Preparation, characterization and photocatalytic performance of Co/Ni Co-doped TiO₂ nanopowders

L. C. Zhang · K. F. Cai · X. Yao

Abstract Co/Ni co-doped TiO₂ nanopowders (dopant amount varying from 0 to 0.75 mol.% Co/0.75 mol.% Ni) were prepared by sol-gel method. The nanopowders were characterized by means of X-ray diffraction and transmission electron microscopy, respectively. The results showed that the structure of all the powders was anatase and that the particle size of the powders was in the range of 40–50 nm. The photocatalytic performances of the nanopowders were studied by examining the degradation of methyl orange. The results showed that the dopant amount was a key factor affecting photocatalytic performance. 0.05 mol.% Co/ 0.05 mol.% Ni co-doped TiO₂ nanopowders had the best photocatalytic performance, and the photocatalytic performance of which was also better than that of 0.1 mol.% Co- or 0.1 mol.% Ni-doped TiO₂ nanopowders.

Keywords Titanium dioxide · Photocatalyst · Sol-gel · Doping

1 Introduction

Titanium dioxide (TiO₂) is a wide-band semiconductor with band gap energy of about 3 eV. Irradiation of TiO₂ with UV light can activate electrons from valence band to conduction band, which results in its strong oxidizability. The photoactivity of many metal oxides has been studied, and TiO₂ has the highest photoactive oxidation rate [1–5].

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Moreover, TiO₂ exhibits some other attractive characteristics, such as chemical stability, nontoxicity, and low cost. All these make TiO₂ be a promising and extensively studied photocatalyst. However, pure TiO₂ requires near-UV light to photoactivate its photocatalytic capability, and its photocatalytic performance is not good enough.

The basic principle of the photocatalytic reaction of TiO₂ is: when the TiO₂ is irradiated by light whose energy is equal to or higher than the band gap energy of the TiO₂, e^- in the conduction band and h^+ in the valence band are generated as the electrons transfer from the valence band to the conduction band, which can be described as follows:

$$TiO_2 + h\upsilon \rightarrow TiO_2 + e^- + h^+$$
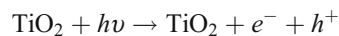
The valence band holes are powerful oxidants (+1.0 to +3.5 V vs. normal hydrogen electrode (NHE), depending on the semiconductor and pH value), while the conduction band electrons are good reductants (+0.5 to −1.5 V vs. NHE) [6]. So molecules or some groups of the molecules that contact with the photocatalyst can be oxidized or reduced, and the molecules are finally degraded. Creation and recombination of the electron-hole pairs are two reverse processes that determine the catalytic performance. As a suitable scavenger or surface defect state is available to trap the electrons or holes, it will prevent the electrons and holes from recombination and subsequent redox reactions take place. In order to slow down the recombination rate of the electron-hole pairs and enhance interfacial charge-transfer efficiency, the properties of TiO₂ particles have been modified by selective surface treatments such as surface chelation, surface derivatization, platinization, or doping TiO₂ with selective metal ions [7–10]. In recent years, much attention has been paid to enhance the performance of TiO₂ by doping metal ions.
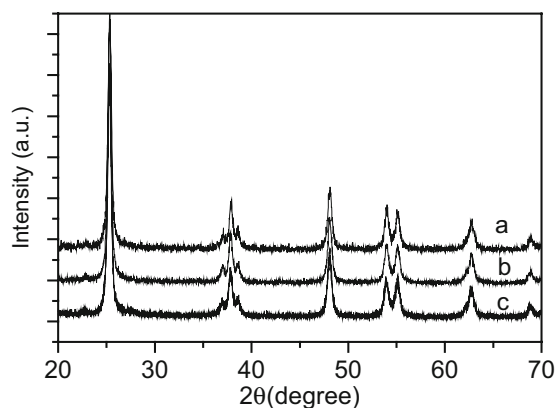
Fig. 1 XRD patterns of the powders (*a*) pure TiO_2 (*b*) 0.05 mol.% Co/0.05 mol.% Ni co-doped TiO_2, (*c*) 0.75 mol.% Co/0.75 mol.% Ni co-doped TiO_2

Most reported work, however, focused on doping one kind of metal ion into TiO_2 [11–15]. In this paper, we co-dope Co/Ni into TiO_2 via sol-gel process and investigate the influence of the dopant concentration on photocatalytic performance of TiO_2. The photocatalytic performance of the Co/Ni co-doped powders is investigated by measuring the degradation of methyl orange. Co- or Ni-doped TiO_2 nanopowders are also prepared and their photocatalytic performance is also studied for comparison.

2 Experimental procedure

All the starting materials were reagent grade and were used without further purification.

In a typical experiment, 17 ml of $Ti(OC_4H_9)_4$ was dispersed in 40 ml anhydrous ethanol by magnetic stirring for 10 min to produce solution A. Appropriate amount of $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ ($CoCl_2 \cdot 6H_2O/NiCl_2 \cdot 6H_2O=$ 1:1 molar ratio) were dissolved into appropriate amount of deionized water to prepare solution B. 10 ml acetic acid and 40 ml anhydrous ethanol were added into solution B with stirring to produce solution C. Solution A was dropped into solution C with vigorous stirring at room temperature. The solution was further stirred for about 30 min after dropping. The resultant sol was dried at 100 °C in an oven to get xerogel. The xerogel was ground and then calcined at 500 °C in air for 2 h.

Put 0.5 g of the TiO_2 powders with different doping concentrations into 6×10^{-5} mol/l methyl orange aqueous solutions and stirred for 5 min to ensure equilibration of methyl orange over the oxide surface. Then the methyl orange aqueous solutions were irradiated by the 365 nm UV light for 30, 60, 90 and 120 min, respectively. After irradiation the solution was centrifuged to remove all the catalyst. The light absorption of methyl orange solution was

quantified by UV-Vis Spectrophotometer (V-570, Jasco). Degradation rate of the methyl orange was calculated by the equation: $D = [(A_0 - A)/A_0] \times 100\%$, ($A_0$ is the light absorption of methyl orange solution at 465 nm wavelength, and A is the light absorption of methyl orange solution at the maximum absorption wavelength measured by the UV-Vis Spectrophotometer).

X-ray diffraction (XRD) patterns of the powders were obtained with a diffractometer (Brucker D8 advance), using CuK_α radiation. A JEM-1230 transmission electron microscopy (TEM) was used to observe the morphology of the powders.

3 Results and discussion

Figure 1 shows XRD patterns of pure TiO_2, 0.05 mol.% Co/0.05 mol.% Ni doped TiO_2, and 0.75 mol.% Co/ 0.75 mol.% Ni doped TiO_2 powders. All the peaks in the XRD patterns correspond to the reported data of anatase (JCPDS card file, No. 04-0477, lattice constants $a=$ 3.783 Å, $c=9.51$ Å). The crystal lattice constants of all the three samples are almost the same. As we know, there are three different phase structures of TiO_2: anatase, rutile and brookite. A lot of researches have proved that among these three phase structures, TiO_2 with anatase structure has the best photocatalytic properties. The average grain size calculated from the broadening of the (101) peak using Scherrer's equation is about 51 nm. Because the radius of Co^{2+} and Ni^{2+} (Co^{2+} 0.078 nm, Ni^{2+} 0.076 nm) is close to that of Ti^{4+} (0.068 nm), according to Pauling's principle, it is easy for Co^{2+} or Ni^{2+} ion to incorporate into the matrix of the TiO_2 without causing much crystalline distortion.

Figure 2 is a TEM image of 0.05 mol.% Co/0.05 mol.% Ni co-doped TiO_2 nanopowders. It can be seen from Fig. 2
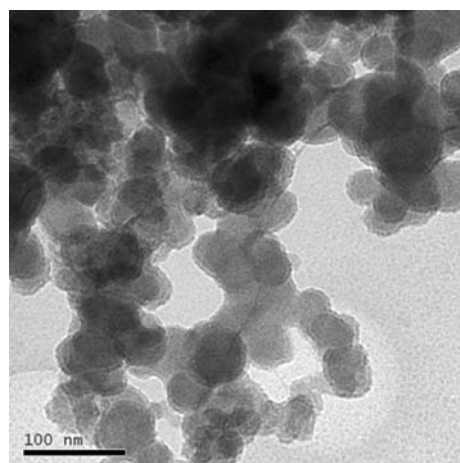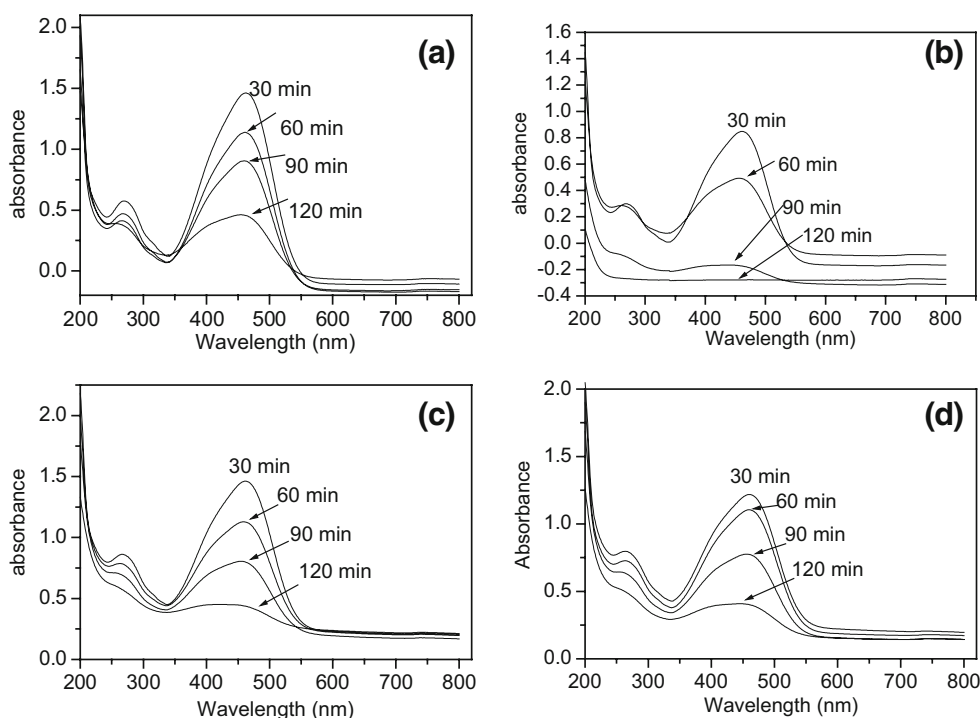

Fig. 2 TEM image of the 0.05 mol.% Co/0.05 mol.% Ni co-doped TiO_2 powders

that the average particle size of the powders is about 40–50 nm, which is in good agreement with the XRD results. Other powders have similar grain sizes known from TEM observation (TEM images for other powders are not shown here).

Figure 3(a), (b), (c) and (d) are, respectively, UV-Vis absorption spectra of methyl orange photocatalyzed by pure TiO$_2$, 0.05 mol.% Co/0.05 mol.% Ni co-doped TiO$_2$, 0.1 mol.% Co-doped TiO$_2$, and 0.1 mol.% Ni-doped TiO$_2$ powders for 30, 60, 90 and 120 min. It can be seen from Fig. 3 that the photocatalytic performance of TiO$_2$ can be improved by doping Co, Ni or Co/Ni, and that the 0.05 mol.% Co/0.05 mol.% Ni co-doped TiO$_2$ nanopowders have the best photocatalytic performance.

The influence of dopant concentration on degradation rate of methyl orange was evaluated and the results are shown in Fig. 4. It can be seen from Fig. 4 that doping concentration has a significant effect on the photocatalytic performance of TiO$_2$. There exists an optimum doping concentration at around 0.05 mol.% Co/0.05 mol.% Ni. This phenomenon can be explained as follows: as the dopant concentration increases, the surface barrier becomes higher and the space charge region becomes narrower, and the electron-hole pairs within the region are efficiently separated by the large electric field before recombination. On the other hand, when the dopant concentration is too high, the space charge region becomes very narrow and the penetration depth of light into TiO$_2$ greatly exceeds the space charge layer [16], therefore the recombination of the photo-

generated electron-hole pairs in semiconductor becomes easier. Consequently, there is an optimum dopant concentration to make the thickness of space charge layer substantially equal to the light penetration depth.

As TiO$_2$ is doped with Co, or Ni, an impurity energy level forms within the band gap, above yet very close to the top of the valence band, which increases the concentration of holes. Therefore, the photocatalytic performance of TiO$_2$ has been improved by doping Co or Ni. As co-doped with Co/Ni, the impurity energy levels introduced by Co and Ni may overlap to some extent to form an impurity energy band, which probably prevents the electrons and holes from recombination, therefore the 0.05 mol.% Co/0.05 mol.% Ni
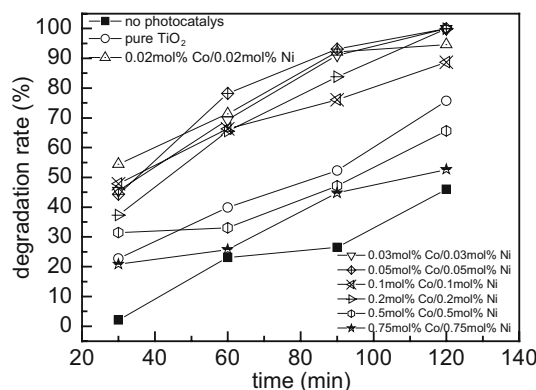

Fig. 4 Degradation rate of methyl orange catalyzed by TiO$_2$ doped with different amount of Co/Ni

co-doped TiO$_2$ nanopowders have better photocatalytic performance than 0.1 mol.% Co- or 0.1 mol.% Ni-doped TiO$_2$ nanopowders.

4 Conclusions

Co/Ni co-doped TiO$_2$ with anatase phase structure can be prepared with sol-gel method followed by an appropriate calcination treatment. Photocatalytic performance investigation shows that lower doping concentration enhances the photocatalytic performance of TiO$_2$, while higher doping concentration decreases its photocatalytic performance. The optimum doping concentration is about 0.05 mol.% Co/ 0.05 mol.% Ni. The 0.05 mol.% Co/0.05 mol.% Ni co-doped TiO$_2$ nanopowders have better photocatalytic performance than 0.1 mol.% Co- or 0.1 mol.% Ni-doped TiO$_2$ nanopowders.

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