Nitrogen-doped titania photocatalysts induced by shock wave

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1. Introduction

It is well known that titania is widely applied in the purification of air and water by photocatalysis, solar energy conversion device, etc. as a most effective photo-functional material [1,2]. But since the band gap of TiO_2 is large (E_g = 3.2 eV), it is only active in the ultraviolet region, which is 3–5% of the overall solar intensity. Therefore, it is much more important to enhance the visible light activity of the TiO_2 photocatalyst. For this reason, many modifications have been made on TiO_2 matrix by doping with metal ions [3] or non-metal ions [4]. Anpo et al. [5] used ion implantation to dope a series of transition metals, such as V, Cr and Ni into TiO_2 films with the band gaps shifting to visible light region. Zhao et al. [6] prepared a V/TiO_2 film and found that the increase of doping amount of vanadium resulted in further redshift in UV–vis region. In 2001, Asahi et al. [7,8] reported that nitrogen-doped titanium oxide with high visible light photocatalytic activities could be prepared by sputtering a TiO_2 target in N_2 (40%)/Ar gas mixture followed by annealing in N_2 gas at 550 °C or by treating anatase TiO_2 powder in NH_3 (67%)/Ar atmosphere at 600 °C. Irie et al. [9] prepared TiO_2-N_x with different nitrogen concentrations in NH_3 atmosphere at 550–600 °C. They also prepared C-doped TiO_2 by oxidative annealing of TiC in air/O_2 at 600 °C for 5 h [10]. Umebayashi et al. prepared S-doped titania by oxidation annealing of TiS_2 in air at 500–600 °C [11,12].

Shock wave action of high temperature, high pressure and high strain rate lasting for very short time (~10^{-6} s) will cause a series of catastrophic changes of chemical and physical properties of materials [13]. So the shock doping combined with shock-induced chemical reaction and phase transition under shock wave action may be a new method to improve the activity of the TiO_2 photocatalyst. Yakovyna et al. [14] found that the photoelectric properties of Hg_{1-x}Cd_xTe semiconductor can be greatly changed under shock wave action induced by laser. Furthermore, a high-dispersed Al_2O_3-doped Cr^3+ with the same optical property of ruby was obtained by treating the mixtures of aluminum powder and ammonium chromate under shock wave action [15]. But at present, there has been no report on the doping semiconductor-photocatalyst by shock wave loading.

In this study, the steel flyer plate was driven by the detonation of nitromethane (CH_3NO_2), in order to produce high temperature and high pressure to complete shock-induced nitrogen-doped titania. Under shock action, the organic dopant containing nitrogen can be decomposed and diffused into the lattice of TiO_2 narrowing its energy gap. The structures and photocatalytic activities of the doped TiO_2 were characterized and evaluated, respectively.

2. Experimental

2.1. Shock loading apparatus

P25 TiO_2 (Degussa Co., Germany) was chosen as a precursor, as it is a standard photocatalyst used in the world and has well-known structure and photocatalytic data. Hexamethylene...
tetramine (HMT, C₆N₄H₁₂) and dicyandiamide (DCD, C₂N₄H₄) were used as doping nitrogen resources. The sample was the mixture of P25 TiO₂ and doping nitrogen resources in a mass ratio of 9:1. The experimental conditions are shown in Table 1. The scheme of shock-loading apparatus is shown in Fig. 1. The steel flyer impacted the container above the liquid level. Aqueous suspensions of rhodamine B (RB) dye (100 mL, with an initial concentration of 1.0 × 10⁻⁶ M) and photocatalyst powder (50 mg) were placed in a beaker (250 mL). Prior to irradiation, the suspensions were magnetically stirred for 10 min under dark condition to establish an adsorption/desorption equilibrium between dye and photocatalyst surface. Under stirring, aliquots of a small amount of suspension (about 4 mL) was taken out at every 10 min under visible light irradiations, then centrifuged and analyzed using a 721 spectrophotometer (made in China).

\begin{table}[h]
\centering
\caption{The experimental conditions.}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
No. & Sample type & Initial density ρ₀ (g/cm³) & ρ₀/ρ₀ (%) & Impact velocity (km/s) & First shock pressure (GPa) & Peak pressure (GPa) & Shock temperature (K) & Sample colors & Phase composition of TiO₂
\hline
\hline
bit-1 & A & 2.38 & 73 & 2.25 & 21 & 56 & 2941 & Grey & 83.0 17.0
\hline
bit-2 & A & 2.51 & 77 & 1.20 & 8 & 26 & 1449 & Grey & 84.6 15.4
\hline
bit-3 & B & 2.29 & 68 & 2.25 & 25 & 56 & 2853 & Grey & 82.6 17.4
\hline
bit-4 & B & 2.10 & 63 & 1.20 & 8.5 & 26 & 1709 & Grey & 83.7 16.3
\hline
\end{tabular}
\end{table}

\textsuperscript{1} A: P25TiO₂ + HMT; B: P25TiO₂ + DCD.

2.3. Evaluation of photocatalytic activity

A 500-W Xe lamp was used as the light source and the visible wavelength was controlled through a 420-nm cut filter (LF420, China), which was hanged in a dark box and kept at about 15 cm above the liquid level. Aqueous suspensions of rhodamine B (RB) dye (100 mL, with an initial concentration of 1.0 × 10⁻⁶ M) and photocatalyst powder (50 mg) were placed in a beaker (250 mL). Prior to irradiation, the suspensions were magnetically stirred for 10 min under dark condition to establish an adsorption/desorption equilibrium between dye and photocatalyst surface. Under stirring, aliquots of a small amount of suspension (about 4 mL) was taken out at every 10 min under visible light irradiations, then centrifuged and analyzed using a 721 spectrophotometer (made in China).

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the samples doped by HMT at different shock pressures are shown in Fig. 2. It is found that the odor of ammonia could be smelled when the sample container was opened by lathing. It indicates that the dopant of HMT has already decomposed under shock action. But there was also the undecomposed HMT in the sample as shown in Fig. 2. By carefully analyzing the diffraction pattern, we can get the phase content of anatase and rutile according to the calculation equations reported by Liu et al. [17] as listed in Table 1. It can be seen that a little anatase transform to rutile under shock action and increase with increasing flyer velocity at higher shock temperature. But the conversion is very low that indicates the rutile and anatase phases of P25 TiO₂ are basically stable at present conditions.

The XRD patterns of the samples doped by DCD at different shock pressures are shown in Fig. 3. Compared with the starting dopant of DCD (Fig. 3(d)), there are some diffraction peaks appeared in the doped samples which should be attributed to the undecomposed DCD. The intensity of diffraction peaks of the undecomposed DCD decreased with increasing shock pressure and temperature. It indicates the DCD dopant is unstable and partially decomposed.

It is well known that the both of anatase and rutile are tetragonal system with the unit cell of a ≠ b ≠ c, α = β = γ = 90°. So a and c of the unit cell of TiO₂ can be calculated from the data of XRD spectra (Figs. 2 and 3) containing crystal spacing (d values) and crystal plane (h k l) according to Eq. (1) as shown in Table 2.

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]  

Compared with the unshocked P25 precursor, all the a and c axis of anatase and rutile prolongs a little after shock loading that...
indicates the N\textsuperscript{3−} ions (1.46 Å) with a larger ionic radius than the O\textsuperscript{2−} ions (1.40 Å) were substituted into the TiO\textsubscript{2} lattice and led to the expansion of the TiO\textsubscript{2} lattice constant [18]. However, the reduction of unit cell axis is along with increasing flyer velocity, suggesting that the contraction of the TiO\textsubscript{2} lattice to some extent originated from shock compression occurred under even more intense shock loading [19]. Besides, the changes of \(a\) and \(c\) axis of rutile is independent of dopant type and flyer velocity because rutile is a thermodynamic stable phase with high density \(\rho_0 = 4.28\, \text{g/cm}^3\) and not easier to be doped and compressed than the metastable anatase with low density \(\rho_0 = 3.92\, \text{g/cm}^3\) under the same shock conditions.

### 3.2. UV–vis spectra

Fig. 4 shows the UV–vis spectra of doped and undoped TiO\textsubscript{2}. It can be seen clearly that all the four samples of doped TiO\textsubscript{2} by shock wave have exhibited obvious red shifts to the absorption edge of about 450 nm compared with that of 400 nm of unshocked P25 TiO\textsubscript{2}. Furthermore, the doped samples by shock wave exhibited strong absorption tails above 450 nm, which cover the whole visible light region, corresponding to the color changes from white to grey as given in Table 1 after recovery. By comparison, the sample bit-3 (Fig. 4(c)) with the dopant of C\textsubscript{2}N\textsubscript{4}H\textsubscript{4} shows the most strongest second absorption, it may be explained by that it possesses more nitrogen content in the per molecular unit because the diffusion of N species decomposed by DCD into the lattice of TiO\textsubscript{2} was accelerated to achieve higher N doping concentration under higher shock pressure and temperature that can be confirmed by the following XPS characterizations. These results indicate that the shock doping is a new and effective method to get doped TiO\textsubscript{2} photocatalyst responding to visible light.

### 3.3. XPS studies

The XPS spectra for samples of bit-3 and bit-4 has been measured, as shown in Fig. 5. The N 1s peaks of binding energy around 400 eV appear clearly which can be attributed to several N bonds including O–Ti–N, TiN, NO\textsubscript{x} which may narrow the energy gap of TiO\textsubscript{2} by replacement or interstitial substitution for O atom [20]. The nitrogen atom contents in the samples of bit-3 and bit-4...
are 31.6% and 26.5% (at.%) calculated from the XPS survey spectra. With increasing flyer velocity, the nitrogen content increases, it indicates that high flyer velocity leads to high shock pressure and temperature (Table 1) which promotes the decomposition of dopant C2N4H4 to entering the lattice of TiO2 by the diffusion of N species enforced by shock wave for doping.

3.4. Photocatalytic activity

It is clearly seen from Fig. 6 that the undoped P25 TiO2 has no photocatalytic activity under visible light irradiation as it only absorbs the ultraviolet light (< 400 nm). But the samples of bit-3 and bit-4 doped by shock wave exhibit obvious photocatalytic degradation activity under visible light irradiation and the photocatalytic degradation activity increases with increasing the flyer velocity. It can be explained by that the higher flyer velocity leads to higher shock pressure and temperature (Table 1) that leads to getting the samples with high doping concentration of N atom in TiO2 and broadening the response to visible light as shown in Fig. 4. At last, the photocatalytic activity of sample bit-4 is effectively improved.

4. Conclusions

The nitrogen-doped TiO2 photocatalysts response to visible light can be obtained by shock-induced chemical reaction of dopant containing nitrogen of hexamethylene tetramine and dicyandiamide. The absorption edges of the nitrogen-doped TiO2 photocatalysts by shock wave are extended to 450 nm. The photocatalytic activity of the samples doped with the dicyandiamide increases with increasing the flyer velocity. The present experimental results suggest that the shock doping is a new and effective method to get TiO2 photocatalyst responding to visible light.

References