



Nitrogen-doped titania photocatalysts induced by shock wave

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ABSTRACT

The nitrogen-doped titania photocatalysts were prepared by shock wave with detonation-driven flyer impact. The samples were shocked at different flyer impact velocities and recovered successfully. The phase composition, light absorption spectra and N doping status of the recovered samples with different flyer velocities and two nitrogen resources containing hexamethylene tetramine (HMT) and dicyandiamide, respectively, were characterized. The absorption edge of the N-doped TiO₂ photocatalysts by shock wave was extended to 450 nm corresponding to visible light region. The photocatalytic degradation to rhodamine B of the samples doped with dicyandiamide increased with increasing flyer velocity due to the higher N doping concentration and wider response to visible light.

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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 TiO₂ 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 TiO₂ photocatalyst. For this reason, many modifications have been made on TiO₂ 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 TiO₂ films with the band gaps shifting to visible light region. Zhao et al. [6] prepared a V/TiO₂ 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 TiO₂ target in N₂ (40%)/Ar gas mixture followed by annealing in N₂ gas at 550 °C or by treating anatase TiO₂ powder in NH₃ (67%)/Ar atmosphere at 600 °C. Irie et al. [9] prepared TiO_{2-x}N_x with different nitrogen concentrations in NH₃ atmosphere at 550–600 °C. They also prepared C-doped TiO₂ by oxidative annealing of TiC in air/O₂ at 600 °C for 5 h [10]. Umabayashi et al. prepared S-doped titania by oxidation annealing of TiS₂ 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 ($\sim 10^{-6}$ 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 TiO₂ 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 Al₂O₃-doped Cr³⁺ 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 (CH₃NO₂), 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 TiO₂ narrowing its energy gap. The structures and photocatalytic activities of the doped TiO₂ were characterized and evaluated, respectively.

2. Experimental

2.1. Shock loading apparatus

P25 TiO₂ (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

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Table 1
The experimental conditions.

| No. | Sample type ^a | Initial density ρ_{00} (g/cm ³) | ρ_{00}/ρ_0 (%) | Impact velocity (km/s) | First shock pressure (GPa) | Peak pressure (GPa) | Shock temperature (K) | Sample colors | Phase composition of TiO ₂ | |
|-------|--------------------------|--|------------------------|------------------------|----------------------------|---------------------|-----------------------|---------------|---------------------------------------|------------|
| | | | | | | | | | Anatase (%) | Rutile (%) |
| P25 | TiO ₂ | – | – | – | – | – | – | White | 85.3 | 14.7 |
| bit-1 | A | 2.38 | 73 | 2.25 | 21 | 56 | 2941 | Grey | 83.0 | 17.0 |
| bit-2 | A | 2.51 | 77 | 1.20 | 8 | 26 | 1449 | Grey | 84.6 | 15.4 |
| bit-3 | B | 2.29 | 68 | 2.25 | 25 | 56 | 2853 | Grey | 82.6 | 17.4 |
| bit-4 | B | 2.10 | 63 | 1.20 | 8.5 | 26 | 1709 | Grey | 83.7 | 16.3 |

^a A: P25TiO₂ + HMT; B: P25TiO₂ + DCD.

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 was propelled to a high velocity ranging from 1 to 3 km/s depending on the flyer thickness and the height of main charge by detonation of the main charge of nitromethane (CH₃NO₂), initiated by booster charge of 8701 explosive. The steel flyer impacted the container with the samples subjecting to shock wave compression. The approximate calculation on the shock pressure and temperature in Table 1 can be described elsewhere in detail [16].

2.2. Characterization of photocatalyst

The phase composition of the products was determined on an X-ray diffractometer (XRD) (Rigaku D/MAX-2500) using Cu K α radiation ($\lambda = 0.15406$ nm) at 40 kV work voltage and 200 mA work current. The light absorption spectra of the products were determined using a UV–vis diffuse reflectance spectrophotometer

(Shimadzu UV–vis 250 IPC). Nitrogen doping was analyzed by X-ray photoelectron spectrometry (XPS) (Thermo ESCA LAB 250).

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^{-4} 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 $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$. 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 (hkl) according to Eq. (1) as shown in Table 2

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Compared with the unshocked P25 precursor, all the a and c axis of anatase and rutile prolongs a little after shock loading that

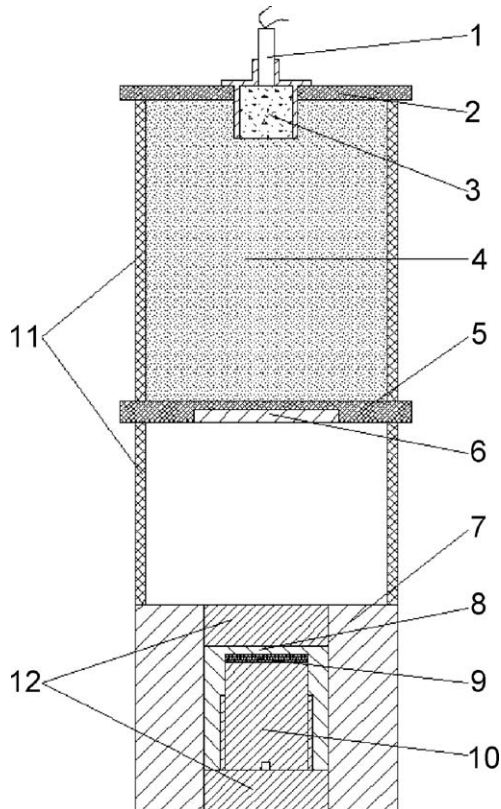


Fig. 1. Scheme of shock-loading apparatus. (1) detonator; (2) upper cover; (3) booster charge; (4) nitromethane; (5) bottom cover; (6) flyer; (7) steel protection tube; (8) copper sample container; (9) sample; (10) copper screw lid; (11) PVC plastic tube; (12) steel momentum block.

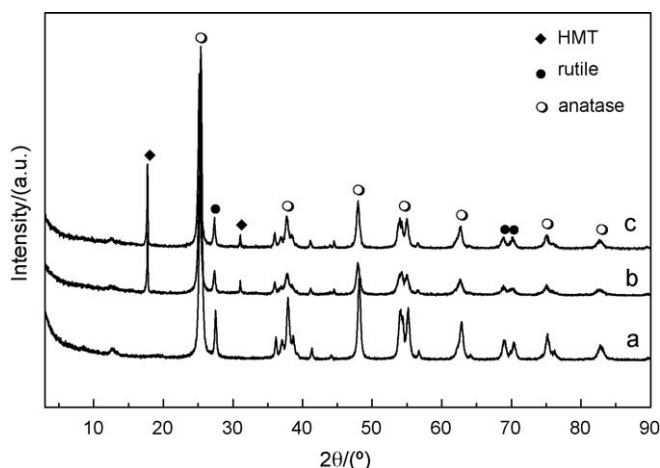


Fig. 2. XRD patterns of the unshocked P25 TiO₂ (a), bit-1 (b) and bit-2 (c).

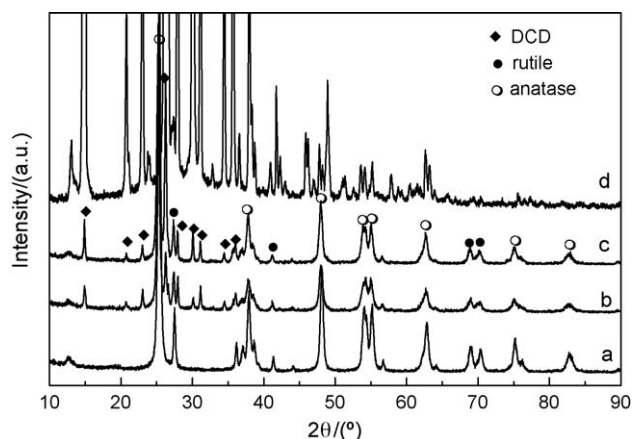


Fig. 3. XRD patterns of the unshocked P25 TiO₂ (a), bit-3 (b), bit-4 (c) and DCD (d).

indicates the N³⁻ ions (1.46 Å) with a larger ionic radius than the O²⁻ ions (1.40 Å) were substituted into the TiO₂ lattice and led to the expansion of the TiO₂ lattice constant [18]. However, the reduction of unit cell axis is along with increasing flyer velocity, suggesting that the contraction of the TiO₂ 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.

Table 2
Changes of unit cell parameters of anatase and rutile after shock loading.

| No. | Sample type ^a | Impact velocity (km/s) | Unit cell parameter (Å) | | | |
|-------|--------------------------|------------------------|-------------------------|----------|----------|----------|
| | | | Anatase | | Rutile | |
| | | | <i>a</i> | <i>c</i> | <i>a</i> | <i>c</i> |
| P25 | TiO ₂ | – | 3.77 | 9.48 | 4.58 | 3.03 |
| bit-1 | A | 2.25 | 3.80 | 9.51 | 4.61 | 3.02 |
| bit-2 | A | 1.20 | 3.81 | 9.53 | 4.61 | 3.02 |
| bit-3 | B | 2.25 | 3.79 | 9.50 | 4.59 | 3.02 |
| bit-4 | B | 1.20 | 3.80 | 9.52 | 4.61 | 3.02 |

^a A: P25TiO₂ + HMT; B: P25TiO₂ + DCD.

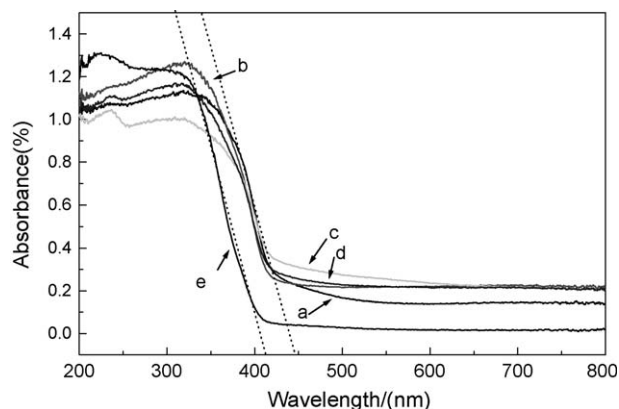


Fig. 4. UV–vis spectra of the samples of bit-1 (a), bit-2 (b), bit-3 (c), bit-4 (d) and unshocked P25 TiO₂ (e).

3.2. UV–vis spectra

Fig. 4 shows the UV–vis spectra of doped and undoped TiO₂. It can be seen clearly that all the four samples of doped TiO₂ 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 TiO₂. 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 C₂N₄H₄ 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 TiO₂ 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 TiO₂ 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_x which may narrow the energy gap of TiO₂ by replacement or interstitial substitution for O atom [20]. The nitrogen atom contents in the samples of bit-3 and bit-4

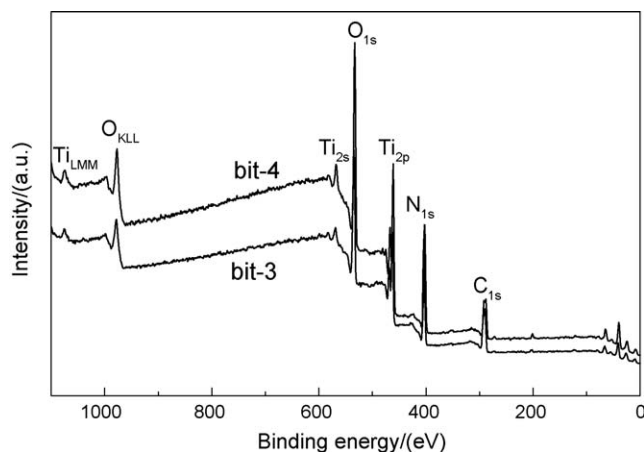


Fig. 5. XPS spectra of the samples of bit-3 and bit-4.

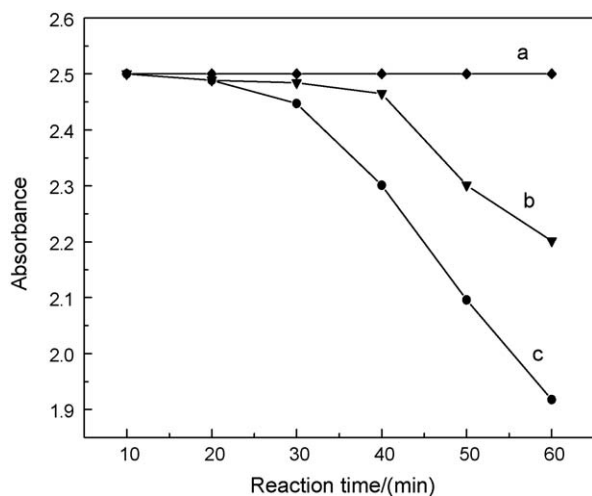


Fig. 6. Photocatalytic degradation curves of rhodamine B on different photocatalyst samples: (a) undoped P25 TiO₂; (b) bit-4; (c) bit-3.

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.

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