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Composition dependence of structural, optical, and photoelectrochemical properties of nanocrystalline neodymium-doped titania photocatalyst

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ABSTRACT

Neodymium-doped titanium dioxide (Nd/TiO_2) films with different Nd concentration *x* from 2 to 10% are fabricated on silicon by chemical solution deposition and a subsequent cathodic electrochemical process using neodymium nitrate solution as the Nd source. The Nd dopant effects on the structural, optical, electrical, and photoelectrochemical properties of the Nd/TiO_2 films are investigated by X-ray diffraction, ultraviolet Raman scattering, UV–vis diffuse reflectance spectra (DRS), and electrochemical methods at room temperature. XRD shows the polycrystalline anatase phase with Nd atoms incorporated into the TiO_2 matrix. The grain size decreases with increasing Nd concentrations. The intensity of the Raman-active mode B_{1g} increases with Nd concentration. The diffuse reflection absorption spectra (DRS) indicate that the absorbance edge of all the Nd/TiO_2 samples shifts to the visible region. The Nd dopant decreases the band gap of TiO_2 consequently enhancing the visible light absorption ability of the photocatalyst. The photoelectrochemical results indicate that in the same electrolyte, Nd can significantly enhance the photoconversion efficiency of the TiO_2 electrode as well as the photocurrent density. The Nd/TiO_2 electrode shows higher efficiency in photoelectrocatalytic (PEC) degradation of p-nitrophenol (PNP) than the undoped TiO_2 electrode under the same conditions.

1. Introduction

Since the first report by Fujishima and Honda [1], titanium dioxide or titania (TiO_2) has been considered one of the efficient photocatalysts. TiO_2 has also been used to convert solar energy into electricity in the worldwide efforts to reduce the dependence on fossil fuels [2–4]. Titania has three common crystalline forms: rutile, anatase, and brookite [5]. The anatase form usually has more efficient photoactivity than rutile and brookite [6–8]. Nevertheless, as a wide band gap n-type semiconductor, the band gap of anatase is 3.2 eV and so the materials cannot absorb sunlight sufficiently. Therefore, it is critical to decrease the band gap in order to improve the efficiency of TiO_2 in photocatalytic applications. There have been many suggested approaches, for example, modifications of the cationic and anionic sublattices, application of organic dyes and noble metals, etc. [9–11]. For instance, in 2001, Asahi et al. incorporated anions and transition metals into the TiO_2 anionic sublattice to narrow the energy band gap and increase the solar energy conversion efficiency [12]. Zhao et al. doped transition metals into TiO_2 to form compound photocatalyst to improve TiO_2 photocatalytic activity [13].

Titanium dioxide doped with rare-earth ions has attracted considerable interest recently because of the unique 4*f* electronic configuration and special luminescent and catalytic properties. Multiple electronic configurations can be easily generated and the oxide is polymorphism exhibiting strong adsorption selectivity and good thermal stability. In particular, there is considerable shift to the visible range after doping. Xie et al. reported the relationship between the photocatalytic activity and dye sensitization or electronic removal in Re^{3+} doped TiO_2 [14]. Li et al. reported that Ce^{3+} doped in to TiO_2 enhanced the adsorption capacity to pollutants (MBT) and improved the photocatalytic activity in the ultraviolet and visible regions [15]. Xu et al. had researched the photocatalytic activity of the neodymium-doped TiO_2 nanotubes neodymium-doped TiO_2 nanotubes, however, the lattice vibration of Nd^{3+} doped TiO_2 is not well understood and it is also important to investigate the dependence of the Nd concentration on the physical and chemical properties of neodymium doped TiO_2 films for photocatalytic activity.

Many techniques such as pulsed laser deposition (PLD), pyrolysis, and the sol–gel method are employed to prepare Nd/TiO_2 films but the preparation of Nd doped TiO_2 films

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electrochemically has seldom been reported. In this work, Nd/TiO_2 films with Nd concentration varying from 2 to 10% are prepared on silicon by chemical solution deposition and cathodic electrochemical process and the structural, optical, and photoelectrochemical characteristics are studied systematically. The doped photocatalyst shows significantly enhanced photoelectrochemical and PEC properties compared to the undoped samples under the same conditions.

2. Experimental details

2.1. Preparation of TiO_2 films

The TiO_2 thin films were deposited directly on p-type Si (1 0 0) substrates using the sol–gel method. The substrates were cleaned in pure ethanol ultrasonically and rinsed several times with deionized water. The wafers were dried under flowing nitrogen before film deposition.

Analytically pure titanium butoxide [Ti $(OC_4H_9)_4$], anhydrous ethanol (C_2H_5OH), and acetic acid (CH_3COOH) were the starting materials. Acetyl acetone and an equimolar amount of titanium butoxide were added dropwise to the solution to the required volume ratio of C_2H_5OH:CH_3COOH (16:1) under vigorous stirring at room temperature. Caution was exercised because the reaction was rather violent. The acetate and acetyl acetone were used to adjust the pH and stabilize the titanium butoxide, respectively. The solution was stirred for 2 h at 50 °C to increase the homogeneity. The 0.3 M precursor solution was transparent without precipitates even after two months. Before deposition of the TiO_2 films, the silicon wafers were cut into chips with dimension of 1 cm × 1 cm and cleaned using the standard RCA process. The TiO_2 films were deposited by spin coating the solution on the Si sample at 4000 rpm for 20 s. Finally, the thin films were dried at 180 °C for 200 s, pyrolyzed at 380 °C for 240 s to remove residual organic compounds, and annealed at 500 °C for 1 h in ambient air. The deposition and annealing treatment procedures were repeated eight times in order to obtain the desired thickness [16].

2.2. Preparation of Nd-doped TiO_2 films

The Nd-doped TiO_2 films were prepared using a cathodic electrochemical process. The TiO_2 films were used as the cathode and graphite served as the anode. The 0.05 M neodymium nitrate hexahydrate ($Nd(NO_3)_3{\cdot}6H_2O$) solution was the electrolyte. The plating bath was kept at 60 °C and rigorously stirred. The voltage was kept at 2 V. After deposition, the samples were rinsed with double-distilled water, dried in air, and then annealed at 500 °C in air for 1 h. Different amounts of Nd were incorporated by varying the electrochemical process time [17].

2.3. Characterization of Nd-doped TiO_2 films

The crystalline structure of the Nd/TiO_2 films was determined by X-ray diffraction (XRD) using Cu Kα radiation (Rigaku, RINT2000, Japan). A vertical goniometer (Model RINT2000) was used and the continuous scanning mode ($2\theta/\theta$) with an interval of 0.02° and scanning rate of 10°/min was adopted. Ultraviolet Raman scattering was performed at room temperature on a micro-Raman spectrometer with a spectral resolution of 1.5 cm^{-1} (Jobin-Yvon LabRAM HR 800 UV). The 325 nm (3.82 eV) line of a He-Cd laser with output power of 30 mW was the excitation source. The light absorption properties were determined by monitoring the UV–vis diffuse reflectance spectra in the wavelength range of 200–800 nm.

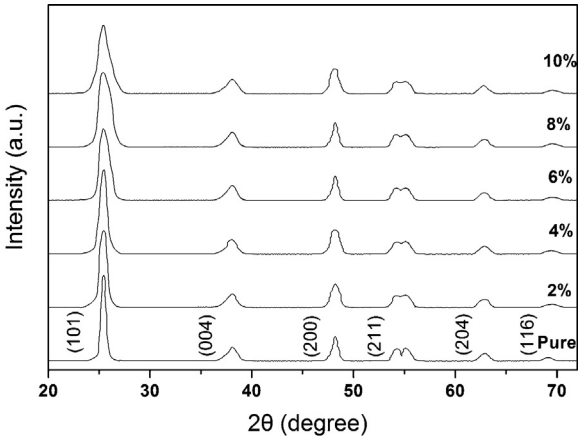

Fig. 1. XRD patterns of the Nd/TiO_2 films containing 2, 4, 6, 8, and 10% of Nd prepared on Si (1 0 0).

2.4. Photoelectrochemical and photoelectrocatalytic degradation

The photoelectrochemical experiments were carried out in a conventional three-electrode cell controlled by the LK3200A electrochemical workstation. The Nd/TiO_2 nanocomposite electrode was the photo-anode. A platinum wire electrode was adopted as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. The electrolytes consisted of 50 mL of 0.1 M Na_2SO_4 and 50 mL of a mixture containing 20 mg L^{-1} of PNP with 0.1 M Na_2SO_4. A 350 W xenon lamp with an illumination intensity of 100 mW cm^{-2} was the light source. All the experiments were performed at 25 °C. The photoelectrocatalytic degradation experiments were also conducted in the three-electrode cell controlled by the LK3200A electrochemical workstation. The photo-anode, cathode, reference electrode, and electrolytes were the same as in the photoelectrochemical experiments. The experiments were performed with magnetic stirring at room temperature and the pH of the solution was adjusted by H_2SO_4 or NaOH.

3. Results and discussion

The XRD patterns acquired from the Nd/TiO_2 films with different Nd concentrations are depicted in Fig. 1. All the films are polycrystalline with strong (1 0 1) diffraction which position shifts from 25.3° to 25.5° with Nd incorporation. It can be explained by that the radius of Nd is larger than that of Ti. Besides this salient feature, there are several weaker diffraction peaks of (0 0 4), (2 0 0), (2 1 1), (2 0 4), and (1 1 6) at about 37.8°, 48.0°, 55.1°, 62.75°, and 68.84° but no impurity phases are observed confirming the pure anatase structure. The polycrystalline grains with different orientations are formed in the anatase films and Nd atoms exist in the TiO_2 matrix. The (1 0 1) peak intensity decreases and peak width increases with increasing Nd concentrations implying Nd plays an important role in the crystalline lattice. On the basis of the (2 0 0) and (0 0 4) diffraction peaks, the lattice constants $a = b$ and c of the Nd-doped TiO_2 films are estimated to be slightly larger than the theoretical values of pure anatase ($a = b = 3.747$ Å, $c = 9.334$ Å) as a result of Nd substitution. The difference in the lattice constant suggests that there are different lattice distortions in the anatase films doped with Nd. The average crystalline size r can be calculated from the (1 0 1) diffraction peak according to the Scherrer equation $r = K\lambda/\beta\cos\theta$, where $K \approx 1$ is the shape factor, $\lambda = 1.540$ Å is the average wavelength of Cu Kα radiation, β is the full width at half-maximum, and θ is the diffraction angle. That shown the average grain size is about 31.4 nm and the grain size diminishes with increasing Nd concentration while the cell parameter is not varied.