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An enhanced visible-light photocatalytic activity of TiO_2 by nitrogen and nickel–chlorine modification

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ABSTRACT

A series of nitrogen and nickel–chlorine co-modified TiO_2 photocatalysts (TiO_2-N–x%Ni) with visible-light response have been synthesized by a sol–gel method. The results of photocatalytic degradation of 4-chlorophenol (4-CP) suggest that TiO_2-N–x%Ni photocatalyst shows a higher activity than both pure TiO_2 and nitrogen doped TiO_2 (TiO_2-N) under visible-light irradiation. The structure and properties of the photocatalysts have been investigated by XRD, XPS, UV–vis diffuse reflectance spectra (DRS), and photoluminescence (PL) spectra. It was found that unique chemical species, such as N–O_x and O–Ni–Cl, existed on the surface of TiO_2-N–x%Ni. The energy levels of N–O_x and O–Ni–Cl surface states locate above the valence band and below the conduction band of TiO_2, respectively. This could lead to strong visible-light absorption and an enhanced charge carrier separation compared with both pure and TiO_2-N. Our results offer a paradigm for preparation of photocatalyst with a high visible-light activity by simultaneously doping TiO_2 with two or more different elements.

1. Introduction

Doping TiO_2 with metal or nonmetal ions [1–4] is considered as one of the most promising methods to efficiently develop TiO_2-based photocatalysts sensitive to visible light. So far, many efforts have been made in this field [5,6] and a breakthrough was made in 2001 by substitutional doping of nitrogen in TiO_2 which shows a superior visible-light activity to pure TiO_2 [7]. Since then, extensive research has been carried out on the TiO_2-N catalysts owing to its great potential for enhancing the visible-light response of TiO_2 [8–12]. Doping nitrogen is considered as an effective method because N2p states would mix with O2p states and contribute to the formation of valence band. However, only a small amount ($\leqslant$2%) of nitrogen can be incorporated into TiO_2 catalysts, resulting in a limited visible-light absorption and a low visible-light photocatalytic performance. Therefore, it is still of great importance to further improve the photocatalytic activity of TiO_2-N.

In recent years, nickel doped TiO_2 has also been attracting more and more attention due to its effects on increasing the photocatalytic activity of TiO_2 [13–18]. Zhao and coworkers investigated the photocatalytic properties of B doped TiO_2 loaded with Ni_2O_3 [4]. Murakami et al. prepared TiO_2 with modified Ni^{2+} ions by the impregnation method and found Ni^{2+} ions acted as an electron acceptor [14]. Yoshinaga et al. reported that nickel nanoparticles deposited on the surface of TiO_2 film by chemical vapor reductive deposition method remarkably increased the photocatalytic activity of TiO_2 film [15]. Niishiro et al. found that substitutional doping of nickel was effective in producing a visible-light response for TiO_2 which was due to the transimation from the donor levels formed by Ni^{2+} ions to the conduction band [16]. Visinescu et al. reported that Ni ions would accommodate in the titania matrix synthesized by dc reactive sputtering method [17]. Kim et al. synthesized nickel doped TiO_2 by mechanical alloying and investigated its energy states [18]. However, the doping modern and doping energy of nickel doped TiO_2 have not been well explored up until now.

Thus, in this work we prepared a series of TiO_2 photocatalysts with N and Ni–Cl modification by a sol–gel method. It is revealed that the doping N, Ni and Cl ions exist as unique surface species, such as N–O_x and O–Ni–Cl on surface of TiO_2. Our findings suggest that surface modification of O–Ni–Cl species can further extend the spectral response to the visible region and enhance the photocatalytic activity of TiO_2-N. The goals of both extending the TiO_2 spectral response to the visible region and improving its catalytic activity are achieved by modification with two species, N–O_x and O–Ni–Cl. The detailed discussion is presented in the text. We suggest that the co-modified TiO_2 is an effective method to improve the visible-light activity of TiO_2-based photocatalysts.

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2. Experimental section

2.1. Catalyst preparation

Different amount of nickel chloride ($NiCl_2 \cdot 5H_2O$), 15 mL of tetrabutyl titanate and 4.16 mL of concentrated hydrochloric acid (12 M) were mixed with 40 mL of ethanol under vigorous stirring. After aging at room temperature for 12 h, 3 mL of ammonia was added into the mixture under continuously stirring dropwise, and a white precipitate formed immediately. After stirring for 3 h, the resultant gel was dried at 100 °C, annealed at 450 °C for 2 h. The TiO_2 photocatalysts with N and Ni–Cl modification were thus obtained, denoted as TiO_2-N–x%Ni (x represents the nominal molar ratio of Ni to (Ni + Ti), $x = 1.5, 6, 10$, molar amount of Cl is equal to that of Ni). The nitrogen doped TiO_2 and pure TiO_2 catalysts were prepared by using the same protocol, but with and without adding the respective doping reagent.

2.2. Characterization

The UV–vis DRS were collected with a UV–vis spectrometer (U-4100 Spectrophotometer, Hitachi). The XRD measurements were carried out at room temperature using a Rigaku D/MAX-2500 diffractometer with Cu Kα radiation ($\lambda = 0.154056$ nm). The BET surface areas of the samples were determined by nitrogen adsorption–desorption isotherm measurement at 77 K (Micromeritics Automatic Surface Area Analyzer Gemini 2360, Shimadzu). XPS measurements were performed with an ESCA Lab 220i-XL spectrometer by using an unmonochromated Al Kα (1486.6 eV) X-ray source. All the spectra were calibrated using the binding energy of the adventitious C1s peak at 284.8 eV. The fluorescence generated by illuminating the samples with a nanosecond Nd:YAG laser (NL303G, 325 nm) at an ambient temperature was collected and focused into a spectrometer (Spex 1702), and detected by a photomultiplier tube (PMT; Hamamatsu R943).

2.3. Calculation

The density functional theory (DFT) calculations were carried out using the Castep package within the generalized gradient (GGA) approximation. For the periodic plane-wave approach, Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional and ultrasoft pseudopotentials were used. The anatase (1 0 1) surface was modeled with a periodically repeated slab. The vacuum was taken as 7 Å. The energy cutoff was set as 340 eV. The k-point sampling of Brillouin zone was limited to a low-symmetry k-point.

2.4. Photoreactivity experiments

The photocatalytic degradation of 4-CP was performed with 10 mg catalyst suspended in a 40 mL of aqueous 4-CP solution (5×10^{-5} mol/L) under visible-light irradiation. A 400 W sunlamp (Philips HPA 400/30S, Belgium) placed at about 15 cm from the reaction vessel was used as the light source with a 400 nm cutoff filter. The reaction temperature was maintained at 28 ± 2 °C during the whole experiment. Prior to the irradiation (i.e., photocatalytic reaction), the suspension was first magnetically stirred for 30 min in the dark to reach absorption–desorption equilibrium of 4-CP. The oxygen gas was continuously bubbled into the suspension at a flux of 5 mL min^{-1} during the reaction. The concentration of 4-CP at different times under the illumination was monitored by using a UV–vis spectrometer (UV-16PC, Shimadzu) with the help of 4-aminoantipyrine as the chromogenic reagent.

3. Results and discussions

3.1. UV–vis DRS spectra

The UV–vis DRS spectra of pure TiO_2, TiO_2-N and TiO_2-N–x%Ni samples are shown in Fig. 1. For pure TiO_2, only a strong absorption is observed in the ultraviolet-light region of the spectra, which is attributed to the band–band transition, corresponding to a band gap of 3.1 eV. Besides this intrinsic absorption band, TiO_2-N also shows a significant absorption ranging from 400 to 550 nm, which may be attributed to the electron transition from energy levels of N surface species, locating at 0.25 eV above the valence band of TiO_2, to the conduction band of TiO_2 [19,2]. For TiO_2-N–x%Ni sample, an even more intense and broader absorption in the visible region of 400–600 nm is observed. Hence, TiO_2-N–x%Ni samples are more sensitive to visible light than pure TiO_2 and TiO_2-N. In addition, it is noted that this absorption becomes more and more intense with the increase of the doping amount of Ni and Cl, which could be related to the Ni and Cl surface species formed by the introduced Ni and Cl ions in the TiO_2-N–x%Ni samples. The difference DRS spectra were obtain by subtracting the absorbance spectra of TiO_2-N–1.5%Ni (curve c) from the spectra of TiO_2-N–6%Ni and TiO_2-N–10%Ni (curves d and e) in Fig. 1, which is shown in the inset of Fig. 1. The position of the absorption maximum was around 420 nm, corresponding to an energy level gap of 2.95 eV. Thus, the visible-light absorption observed in TiO_2-N–x%Ni is attributed to the electron transition from TiO_2 valence band to the energy level of Ni and Cl surface states, which locate at about 0.15 eV below the TiO_2 conduction band.

3.2. Calculation

Fig. 2A shows density of states (DOS) of TiO_2–x%Ni calculated by using DFT. The projected contributions to the total DOS from O ($2s^22p^4$), Cl ($3s^23p^5$), Ti ($3s^23p^63d^24s^2$) and Ni ($3d^84s^2$) are also included in the figure. It is found that, as expected, the valence band is mainly composed of O2p electronic states, strongly hybridized with Ni 3d, Ti 3d and Cl 3p states. The conduction band is dominated by Ti 3d electronic states, strongly hybridized with O2p. A new energy band appears below the conduction band, which is mainly composed of Ni 3d electronic states, hybridized with Cl 2p. This is attributed to the Ni and Cl surface states which would be confirmed by XRD and XPS.

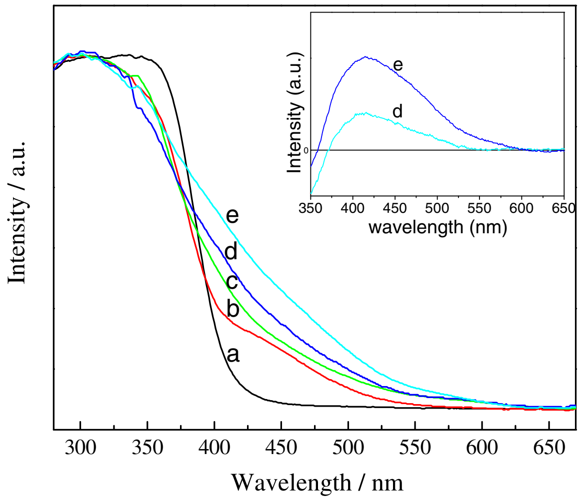

Fig. 1. Diffuse reflectance UV–vis absorption spectra of (a) TiO_2, (b) TiO_2-N, (c) TiO_2-N–1.5%Ni, (d) TiO_2-N–6%Ni and (e) TiO_2-N–10%Ni. The inset gives the difference DRS spectra of TiO_2-N–6%Ni and TiO_2-N–10%Ni (curves d and e).