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Photocatalytic water splitting for hydrogen production under visible light on Ir and Co ionized titania nanotube

M. Alam Khan [1], O-Bong Yang [*]

School of Semiconductor and Chemical Engineering, Solar Energy Research Center, Chonbuk National University, Dukjin dong, Dukjin Gu, Jeon-ju 561-756, Republic of Korea

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ABSTRACT

Highly dispersed iridium and cobalt metal particles (average 3 nm) were introduced in the texture of the synthesized titania nanotube (TiNT) by ion-exchange method, which were found to be effective photocatalysts for the production of stoichiometric hydrogen and oxygen by the splitting of water under the visible light irradiation. Thus prepared Ir(IE)/TiNT and Co(IE)/TiNT catalysts evolved hydrogen at the rate of 7.05 μmol/h/0.5 g and 1.27 μmol/h/0.5 g in aqueous methanol and 2.73 μmol/h/0.5 g and 0.67 μmol/h/0.5 g in pure water, respectively. The band gap energies were decreased to 2.5 eV and 2.6 eV from 3.1 eV of bare TiNT by introducing highly dispersed Ir and Co nanoparticles in the texture of TiNT, respectively, resulting in the improved photo-response towards visible light. However, visible light photo-activity for water splitting was not observed on the large aggregated Ir and Co particles on TiNT prepared by impregnation method. The prepared catalysts were characterized by FE-SEM, HR-TEM, SEMEDX, XRD, UV–vis DRS spectra, photocurrent density and BET surface area.

1. Introduction

Nanomaterials have been shown to behave quite differently from their bulk counterparts due to the effect of their quantum confinement imposed upon the charge carriers [1]. Since the photo-induced decomposition of water on TiO_2 electrodes was discovered by Fujishima and Honda [2], titania-mediated semiconductor photocatalyst has attracted extensive interest towards the process of splitting of water into hydrogen and oxygen with the use of sunlight due to their low cost method of hydrogen production [3]. One particular focus point is the development of titania-based photocatalysts capable of using visible light. However, its widespread use is impaired by the wide band gap energy (3.2 eV), which requires UV irradiation for its photocatalytic activations. Furthermore, UV light accounts for only 6% compared to 45% visible light in solar radiation. Despite of these limitations, TiO_2 still remains the most promising photocatalyst owing to its low cost, chemical inertness, nontoxic, high efficiency and high photostability [4–7]. Especially, TiO_2 nanoparticles less than 10 nm show significant photo-activity due to quantum size effects [8,9]. So, any shift in the optical response from UV to visible range spectra will have profound positive effect on the photocatalytic efficiency of the TiO_2-based photocatalysts [10]. A series of semiconductor and metal nanoparticles have been shown to facilitate charge rectification and extend the photo-response [11–15]. For that purpose, two approaches have been applied to extend the shift towards visible range: one is metal doping into TiO_2, which suffers from the thermal instability of doped metal [16]; the other is high energy ion implantation by bombarding metal ions [17,18], which is considered as an expensive method even though very effective tool. Justicia et al. demonstrated that the titania in anatase phase with large oxygen deficiency can act as an efficient photocatalyst [19]. The reduced form of titania may introduce the localized oxygen vacancy states located at 0.75–1.18 eV below the conduction band minimum of TiO_2 [20], which may improve the photo-response of the titania materials.

In our previous work, well-grown titania nanotube, and TiNT (with ca. 8 nm diameter and 500–700 nm length) possess oxygen deficiency with sodium counter cation [21], which may facilitate ion-exchange or proton exchange to introduce precious metals inside or outside of their tubular network. In the present study, we have applied reduced forms of TiO_x nanotube ($x < 2$) along with the metal doping (Ir and Co) to enhance the optical response towards visible. It was found that the photo-response in visible light was drastically improved by introducing the highly dispersed Ir and Co in the texture of TiNT by ion-exchange method, resulting in the significant activity in the water splitting reaction to produce stoichiometric hydrogen and oxygen under visible light.

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[*] Corresponding author. Tel.: +82 63 270 2313; fax: +82 63 270 2306.
E-mail address: obyang@chonbuk.ac.kr (O.-B. Yang).

[1] Present address: School of Display and Chemical Engineering, Yeungnam University, Gyeongsan, Republic of Korea.

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2. Experimental

2.1. Preparation of catalyst

The titania nanotubes (TiNTs) were synthesized from the TiO_2 nanoparticles that were prepared by sol–gel method as follows. The mixture of TiO_2/SiO_2 mole ratio of 90:10 was obtained by mixing 26 ml titanium isopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, >99%, Junsei Chemical Co.) and 2.6 ml tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$ >99%, Acros Organics), and was dissolved in the 26 ml ethanol (99.5%). After refluxing the resulting solution at room temperature for 1 h, the other mixture of 26 ml ethanol and 20.3 g of 4 M aqueous HCl (36%, Showa Chemical Co.) was added slowly to the TTIP containing the former solution and further stirred at room temperature for 1 h. To form the precipitation of xerogel, thus prepared sol was put into the incubator at 80 °C for 48 h. Then, xerogel was dried and calcined in the air at 600 °C for 3 h, which were the high crystalline TiO_2 nanoparticles with an anatase phase and ca. 20 nm size.

TiO_2 nanotube (TiNT) in this study was prepared similar to Kasuga et al. [22] except the hydrothermal temperature in an aqueous NaOH (8 M) was maintained at 130 °C for 20 h in a Teflon lined autoclave vessel under continuous stirring at 200 rpm. After natural cool down to the room temperature of the autoclave, the obtained titanium dioxide white powder of nanotubular matrix was transferred into a vessel (round flask) containing distilled water and decantated in this vessel by pouring the fresh distilled water for several times. After the filtering and washing, the obtained white powder was dried and calcined in air at 80 °C and 250 °C, respectively. The obtained sample was denoted as titania nanotube.

The Ir and Co metals were introduced on TiNTs by ion-exchange or impregnation method. Chloropentaammineiridium(III) chloride ($[IrCl(NH_3)_5]Cl_2$, 99.9%, Alfa Aesar) and cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 99.9%, Aldrich) were used as a cation exchange precursors of Ir and Co metal, respectively. For the cation exchange of TiNT containing 2.7% Na^+ ion, 0.025 M aqueous solution of Ir or Co metal were introduced in the flask containing TiNT, which was stirred and maintained at the pH 10 by adding the aqueous ammonia solution at room temperature for 20 h. $IrCl(NH_3)_5{}^{2+}$ or Co^{2+} exchanged TiNTs were filtered, washed, dried and calcined at 250 °C in an air for 2 h, which were denoted as Ir(IE)/TiNT and Co(IE)/TiNT. The Ir and Co metal loading was 1.8 wt% according to the measurement of FE-SEMEDX.

Dihydrogen hexachloroiridate(IV) hydrate ($H_2IrCl_6{\cdot}xH_2O$, 99.9%, Alfa Aesar) and cobalt(II) nitrate hexahydrate (Co(N-

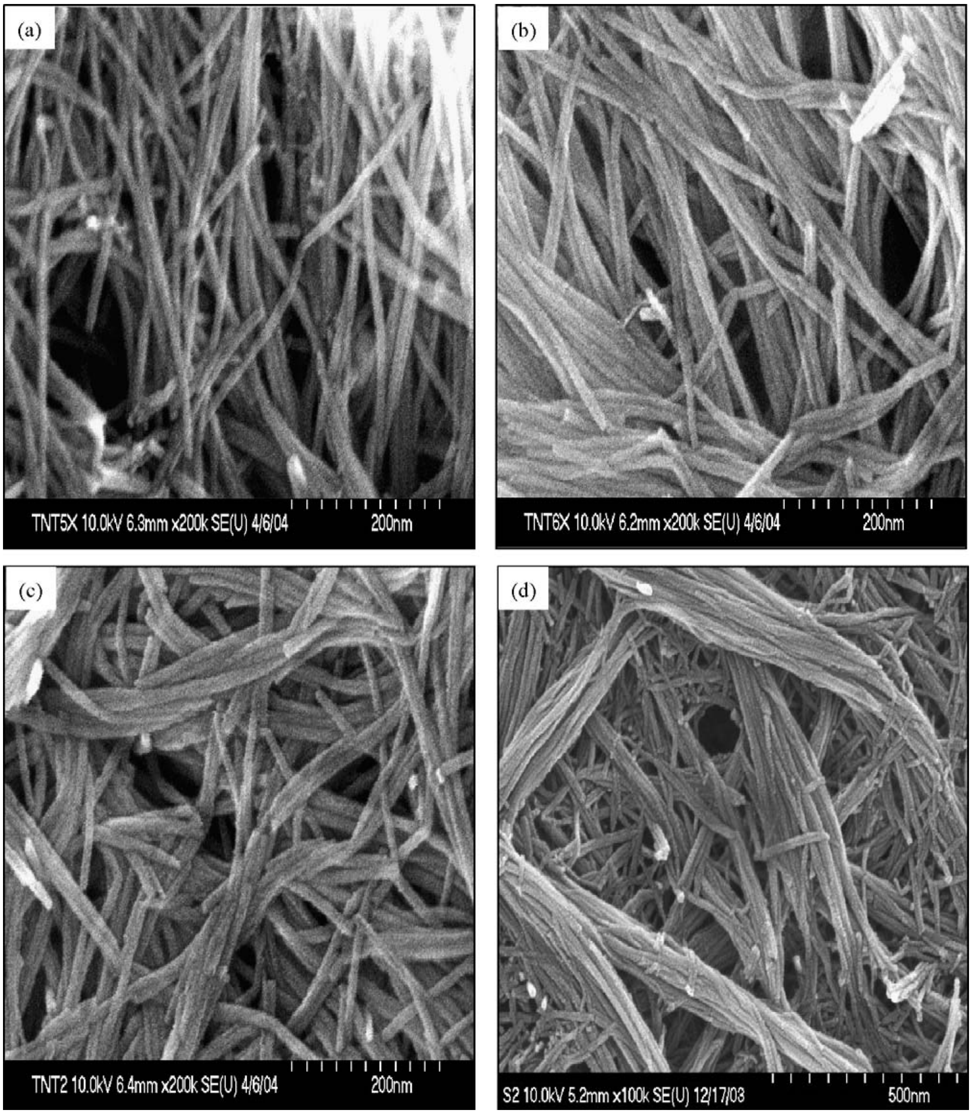

Fig. 1. FE-SEM images of (a) Ir(IE)/TiNT, (b) Co(IE)/TiNT, (c) Ir(IM)/TiNT and (d) Co(IM)/TiNT.