Photocatalytic Activity of (Copper, Nitrogen)-Codoped Titanium Dioxide Nanoparticles

Kaixi Song, Jiahong Zhou, Jianchun Bao, and Yuying Feng

Key Lab of Biofunctional Materials of Jiangsu Province, Nanjing Normal University, Nanjing 210097, China

Department of Chemistry and Environmental Science, Nanjing Normal University, Nanjing 210097, China

(Copper, Nitrogen)-codoped titanium dioxide (TiO₂) nanoparticles have been prepared via a sol–gel route, followed by heat treatment at an elevated temperature. Such (Cu, N)-codoped TiO₂ nanoparticles showed a strong absorption in the visible region and a red shift in the band gap transition and exhibited an enhanced photocatalytic activity as compared with the pure, N-doped and Cu-doped TiO₂ for xylene orange decomposition.

I. Introduction

Due to the last two decades, the photocatalysis on semiconducting TiO₂-based materials has been the focus of considerable attention because the use of TiO₂ as a photocatalyst has several advantages: high activity, good chemical inertness, safety, non-toxicity, and low costs. Thus, it has been considered as the most promising environment protective photocatalyst. However, pure TiO₂ exhibits relatively high activity only under ultraviolet (UV) light irradiation (Eg = 3.2 eV), leading to a low utilization of solar light. In this case, the overall efficiency of pure TiO₂ is quite low, limiting the practical application of TiO₂.

To improve the absorption ability of TiO₂ in the visible region, several strategies have been involved including the decrease of TiO₂ particle size and the doping with other species. Among them, doping could be an efficient approach to increase the absorption ability of TiO₂ in the visible region. The doping of various noble/transition metal elements or metal oxides into TiO₂ has been extensively attempted to extend the absorption edge and the results demonstrated that doping would result in a red-shift in the absorption edge. In most cases, however, the photocactivity of these doped samples is insufficient, due to low thermal stability and an increase in the carrier-recombination centers.

First report by Asahi et al. has proved that the absorption edge of the N-doped TiO₂ prepared by sputtering TiO₂ target in either N₂/Ar or NH₃ ambience red shifted from 387 to 500 nm. It was believed that nitrogen atoms have substituted the oxygen atom sites of TiO₂, leading to a narrow band gap by mixing the N 2p and O 2p states. Since then, studies on doping of nonmetal elements like N, S, P into TiO₂ lattice have become one major focus. The doping with metal or nonmetal elements has its respective advantages. If metal and nonmetal elements are codoped into TiO₂, the sample may possess the better photocatalytic performance. To date, however, only a few papers dealt with the codoping of metal and nonmetal elements into TiO₂.

II. Experimental Procedure

(1) Preparation

The synthesis of (Cu, N)-codoped TiO₂ nanoparticles involved the following steps: (1) 4 mL of acetic acid and 4 mL of tetrabutyl titanate (C₆H₁₃O₄Ti) were dissolved into 20 mL of ethanol. (2) The appropriate amounts of Cu(NO₃)₂ and CO(NH₂)₂, acetic acid and water were dissolved in 10 mL of ethanol. (3) The homogeneous solution prepared in step 2 was dropped into the step 3 mixture. (4) The colloid was first dried at 80 °C and calcined in a muffle at 450 °C for 3 h. Then, the (Cu, N)-codoped TiO₂ sample can be obtained. For the sake of comparison, pure, Cu and N-doped TiO₂ were also prepared by the similar procedure.

(2) Characterization

Ultraviolet-visible (UV-vis) diffuse reflectance spectra were performed using VARIAN Cary-5000 UV/vis/NIR spectrophotometer. BaSO₄ was used as a reflectance standard sample. X-ray diffraction (XRD) measurements utilized a Rigaku (Tokyo, Japan) D/MAX-2500 diffractometer with a CuKα radiation (1.54056 Å). The tube voltage was maintained at 60 kV and tube current at 300 mA. X-ray photoelectron spectra (XPS) were determined using PHI-550 multifunction X-ray photoelectron spectrophotometer (Physical Electronics, Chanhassen, MN).

(3) Photocatalytic Experiment

The photocatalytic activity of the sample was evaluated by measuring the degradation ratio of xylene orange. The light source used was a 500 W high-pressure mercury lamp equipped with a 380 nm cut-off filter and circulating cold water. The degradation ratio was determined using a spectrophotometer and the absorbance at 433 nm was recorded. For comparison, the photocatalytic reaction on pure TiO₂, Cu and N-doped TiO₂ was also evaluated.

III. Results and Discussion

(1) Diffuse Reflectance Spectra of the Photocatalysts

Figure 1 is a comparison of the UV-vis diffuse reflectance spectra of four samples. Comparing these curves, the absorption edges of the doped samples were shifted to longer wavelength region as compared with that of pure TiO₂ (curve a). The strongest absorption was observed on (Cu, N)-codoped TiO₂ nanoparticles. In this communication, (Cu, N)-codoped TiO₂ nanoparticles were synthesized by sol–gel method and the influence of the amount of Cu and N codoped into TiO₂ on its photocatalytic activity was discussed. This work may provide a new insight into the preparation of highly photocative (Cu, N)-codoped TiO₂ nanoparticles.

P. Yang—contributing editor

Manuscript No. 23625. Received August 18, 2007; approved December 10, 2007.
This work was financially supported by the Natural Science Foundation of China (grant no.200603018).
Author to whom correspondence should be addressed. e-mail: yuyfeng@163.com

DOI: 10.1111/j.1551-2916.2008.02291.x
© 2008 The American Ceramic Society
(curve d) with a red shift to 590 nm. This may be caused by two reasons. One reason is that N 2p hybridizing with O 2p leads to a decrease in band gap energy. Another reason is that Cu2⁺ partly replaces Ti4⁺ in TiO2 crystal lattice and copper oxide can absorb light with longer wavelength so that the absorption intensity is increased. The mechanisms need to be further clarified in more details.

(2) Structural Analysis of the Photocatalysts

The power XRD patterns of four samples are shown in Fig. 2. All the XRD patterns clearly show five main characteristic peaks of anatase phase structure of TiO2, namely, the planes (101), (004), (200), (105), and (211), at 2θ values of ca. 25.3°, 37.8°, 47.9°, 53.9°, and 55.2°, respectively, which all are in good accordance with (American Society for Testing and Materials, ASTM) standard no. 21-1272. It indicates that all the samples are principally single-phase structures. The lattice parameters of doped TiO2 samples, calculated using the (101) crystal face, are slightly smaller than those of undoped TiO2, indicating that nitrogen and copper are doped into TiO2. The average particle sizes of pure, N-doped, Cu-doped and (Cu, N)-codoped TiO2 are 7.0, 6.4, 6.1, 4.9 nm, respectively, as estimated using Scherrer’s equation. It implies that the doping might inhibit the growth of TiO2 crystallites.

(3) XPS Studies

In order to verify the doping of N and Cu species into nanosized TiO2, XPS measurements were conducted. Figure 3 shows the XPS spectra of pure and (Cu, N)-codoped TiO2. There are three main peaks for pure TiO2. The first two peaks located at ca. 460.0 and 474.5 eV can be assigned as the Ti 2p3/2 and Ti 2p1/2 of TiO2. Another peak at 530.3 eV is attributable to O 1s. For the (Cu, N)-codoped TiO2 sample, three additional peaks were observed. Two peaks located at 950.6 and 931.4 eV can be assigned as the Cu 2p3/2 and Cu 2p1/2, and the weak peak at 397.2 eV can be ascribed to N 1s. Obviously, the XPS results clearly proved that the N and Cu species have been doped into TiO2.

(4) Evaluation of Photocatalytic Activity

Based on the good absorption ability of the (Cu, N)-codoped TiO2 in the visible light region, xylenol orange degradation was used to determine the photocatalytic activity of the (Cu, N)-codoped TiO2 sample. The doping quantity of the elements usually has a significant influence on the photocatalytic activity of TiO2. Efforts to this end, we first optimize the amount of N and Cu doped into TiO2. Figure 4 shows the effects of doping amount of N and Cu on the photocatalytic degradation of xylenol orange. Clearly, the optimized weight percent of N for the N-doped TiO2 is ca. 0.6 wt% in curve (a). Enhanced photocatalytic activity of N-doped TiO2 could be due to a narrowed band gap derived from the mixing of N 2p and O 2p.
states. By fixing N content at 0.6 wt%, the effect of Cu doping amount within (Cu, N)-codoped TiO₂ on its photocatalytic activity is given in curve (b) of Fig. 4. The highest photocatalytic activity was obtained with a Cu content of 0.8 wt%, Cu²⁺ could inhibit the recombination between photogenerated electrons and holes by capturing the photogenerated electrons with the increase in Cu content doped into TiO₂,¹⁸,¹⁹ thus leading to an enhanced photocatalytic efficiency. However, when the Cu content exceeded 0.8 wt%, Cu species became the recombination center of photogenerated electrons and holes, resulting in a decreased photocatalytic activity. This explanation is in agreement with previously published papers.²⁰,²¹

Figure 5 shows a comparison of xylenol orange degradation ratio with time on four photocatalysts. The xylenol orange degradation ratios after 40 min irradiation on pure, N-doped, Cu-doped and (Cu, N)-codoped TiO₂ samples were 10%, 19%, 45% and 51%, respectively, clearly indicating that the doping significantly enhances the photocatalytic activity of TiO₂. Among four samples, the (Cu, N)-codoped TiO₂ sample exhibited the highest photocatalytic activity, which could be due to the synergistic effects of nitrogen and copper codoped into TiO₂. As discussed above, the codoping of both N and Cu resulted in a narrowed band gap and a red shift of absorption edge of TiO₂. Upon irradiating, more holes and active radicals are created on the codoped sample. As a result, the photocatalytic activity is enhanced greatly.

IV. Conclusions

The (Cu, N)-codoped TiO₂ nanoparticles were firstly synthesized by a simple sol-gel method. The absorption edge of the (N, Cu)-codoped TiO₂ has been extended to the visible light region at ca. 590 nm. The photocatalytic degradation experiments of xylenol orange proved that (Cu, N)-codoped TiO₂ nanoparticles have a higher photocatalytic activity than pure, N- and Cu-doped TiO₂, thus showing the potential applications for the degradation of organic pollutants.

References