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V and N co-doped nanocrystal anatase TiO_2 photocatalysts with enhanced photocatalytic activity under visible light irradiation

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Abstract

Vanadium and nitrogen co-doped TiO_2 nanocrystal (4–5 nm) photocatalysts were prepared through direct nitridation of the controlled hydrolysis product of Tetrabutyl titanate in V (IV) ions solution. The catalysts were characterized by XRD, BET surface area, XPS, and UV–vis diffuse reflectance spectra. The co-doped TiO_2 nanocrystal has a narrower band gap of 2.76 eV than V-doped TiO_2 (2.91 eV) and N-doped TiO_2 (2.92 eV). The co-doped TiO_2 photocatalysts show enhanced photocatalytic activity for the degradation of methylene blue under visible light irradiation ($\lambda > 420$ nm) compared with V-doped TiO_2 and N-doped TiO_2.

Keywords: Titanium dioxide; Co-doping; Vanadium and nitrogen; Visible light; Photocatalytic activity

1. Introduction

More widespread applications of TiO_2 as a photocatalyst have been cumbered with its wide band gap (3.2 eV for anatase TiO_2) [1,2]. This requires ultraviolet irradiation ($\lambda \leqslant 387$ nm) for photocatalytic activity. However, UV light accounts for a small fraction (about 5%) of the sun rays on the surface of the earth. Therefore, many attempts have been made to develop TiO_2 photocatalysts with visible light (vis-) photocatalytic activity. Doping with transition metal ions (Cr, V, and Fe etc.) is one of the important approaches [3–6]. However, doping with transition metal ions generally increases carrier-recombination centers, and consequently debases the quantum efficiency of doped TiO_2 catalysts [3–5]. Moreover, doping with transition metal ions could result in the thermal instability of doped photocatalysts. Another approach is doping with nonmetals. After the first report from S. Sato on NO_x-doped TiO_2 [7], Asahi et al. recently prepared N-doped TiO_2 films and powders with high vis-photocatalytic activity [8]. From then on, the vis-photocatalytic properties of doped TiO_2 with nonmetals (N, C, S, F) have been widely investigated [9–17]. Of these nonmetals, doping with N is the most promising for preparing doped TiO_2 catalysts as a potential candidate for the second-generation photocatalysts with efficient catalytic activities over the UV region and much of the visible light region [8,9,18].

Very recently, Ozaki et al. reported that N-doped silica-modified TiO_2 exhibits high vis-photocatalytic activities for decomposing acetaldehyde [19]. Cong et al. found that nanoparticles of TiO_2 co-doped with N and Fe (III) show greatly-enhanced vis-photocatalytic activities [20]. These results indicate that co-doped TiO_2 with nonmetals and transition metal ions may be a new promising second-generation photocatalysts. Though V-doped TiO_2 and N-doped TiO_2 have already shown efficient vis-photocatalytic activities, few reports are published on V and N co-doped TiO_2 photocatalysts. In this study, V and N co-doped anatase TiO_2 nanocrystal photocatalysts were synthesized through the controlled hydrolysis of Tetrabutyl titanate ($Ti(OBu)_4$) followed by a direct nitridation process at room temperature. The co-doped TiO_2 nanocrystal photocatalysts showed enhanced vis-photocatalytic activity comparing with V-doped TiO_2 and N-doped TiO_2.

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2. Experimental

The V and N co-doped TiO_2 nanocrystal photocatalysts were synthesized by a two-step wet chemical method. Firstly, V-doped TiO_2 nanoparticles were prepared through the controlled hydrolysis of Tetrabutyl titanate ($Ti(OBu)_4$) in V ions solution. A 2.5 mL sample of tetrabutyl titanate, dissolved in isopropyl alcohol with the volume ratio of 1:9, was added dropwise to 500 mL aqueous solution containing 0.2 mM V(IV) ions at pH 1.5 (adjusted with HNO_3) under vigorous stirring at room temperature(about 20 °C). After continuous stirring for 24 h, V-doped TiO_2 nanoparticles were obtained by evaporating at 50 °C and then drying under vacuum. As a reference sample, un-doped TiO_2 nanoparticles were prepared through a similar procedure in deionized water without V ions. Secondly, V and N co-doped TiO_2 nanocrystal powders were prepared at about 20 °C by a direct nitridation process developed by Burda et al. [9]. Nitridation was performed by adding the excess of triethylamine into the V-doped TiO_2 nanoparticle suspension under strong stirring. After continuous stirring for 6 h, brownish V and N co-doped TiO_2 samples were obtained after evaporating at 50 °C and drying for 48 h under vacuum. As a reference sample, Yellowish N-doped TiO_2 nanocrystal powders were obtained via a similar nitridation procedure using above un-doped TiO_2 nanoparticles. For simplification, V and N co-doped TiO_2, V-doped TiO_2, N-doped TiO_2, and un-doped TiO_2 are referred to as V–N–TiO_2, V–TiO_2, N–TiO_2, and TiO_2, respectively.

The X-ray Diffraction (XRD) patterns for all the samples were recorded on a Philips X′pert X-ray diffractometer operated at 40 kV (Cu K_α radiation). The Brunauer–Emmett–Teller (BET) surface areas of the samples were measured with a surface area and pore analyzer (NOVA2000e, Quantachrome Instruments). X-ray photoelectron spectroscopy (XPS) measurements were performed on VG Microlab MK II. Aluminum K_α radiation was used as the excitation source (1486.6 eV). All the binding energies were calibrated by the C1 s peak at 284.6 eV for the adventitious carbon. Ultraviolet–visible (UV–vis) diffuse reflectance spectra were recorded through a UV–vis–NIR spectrophotometer (SHIMADZU, Solidspec-3700).

The photodegradation of methylene blue (MB) was used to evaluate the vis-photocatalytic activities of doped TiO_2 catalysts. A 400 W xenon lamp was used as a visible light source. A colored glass filter (JB420, EOLFH) with cut-off wavelength of 420 nm was used for eliminating UV light. For a photocatalytic experiment, 40 mg of nanocrystal catalysts was ultrasonically dispersed into 100 mL aqueous solution of 0.005 mM MB in a beaker. The distance between the beaker and the light source is about 25 cm. Before irradiation, the suspensions containing MB and catalysts were magnetically stirred for 30 min at dark in order to reach an absorption–desorption equilibrium. The decolorization of MB solution was determined by a UV–vis spectrometer at the wavelength of 661.0 nm.

3. Results and discussion

The XRD powder diffraction patterns for all the samples are shown in Fig. 1. All the samples are only of anatase form. Since a Rietveld refinement technique is very effective for providing the quantitative structural information of crystalline materials [21,22], it is used to exactly determine the crystallographic parameters of all the samples in this study. Rietveld refinement of the XRD profiles was carried out using the DBWS Rietveld refinement program with a Cerius-2 interface. According to the refinement results, the grain sizes and lattice parameters for all the samples are listed in Table 1. Obviously, all the as-prepared samples are nanocrystals with the average grain size of 4–5 nm. The doping has little effect on the grain size. V–N–TiO_2 shows the expansion of the lattice parameters along both "*a*" and "*c*" axes comparing with TiO_2. This indicates that V and N species have been incorporated into the lattice of anatase TiO_2.

Since the specific surface area is one of the important factors for the photocatalytic properties of catalysts, the BET surface areas of all the samples were measured. The results (as listed in Table 1) show that the specific surface area of V–TiO_2 is close to that of TiO_2, while the specific surface areas of N–TiO_2 and V–N–TiO_2 are less than those of TiO_2 and V–TiO_2. This indicates the nitridation process results in the aggregation of the nanoparticles. In preparing the $TiO_{2-x}N_x$ powders by a similar nitridation route, Gole

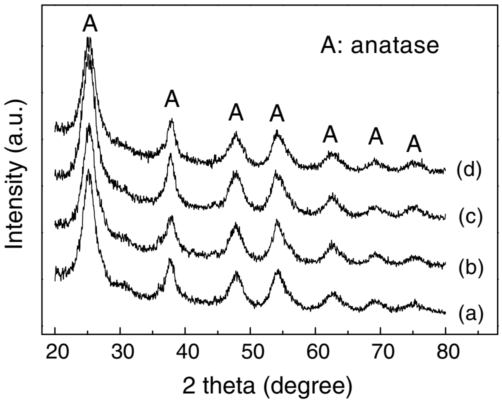

Fig. 1. XRD powder diffraction patterns for (a) TiO_2, (b) N–TiO_2, (c) V–TiO_2 and (d) V–N–TiO_2.

Table 1
XRD data, N concentrations determined from XPS data, and BET surface areas for all the samples

Sample	Lattice Parameters		Grain size (nm)	N concentration (at.%)	Surface area ($m^2 g^{-1}$)
	a (Å)	*c* (Å)			
TiO_2	3.7848	9.4826	4.2	0	216
N–TiO_2	3.7917	9.4868	4.6	3.3	181
V–TiO_2	3.7882	9.4949	4.3	0	203
V–N–TiO_2	3.7996	9.4976	4.2	3.9	172