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Synergistic effect on the photocatalytic activity of N-doped TiO_2 nanorods synthesised by novel route with exposed (110) facet

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ABSTRACT

This paper describes a facile route for the preparation of visible-light-active N-doped TiO_2 nanorods arrays at low temperature by a template-free oxidant peroxide method (OPM) and crystallized under hydrothermal treatment. The samples were characterized for structural, morphological and optical properties by XPS, FE-SEM, HRTEM, XRD, Raman and UV–vis spectroscopy. XPS analysis revealed that N dopant atoms were mainly added at the interstitial sites into TiO_2 lattice structure and few N atoms were present as substitutional sites of nitrogen atoms and/or at molecularly chemisorbed γ-N_2 molecules. FE-SEM and HR-TEM analyses show that doping does not influenced the cylindrical architecture of the nanorods. However, N doping causes an obvious red shift in the band edge which increases visible region absorption. The photocatalytic activity of pristine and N-doped TiO_2 photocatalysts was tested for the degradation of methyl orange (MO) under UV and visible light irradiation. The N-doped TiO_2 photocatalysts showed an efficient photocatalytic activity for methyl orange degradation under UV and visible-light irradiation as compared to pristine TiO_2. Multiple cycles for the MO photodegradation were performed without a decrease in the photocatalytic activity. PEC studies showed that photocurrent densities of 8.2 $\mu A\ cm^{-2}$ and 7.0 $\mu A\ cm^{-2}$ were obtained under UV and visible-light illumination at a potential of 0.8 V.

1. Introduction

Titanium dioxide (TiO_2) is one of the most promising semiconductor with a wide bandgap and is finding extensive attentions due to its unique combination of non-toxicity, structural and physicochemical characteristics in applications such as self-cleaning coatings, solar cells, environmental remediation, photocatalytic degradation of organic pollutants under UV light, sensors, photonic crystals, Li ion batteries, etc. [1–4] However, the effect of morphology is pivotal on the electronic conductivity due to wide bandgap of its anatase phase TiO_2 (3.2 eV) for photocatalytic applications in the visible-light range. Besides this, the relatively high rate of electron–hole recombination for low band-gap semiconductors often results in a poor efficiency of photocatalytic reactions with low quantum yield [3,4].

To deal with the above short-comes, doping of TiO_2 with non-metals and specifically of nitrogen, is considered a promising approach to improve the performance of photophysical and electrochemical properties for TiO_2 in the visible light [5–7]. This could increase its optical activity by shifting the onset of its response from UV to visible region due to enhancement of electrical conductivity [8,9]. Asahi et al. reported first time a visible light-active N-doped TiO_2 photocatalyst. It was noted that band structure was responded to visible-light sensitivity and was expected due to mixing of substitutional N2p states with O2p states [5]. Irie et al. isolated the substitutional N in N-doped TiO_2 for N2p narrow band formed above the O2p valence band that is responsible for the visible-light response [10]. Serpone et al. argued the creation of defects associated with oxygen vacancies for visible light activation of N-doped TiO_2 and gave rise to color-centers [11]. Livraghi et al. applied a combination of experimental and theoretical approaches for N-doped TiO_2 and established that the creation/incorporation of N_b^* centers into the TiO_2 lattice played an essential role in the transition of electrons to the conduction band and in the photo-induced electron transfer to reducible adsorbent that causes the absorption of visible light [12].

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The search for novel and facile synthesis strategy to prepare visible-light-active N-doped TiO_2 photocatalysts (powders and films) is still of great interest. Reported methods adopted for this purpose includes; controlled hydrolysis or sol–gel [13,14], sputtering [5,15], ion implantation [16,17], and chemical treatments of the baer TiO_2 [5,18,19]. In this paper, we have developed a new method to prepare nanorods shaped N-doped TiO_2 photocatalysts using oxidant peroxide route and crystalized via hydrothermal treatment. We have studied the structural, optical and morphological properties of N-doped TiO_2 using X-ray photoelectron spectroscopy, X-ray diffraction, UV–visible spectroscopy and high-resolution transmission electron microscopy. The photocatalytic activity of N-doped TiO_2 photocatalysts has been tested for photodegradation of methyl orange under UV and visible light irradiation.

2. Experimental

2.1. Synthesis

Preparations of N-doped TiO_2 photocatalysts were synthesized from decomposition Ti peroxo-complex in the hydrothermal treatment. Ribeiro el. al [20]. described in detail the synthesis of Ti-peroxo-complex in a mixture of ammonia and hydrogen peroxide mixture solution. Briefly described as; 250 mg of metallic Ti (99.7%, Aldrich) was added into a 3:1 ratio solution of H_2O_2/NH_3 (both 29.0%, Synth) to make 80 mL mixture solution. This solution was placed on cool ice–water bath until to the formation of stable peroxy titanate ion $[Ti(OH)_3O_2]^-$ with the appearance of transparent yellow aqueous solution due to complete dissolution of the metal [21]. Different amount of trimethylamine (as N source) was added to the stable peroxy titanate ion solution ranging from 1 to 5% (w/w compared to TiO_2) to obtain N-doped resins. The samples were marked with an initial content of N as; NTO-2 = 1%, NTO-3 = 2%, NTO-4 = 3%, NTO-5 = 4% and NTO-6 = 5%, whereas NTO-1 denoted the original TiO_2 sample. The resulting solution was set to heating until start boiling and then sent for quick cooling in an ice-water bath to obtain the precipitate, which was set to continuous magnet stirring in order to evaporate all excess of NH_3 and H_2O_2 for 12 h. The precipitate was freeze-dried and 200 mg precursor was suspended into an appropriate amount of water for hydrothermal treatment at 200 °C for 120 min in a controlled reactor to obtain crystallized material. The obtained crystalline material was repeatedly washed to reach a pH value of pure distilled water and to limit the side-effect of any residue (acids, bases or counter-ions) from synthesis environment to the characterization of material. Reference sample TiO_2 Aldrich nanopowder 99.7% purity (Ind.) of the industrial grade was analyzed by XRD analysis comprising 92% of anatase and rutile phase using the relation of planes peak intensities between the two phases [22,23].

2.2. Powder characterization

Rigaku D-Max 2500 diffractometer was used to perform X-ray diffraction analyses, having a Cu anode ($\lambda_{Cu\text{-}K\alpha} = 1.5456$ Å) define the peak position and width with a scanning rate of 1 min at 2θ between the range of 10° and 75°. The exposure time was 1s with the angular pass of 0.02°. The approximate length of crystallographic coherence was calculated from Scherer's equation. Lorentzian approximation gave the full width at half maximum (FWHM) and reflection of monocrystalline Silicon wafer at (101) FWHM was used as reference [24]. Field emission gun scanning electron microscope (FE-SEM) and high-resolution transmission electron spectroscopy (HR-TEM) were used to characterize surface morphology of the nanoparticles. Transmission electron microscopy (TEM) and HRTEM images were obtained from FEI TECNAI F20 microscope operating at 200 kV. Additional HRTEM and HAADF-STEM characterization were obtained from JEOL JEM 2200FS aberration-corrected microscope operating at 200 kV. FT-Raman Bruker RFS100/S spectrometer were used to collect the Raman spectra at room temperature using the 1064 nm line of 450 Y–Al garnet laser with a scans rate of 200 operated for each measurement in the frequency range of 100–1000 cm^{-1}. Micromeritics ASAP 2000 adsorption analyzer was used to obtain the Brunauer–Emmett–Teller (BET) specific surface area (SA) by nitrogen physical adsorption at 77 K. Standard BET surface area procedures to estimate the surface areas (SA, $m^2\ g^{-1}$) and mean particle size of the nanoparticles assuming uniform size of nonporous spheres:

$$d = \frac{6000}{\rho x SA} \tag{1}$$

Where $\rho = 3.99\ g\ cm^{-3}$ denotes the theoretical density of TiO_2. Malvern Zeta sizer Nano ZS potential was used to obtain Zeta potential values of the dilute suspensions and electrophoretic light scattering was used for particle size analyzer in the pH range from 12.0 to 2.0. KOH and/or HCl were used to adjust the pH to determine the isoelectric point (IEP). PerkinElmer Spectrum 1000 instrument was used for Fourier transform infrared spectra (FTIR) and spectra were collected to confirm the surface-adsorbed hydroxyl groups and water groups of photocatalyst samples. The samples were dried in an oven at 100 °C for 12 h and then mixed with 0.3 wt% concentration of potassium bromide (KBr). A 100 mg pellet was obtained by pressing the above mixture up to 6 tons/cm^2 in a pellet presser and then placed in a desiccator prior to FTIR analysis to ensure the same atmospheric conditions for all samples. Ultraviolet–visible–near infrared (UV–vis–NIR) Cary 5G spectrophotometer was used to record the Ultraviolet–visible (UV–vis) absorption spectra.

Photocatalytic activity of the samples was tested for the degradation of methyl orange under UV and visible irradiation. The light sources used for photocatalytic reaction were UV radiation source of Lamps Phillips TUV 15 W having maximum intensity of 254 nm and a visible radiation source of Osram with maximum intensity at 440 nm with a light filter to cut off the light in a thermostated photo-reactor maintained at 18 °C by circulating water jacket to keep it cool from the infrared radiation and preventing from heating out of the suspension. In a typical photocatalytic test, different samples with the same photocatalyst amount were prepared by dispersing 10 mg of photocatalyst into 20 mL MO aqueous solution with a concentration of 10 mg L^{-1} through ultrasonic treatment for 10 min. Pristine and commercially available TiO_2 (Aldrich nanopowder, 99.7%) were tested for photocatalytic activity under the same conditions as the reference photocatalysts [25]. The residual concentration of MO was recorded after every specifically exposed interval by taking 5 mL samples and separated using a centrifugal separation method. The photocatalytic oxidation of organic dyes was monitored by taking UV–vis measurements spectrophotometer (Shimadzu-UV-1601 PC spectrophotometer) in different periods of light exposure to monitor the degradation kinetics for MO solution. All photocatalysts sample were soaked into organic dyes solution for overnight before the photocatalytic test in order to evaluate the possible adsorption effects. Cyclic usages of the treated samples were performed to confirm their usage and stability. For this purpose, the selected samples were washed with double deionized water and dried at 100 °C to remove moisture. After that, the air-dried samples were heat treated for 2 h in an N_2 atmosphere at 400 °C in a furnace. For the cyclic photocatalytic degradation test, NTO-3, NTO-4 and NTO-5 were selected and repeatedly used.