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Effect of Palladium Nanoparticles on Photocatalytic Characteristics of N doped Titania Catalyst

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To improve the photocatalytic efficiency of TiO₂ nanotubular catalyst, N doped and Pd decorated titania nanotubes was successfully synthesized via anodizing, hydrazine hydrate treatment and photoreduction of Pd ions. The small Pd nanoparticles were precipitated on TiO₂ nanotubes through photoreduction of Pd ions, and its distribution is relatively homogeneous. From X-ray photoelectron spectrometry (XPS) result, the N 1s spectrum represents two peaks with binding energy at 399.7 and 400.7 eV, which suggests that the nitrogen elements doped by hydrazine hydrate treatment are located in interstitial sites of the TiO₂ crystalline structure. For N doped TiO₂ nanotubes with Pd particles, a high photocurrent was detected due to increase of interface charge carrier separation rate. Moreover, N doped and Pd decorated TiO₂ nanotubes exhibited much higher dye destruction efficiency and rate constant due to the synergistic effect of the N dopant and the Pd deposition on TiO₂ nanotubes.

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1. Introduction

For application in decontamination, environmental fields, purification and wastewater treatment, photocatalysis is a promising technique, and TiO₂ is known as one of the best photocatalyst for the degradation of organic pollutants. Moreover, the TiO₂ photocatalysis can be also used in hydrogen production^[1,2] by photocatalytic water splitting reaction as well as dye-sensitized solar cells (DSCs)^[3,4]. Especially, nanotubular array TiO₂ photocatalyst, which represents a high specific surface area and allows fast path of charge transfer, has attracted increased attention due to their excellent physical and chemical properties. However, titania photocatalyst has a relatively large band gap (~3.2 eV for anatase) that restricts its utility to the UV region only, moreover, TiO₂ exhibits a low charge transfer efficiency due to easy recombination of photogenerated electron–hole pairs, which act as detrimental effects on photocatalytic efficiency. Therefore, to maximize the photocatalytic efficiency, the absorption band of TiO₂ should be shifted into the visible light region and the recombination of charge carriers should be avoided by separation of photoinduced electrons and holes.

In order to utilize the incident photon energies in visible light region, many strategies are developed, such as metal/nonmetal ion doping^[5–9], co-doping with foreign ions^[10–12] and hybrid/composite^[13–15]. Meanwhile, many efforts have been also paid for enhancement of photocatalytic activity through restriction of the recombination of photogenerated carriers. Recently, the deposition of metal nanoparticles on TiO₂ surface^[16–19] has been shown to be more effective in photocatalytic efficiency. The metal nanoparticles dispersed on TiO₂ surface may act as an electron acceptor due to the formation of a Schottky barrier at the metal/TiO₂ interface, and promote the photocatalytic activity by effective charge carrier separation. In this work, to improve the efficiency of photocatalytic reaction through extension of the absorption band of TiO₂ into the visible light region and restriction of the recombination of photogenerated carriers, N doped titania nanotubes were fabricated by electrochemical anodizing and hydrazine hydrate treatment, and then palladium nanoparticles were synthesized directly on TiO₂ nanotubes through photoreduction of palladium ions. For investigation on surface characteristics, the TiO₂ nanotube photocatalysts were analyzed by X-ray photoelectron spectrometry (XPS), field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) measurement. The dye decomposition reactions for photocatalytic efficiency were evaluated using rhodamine B.

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2. Experimental

2.1. Morphology and structure

A commercial-grade (99.6 wt%) titanium plates were used for anodization. The Ti plate was cleaned in acetone and ethanol, and rinsed with deionized water for 10 min. The anodic TiO₂ nanotubes were synthesized by anodizing in 0.5 wt% NH₄F and 5 wt% H₂O containing ethylene glycol (EG) solution at a constant voltage of 30 V. The crystalline phase of the TiO₂ nanotubes synthesized by anodizing has been identified as an amorphous structure^[20]. In order to achieve efficient photocatalytic properties, the phase of TiO₂ nanotubes should be transformed from amorphous to crystalline structure (anatase, rutile and brookite), using annealing treatment. Among the three phase structures, anatase phase exhibits superior photocatalytic efficiency. For this purpose, the anodic TiO₂ nanotubes were annealed at 500 °C for 1 h. For fabrication of the N doped TiO₂ nanotube, hydrazine hydrate treatment was utilized. At first, the anodized TiO₂ nanotube was immersed in hydrazine hydrate (80%) for 6 h^[21], and then the titania nanotubes were dried at 110 °C for 4 h in oven. Finally, for crystallization, N doped TiO₂ nanotubes were annealed at 500 °C for 1 h. For synthesis of the N doped TiO₂ nanotubes deposited with Pd particles, palladium acetate (Pd(OAc)₂, Sigma–Aldrich) was dissolved in mixture solution of deionized water/ethyl alcohol (50:50 vol.%). The N doped TiO₂ nanotube immersed in 0.02 mol/L palladium acetate solution was exposed under 20 W UV lamp for 5 min, and Pd nanoparticles were precipitated on titania nanotubes through photoreduction of Pd(II) ions in Pd(OAc)₂ solution.

2.2. Surface characteristics of titania nanotubes

To observe the surface of the anodic TiO₂ nanotubes and determine its crystal structure, high resolution scanning electron microscopy (SEM, JEOL JSM 7600F, Japan) and X-ray diffraction (D8 discover, Bruker AXS, Germany) were employed. X-ray photoelectron spectroscopy (SCA 2000, VG Microtech, UK) was used to determine the surface composition and bonding state of the TiO₂ nanotubes.

2.3. Photoactivity evaluation

The photoelectrochemical activity was evaluated by photocurrent response under visible light impulse irradiation. The measurement for photocurrent response was carried out with a standard three-electrode cell system, which consisted of a window glass cell, reference electrode (Hg/Hg₂SO₄), and platinum mesh as a counter electrode. The cell was mounted with a quartz window glass tube, which allows the irradiation of visible light through a fiber optic cable onto the working electrode surface in the electrolyte. An LED light source (LED illuminator, B&B Opto, Korea) with a light filter cutting the light below 400 nm was used as the visible light source. The light intensity reaching the surface of the working electrode is 2 μW cm⁻². 0.5 mol/L K₂SO₄ solution was used as the electrolyte. All electrochemical experiments were controlled by electrochemical work station (CHI 600C, USA).

2.4. Photocatalytic efficiency for dye decomposition

For the dye decomposition test, 0.038 μmol/L rhodamine B (pH 4.884) solution was prepared, and the dye degradation efficiency was evaluated with 8 mL solution in a quartz tube, with irradiating 100 W Hg lamp as the light source. UV–Vis spectroscopy (Unicam 8700) was performed to determine the decomposition rate of the dye at the wavelength of 554 nm.

3. Results and Discussion

3.1. Morphology of titania nanotubes

Fig. 1(a) and (b) show the surface morphology and cross-sectional area of the self-organized TiO₂ nanotubular layer synthesized at 30 V in EG/0.5 wt% NH₄F/5 wt% H₂O mixture for 20 min. In general, the morphology and nanotubular arrangements on the self-organized TiO₂ layer can be controlled by various fabrication parameters. Especially, applied anodic potential and electrolyte composition clearly affect the shape and growth rate of TiO₂ nanotube. In the case of TiO₂ nanotubes fabricated in ethylene glycol mixture solution, the longer tube length can be obtained. The anodic TiO₂ layer, as shown in Fig. 1, consists of nanotubes with an outer diameter of 100 nm and nanotube length of 2000 nm.

Fig. 2 shows the palladium nanoparticles on TiO₂ nanotubular layer, which precipitated by reduction of Pd(II) ions in palladium acetate solution under UV irradiation. The Pd nanoparticle size can be controlled by adjusting concentration of Pd ions and reduction process time. The surface chemical composition of titania nanotubes, as shown in Fig. 2(b), was determined by energy dispersion X-ray (EDX) analysis, and the elemental signals were proved to be peaks of titanium, oxygen, and palladium. The Ti and O peaks were ascribed to the anatase-type TiO₂ nanotubes, and the Pd peak was attributed to the precipitation of palladium nanoparticles on TiO₂ nanotubes. Therefore, Fig. 2 indicates the presence of Pd nanoparticles on TiO₂ nanotubes. The size distribution of Pd nanoparticles is shown in Fig. 3, and the histogram was fitted using Gaussian function. Fig. 3 shows the Pd nanoparticles with the center of size distribution at 3.66 nm and an FWHM of 2.05 nm. From homogeneous distribution of Pd particles with small size, as shown in Fig. 3, high photocatalytic properties are expected.

3.2. Surface characteristics of TiO₂ nanotubes

To investigate the crystal structure, XRD measurement was performed on TiO₂ nanotube as well as N doped TiO₂ nanotube with Pd particles, and the resulting XRD patterns are shown in Fig. 4. For bare TiO₂ nanotubes, the XRD pattern^[22] exhibited the presence of titanium (JCPDS No. 44-1294), anatase (JCPDS No. 21-

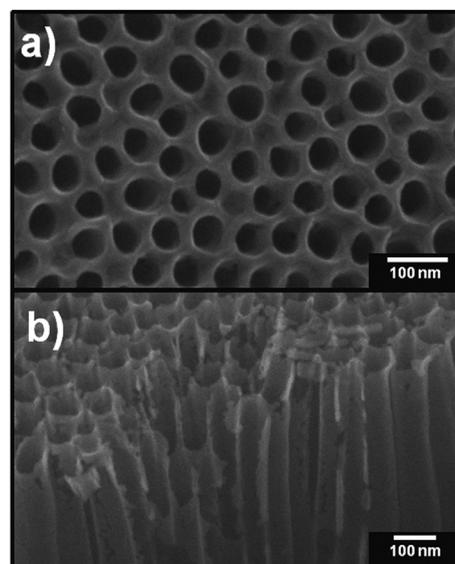


Fig. 1. FE-SEM images exhibit (a) surface and (b) cross-sectional area of anodic titania nanotubes formed at 30 V for 30 min in EG/0.5 wt% NH₄F/5 wt% water mixture.

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