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Enhanced photocatalytic activity of titania with unique surface indium and boron species

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ABSTRACT

Indium and boron co-doped TiO_2 photocatalysts were prepared by a sol–gel method. The structure and properties of photocatalysts were characterized by XRD, BET, XPS, UV–vis DRS and PL techniques. It is found that boron is mainly doped into the lattice of TiO_2 in interstitial mode, while indium is present as unique chemical species of O–In–Cl_x ($x = 1$ or 2) on the surface. Compared with pure TiO_2, the narrowness of band gap of TiO_2 doped with indium and boron is due to the mixed valence band formed by B2p of interstitial doped B ions hybridized with lattice O2p. And the surface state energy levels of O–In–Cl_x ($x = 1$ or 2) and B_2O_3 species were located at about 0.4 and 0.3 eV below the conduction band respectively, which could lead to significant absorption in the visible-light region and facilitated the effectually separation of photogenerated carriers. Therefore, indium and boron co-doped TiO_2 showed the much higher photocatalytic activities than pure TiO_2, boron doped TiO_2 (TiO_2–B) and indium doped TiO_2 (TiO_2–In) under visible and UV light irradiation.

1. Introduction

In recent years, great efforts have been devoted to make TiO_2-based photocatalysts more sensitive to visible light for utilizing solar energy efficiently [1–5]. So far, many strategies have been adopted in this field, such as doping metal or nonmetal elements [6–9], combination with a narrow-bandgap semiconductor [10–14] and surface modification [15]. Doping TiO_2 with metal or nonmetal elements is considered as one of the most promising methods to enhance photocatalytic activity. The introduction of doping states is able to extend catalytic absorption to visible light region, and suppress the recombination of photogenerated charge carriers (electron and hole pairs), due to the narrowness of band gap and/or creation of doping energy levels in band gap [16–19]. However, the amount of doped ions incorporation is usually quite low, which limits visible light absorption and separation efficiency of photogenerated charge carriers. For the boron doped TiO_2 [9], because of only small amounts of boron incorporation, visible light absorption and separation efficiency of photogenerated charge carriers are limited, as a result, the catalysts show a poor visible-light photocatalytic activity.

In addition, it has been proved that modification of unique chemical species on TiO_2 surface can accelerate an improvement of visible-light photocatalytic activity. Our previous work [15] has shown that a unique chemical species, O–In–Cl_x ($x = 1$ or 2), present on the surface of indium doped TiO_2. The surface state energy level of O–In–Cl_x ($x = 1$ or 2) species is located at 0.3 eV below the conduction band of TiO_2, which can lead to the visible-light absorption. Furthermore it allows an efficient transfer of photogenerated electrons to the surface and suppresses the recombination of photogenerated charge carriers. Consequently, the indium doped TiO_2 showed improved photocatalytic activity for photodegradation of 4-chlorophenol compared to pure TiO_2 under visible light irradiation.

Furthermore, the visible-light absorption and photocatalytic activity of photocatalyst can be further improved by doping TiO_2 with multidopants since the contribution can come from all the dopants. This has been demonstrated in several systems, such as (B Ni) [9], (N W) [16] and (N Sn) [17]. Thus, it is expected to establish a promising method to promote photocatalysis by introducing both the doping ions and the surface species into TiO_2. This introduction would be able to further improve the visible light absorption and suppress the recombination of photogenerated charge carriers efficiently. In this work, we prepared a TiO_2-based photocatalyst co-doped with indium and boron prepared via a sol–gel method. Boron is incorporated into the TiO_2 lattice in interstitial mode, and the B_2O_3 species formed by surplus B ions exist on the surface of photocatalyst, while indium exists as surface unique O–In–Cl_x species. Moreover, as expected, it exhibits much better visible and UV light photocatalytic activity than pure TiO_2, indium doped TiO_2 and boron doped TiO_2. The mechanism is also discussed in this contribution.

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2. Experimental

2.1. Catalyst preparation

All chemicals used were of analytical grade and water was deionized water (>18.2 MΩ cm). The modified catalysts were prepared by the following steps. 7.1 mL of $InCl_3$ solution (0.73 mol/L) was mixed with 40 mL of ethanol to prepare solution A, and then an appropriate amount of H_3BO_3 was dissolved into the solution A at room temperature. After mixing continuously for 15 min, 12 mL of tetrabutyl titanate ($Ti(OC_4H_9)_4$) and 1 mL of concentrated HCl solution (12 mol/L) were added dropwise to solution A under vigorous stirring. The mixture was stirred continuously until the formation of TiO_2 gel, which was dried at 100 °C for 10 h after aging for 24 h at room temperature and then annealed at 450 °C for 2.5 h. The boron concentration in the catalysts was adjusted by changing the amount of H_3BO_3, while the indium concentration was the same. The obtained samples were denoted as TiO_2–In–B*X*, where *X*% represented the nominal molar percentage of B^{3+} ions in Ti^{4+} and B^{3+} (B/Ti + B), and equaled to 5%, 10%, 15%, 20% and 25%, respectively. The pure TiO_2, TiO_2–B and TiO_2–In samples were prepared with the same procedure without corresponding precursor, but with and without the addition of the corresponding modification reagent.

2.2. Characterization

The XRD patterns were acquired on a Rigaku *D*/max 2500 X-ray diffraction spectrometer (Cu Kα, $\lambda = 1.54056$ Å). The average crystallite size was calculated according to the Scherrer formula ($D = k\lambda/B\cos\theta$). The BET specific surface areas (S_{BET}) of photocatalysts were obtained by N_2 physisorption at 77 K (Micromeritics Tristar 3000, Shimadzu). XPS measurements were carried out by using a SECA Lab 220i-XL spectrometer with a non-monochromatized Al Kα excitation source (1486.6 eV) and all the binding energies were calibrated to the adventitious C1s peak at 284.8 eV. The Fourier Transform Infra-Red (FT-IR) spectra were recorded for KBr disks containing the powder sample with an FT-IR spectrometer (MAGNA-560). Diffuse reflectance UV–visible (UV–vis) absorption spectra were recorded on a UV–vis spectrometer (U-4100, Hitachi). The photoluminescence (PL) spectra were generated by irradiating samples with a nanosecond Nd:YAG laser (NL303G, 325 nm) at ambient temperature, focused into a monochromator (MS3504) and detected using a photomultiplier tube (PMT, Hamamatsu R943). The whole system includes a single optical parametric system (NT342/3/UV), which consists of the nanosecond Nd:YAG laser and optical parametric oscillator (OPO, PG122), monochromator (MS3504), data acquisition unit (DAQ), digitizer PICO (ADC-200/100), optics for excitation beam guiding and luminescence signal collecting.

2.3. Evaluation of photocatalytic activity

The photocatalytic activity of all photocatalysts was determined by the photodegradation for 4-chlorophenol (4-CP) in glass reactor (100 mL) with 10 mg amounts of catalysts suspended in 4-CP aqueous solution (5×10^{-5} mol/L, 40 mL, pH 5.38) under UV and visible light irradiation. A sunlamp (Philips HPA 400/30S, Belgium) was used directly for the UV-light photocatalytic reaction, while for the visible-light photocatalysis a 400-nm cutoff filter was employed to remove UV light. The reactor was perpendicular to the light beam and located 15 cm away from the light source. All the suspensions were magnetic stirred at 25 ± 2 °C in the dark for 30 min to reach adsorption equilibrium before irradiation, and oxygen gas was continuously bubbled through the solution at a flux of 5 mL min^{-1}. The change in concentration of 4-CP was monitored by a UV–vis spectrometer (UV-1061PC, SHIMADZU) using 4-aminoantipyrine as the chromogenic reagent. The reproducibility of the photocatalytic degradation was evaluated by repeating experiments at least three times with different batches of photocatalysts prepared by the same procedure. The blank experiment was performed under identical conditions but without photocatalyst. The deionized water (18.2 MΩ cm) was used in all experiments.

3. Results and discussion

3.1. Photocatalytic activity

The photodegradation of 4-CP was employed to evaluate the photocatalytic activities of pure TiO_2, TiO_2–B, TiO_2–In and TiO_2–In–B*X* samples under both visible and UV light irradiation. The experiment results are illustrated in Fig. 1, Tables 1 and 2, respectively. For all samples, the $\ln(c_0/c)$ values of 4-CP show a linear relationship with irradiation time, suggesting it be a pseudo-first-order reaction. Under visible light irradiation ($\lambda > 400$ nm) for 8 h (Fig. 1A and Table 1), 4-CP has been scarcely photodegraded in the blank experiment due to photolysis. The photodegraded rate of 4-CP in pure TiO_2 is only 9.1% due to some reason like photolysis. The photodegraded rate of 4-CP for TiO_2–B and TiO_2–In was 31.0% and 41.8%, respectively. TiO_2–In–B*X* photocatalysts exhibited better photocatalytic activity than pure TiO_2, TiO_2–B and

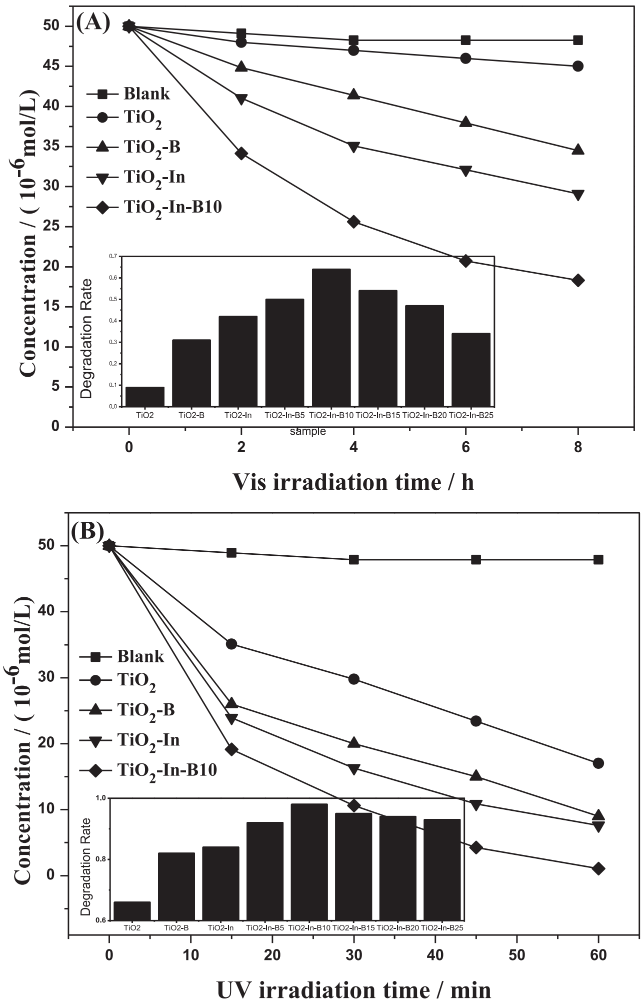

Fig. 1. (A) and (B) The photodegradation of 4-CP in the presence of TiO_2, TiO_2–B, TiO_2–In and TiO_2–In–B10 under both UV and visible light irradiation, respectively. Inset shows the corresponding UV- and visible-light photodegradation rate of 4-CP on all the samples ($I_{UV} = 0.2$ W cm^{-2}, $I_{Vis} = 0.1$ W cm^{-2}).