode. For photocurrent measurements, the electrodes were immersed in a solution of 1 M NaOH (pH = 13.6). The Cr– $\text{TiO}_2$ NTs/Ti electrode was scanned from  $-1000$  to  $+1800$  mV (vs. Ag/AgCl electrode) at a rate of 5 mV/s. The  $\text{TiO}_2$ NTs/Ti or Cr– $\text{TiO}_2$ NTs/Ti electrodes were illuminated with a 200 W xenon lamp equipped with a UV cut-off filter ( $\lambda > 420$  nm). The luminous intensity of the xenon lamp was  $100 \text{ mW}/\text{cm}^2$ . 100% of the light was transmitted by the quartz glass as the xenon lamp shone on the  $\text{TiO}_2$ NTs/Ti or Cr– $\text{TiO}_2$ NTs/Ti photoanodes. Hydrogen evolution was measured for 240 min and  $\text{H}_2$  gas was collected using the water displacement technique.  $\text{H}_2$  gas is produced at the counter-electrode in the photo-electrochemical (PEC) cell. Fig. 2 shows a schematic diagram of the experimental set-up for PEC water splitting. A Pt coil spot-welded to a stainless steel rod served as the cathode. The electrolyte in each compartment was 1 M NaOH. The cathode was inserted into a burette where the hydrogen was collected via electrolyte displacement. The volume of hydrogen was measured by directly reading the variation of the electrolyte level in the burette for various times.

## 3. Results and discussion

The morphology of samples anodized in an ethylene glycol electrolyte containing different concentrations of potassium chromate were observed by SEM. Fig. 3 shows FE-SEM images of  $\text{TiO}_2$ NTs, Cr– $\text{TiO}_2$ NTs-1, Cr– $\text{TiO}_2$ NTs-2 and Cr– $\text{TiO}_2$ NTs-3, respectively, which clearly shows formation of films on the surface of titanium. In figure (a) and (b),  $\text{TiO}_2$ NTs and Cr– $\text{TiO}_2$ NTs-1 samples displayed vertically ordered nanotube arrays that the surface of them was open. It can be seen that the structure two samples consists of a layer of tubes with a diameter in the range of 90–150 nm and wall thickness of 20–40 nm. In Fig. 3c, no nanotubes formed. Porous films were formed instead (Cr– $\text{TiO}_2$ NTs-2 sample). It can be said that when the potassium chromate concentration in anodizing solution increased to 15 mM (Fig. 3c), the formed nanotube array becomes very nonuniform, implying that an appropriate concentration of potassium chromate is important for the structure of nanotube arrays. FE-SEM images of Cr– $\text{TiO}_2$ NTs-3 sample in Fig. 3c shows that a compact film, without porosity, was formed on the surface of titanium. From the cross-sectional view of Cr– $\text{TiO}_2$ NTs-1 sample in Fig. 4 it can be seen that the formed nanotubes are parallel aligned, opened on top and have a length in the range of 16  $\mu\text{m}$ .

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