



Enhanced visible-light absorption of nitrogen-doped titania induced by shock wave

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ABSTRACT

This paper presents a new method to prepare nitrogen-doped titania by detonation-driven flyer impact. The samples were shocked at different flyer impact velocities and recovered successfully. XRD, UV–Vis and XPS spectra were employed to characterize the phase composition, N doping concentration and energy gap of recovered samples. The results show that anatase transforms to rutile and srilankite appears at a higher flyer velocity (1.9–2.52 km/s), and the concentration of doped nitrogen in the recovered samples increases with increasing flyer velocity, while the maximum concentration of nitrogen is 13.45 at.%. The edge adsorption wavelength of nitrogen-doped titania induced by shock wave is shifted from 435 nm to 730 nm and the corresponding energy gap is reduced from 2.85 eV to 1.73 eV. High concentration nitrogen-doped titania is achieved by lattice displacement–atomic exchange mechanism during the formation of srilankite high-pressure phase induced by shock wave.

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1. Introduction

It is well known that titania is widely applied in the environmental remediation and solar energy conversion [1], as a most effective photo functional material. But the main drawback of TiO₂ for photocatalysis is that its band gap is rather large (3.0–3.2 eV), and thus it is only active in the ultraviolet region ($\lambda < 380$ nm) accounting for less than 5% of the total sunlight. Therefore, a large effort has been made to prepare nitrogen-doped TiO₂ with the photocatalytic activity in the visible-light region [2]. In present, nitrogen-doped TiO₂ with the enhanced visible-light absorption has been successfully prepared by different methods including the hydrolysis of titanium precursors in the presence of thiourea, thioacetamide and NH₄OH followed by calcinations [3], gas-phase thin film deposition method [4], atmospheric pressure plasma-enhanced nano-particle synthesis (APPENS) [5], treating anatase in NH₃/Ar atmosphere and sputtering the TiO₂ target in N₂/Ar gas mixture [6]. But present several doping methods are hard to greatly enhance the absorbance of TiO₂ in the visible region and achieve high N-doping concentration. Now the maximum concentration of nitrogen is only 8 at.% by direct amination for nanosized titania particles of 6–10 nm [7].

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 [8]. Under shock wave action, the organic dopant can be decomposed and diffused into the lattice of TiO₂, so the shock doping combined

with shock-induced chemical reaction and phase transition may be a new method to extend the absorption edge into visible light and enhance the photocatalytic activity of TiO₂. Yakovyna et al. [9] 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 [10]. Thus far, there has been no report on the shock doping of TiO₂ semiconductor.

2. Experimental

The sample was the mixture of P25 TiO₂ and doping nitrogen source of dicyandiamide (DCD, C₂N₄H₄) in a mass ratio of 9:1. Steel flyer was propelled by detonation of the main charge of nitromethane (CH₃NO₂), initiated by a booster charge of 8701 explosive to impact the container-enwrapped samples at high-flyer velocity subjecting to shock wave compression. The experimental conditions are shown in Table 1. The details of the approximate calculation on the shock pressure and temperature in Table 1 as well as the shock doping method and shock loading apparatus have been described in Ref. [11] and [12], respectively.

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 working voltage and 200 mA working current. Nitrogen doping was analyzed by X-ray photoelectron spectrometry (XPS) (Thermo ESCA LAB 250). The light absorption spectra of the products were determined using a UV–Vis diffuse reflectance spectrophotometer (Shimadzu UV–Vis 250 IPC).

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Table 1The experimental conditions, A: P25 + C₂N₄H₄ (10%), U: unshocked, S: shocked.

No.	Samples	Mass (g)	ρ_{00} (g/cm ³)	ρ_{00}/ρ_0 (%)	Impact velocity (km/s)	Shock pressure (GPa)	Shock temperature (K)	Edge adsorption wavelength (nm)	Energy gap (eV)	N1s (At.%)	Anatase (%)	Rutile (%)	Srilankite (%)
U	P25							400	3.1	0	85.3	14.7	0
S	P25	3.55	1.77	0.45	2.25	13.8	1809	440	2.82	0	43.0	49.2	7.8
1	A	3.46	1.63	0.49	1.2	4.5	724	435	2.85	3.67	81.9	18.1	0
2	A	2.37	1.59	0.47	1.9	9.5	1280	698	1.78	9.22	67.7	21.0	11.3
3	A	3.49	1.64	0.5	2.25	13.0	1809	710	1.75	11.28	50.7	27.5	21.8
4	A	3.49	1.61	0.48	2.52	15.5	2045	730	1.73	13.45	46.9	30.1	23.0

3. Results and discussion

The XRD patterns of shock-recovered A samples are shown in Fig. 1. The characteristic peaks of anatase, rutile and srilankite phases appeared before and after shock treatments, as marked by various symbols in Fig. 1. The phase contents can be calculated according to a formula given in Ref. [13], as listed in Table 1. It is found that the starting binary mixed phases of anatase and rutile transform to the ternary mixed phase of anatase, rutile and srilankite with increasing flyer velocity. Srilankite appeared at a higher flyer impacting velocity indicating that it is a metastable high-pressure phase.

X-ray photoelectron spectroscopy (XPS) was used to obtain semiquantitative data on chemical compositions of the doped titania with nitrogen. The peak intensity increased gradually with increasing flyer velocity, indicating that the concentration of nitrogen in the recovery samples increased. The nitrogen concentrations of four recovered samples were 3.67 at.%, 9.22 at.%, 11.28 at.% and 13.45 at.% respectively as given in Table 1. The N1s XPS spectra showed a very broad peak between 398 and 402 eV observing a regular shift to lower binding energy with increasing flyer velocity (Fig. 2). Usually, the assignment of doped N1s peaks in the XPS spectra can be classified into two categories, one of the peaks close to 400 eV is assigned to surface chemical adsorption of N₂, NO_x or NH₃ formed by decomposition and oxidation of the N precursors, making no contribution for reducing the energy gap of TiO₂ [14]; another one of the peaks between 396 eV and 399 eV is assigned to interstitial/substitutional N-doping and/or the formation of Ti–O–N species, reducing the energy gap of TiO₂ [15]. According to this, increasing flyer velocity can promote the decomposition of N precursor dicyandiamide under shock wave action and the chemical status of N atoms are changed from surface chemical adsorption to substitutional doping. According to the XRD and XPS analyses, only a small amount of anatase transferred to rutile at a flyer velocity of 1.2 km/s (Table 1). As shock pressure pulse duration (10^{−6} s) is shorter than shock-induced

temperature rising duration, this phase transition under lower shock pressure and temperature can be classified into shock-induced temperature–phase transition, according to non-equilibrium temperature–pressure phase-diagram of TiO₂ [16]. The nitrogen-doped concentration was only 3.67 at.% at a lower flyer impact velocity of 1.2 km/s. The nitrogen-doped mechanism at a lower flyer impact velocity can be attributed to the slower thermal diffusion mechanism of shock-induced temperature rising that is similar to common doping method by heating in gaseous or liquid media. At a higher flyer impact velocity, the shock pressure and temperature were much higher (Table 1), a large amount of anatase transferred to rutile and srilankite high-pressure phase. Anatase transferred to srilankite high-pressure phase by applying a moderate heating at higher pressure [17]. According to the non-equilibrium temperature–pressure phase-diagram of TiO₂ [16], metastable srilankite phase was formed by shock-induced temperature–phase transition and shock-induced pressure–phase transition. In most cases, there is no sufficient time for diffusion transition; thus, martensitic transformations are the most common under shock conditions [18]. The oxygen–titanium coordination was distortedly changed from 6:3 to 8:4 during the shock-induced pressure–phase transition and the higher oxygen coordination was attributed to the srilankite high-pressure phase [19]. The srilankite high-pressure phase is a short-range order in microsecond times under shock conditions and the oxygen–titanium coordination number varies from point to point [19]. Nitrogen species was formed by shock induced chemical reaction of dicyandiamide, as the radius of N^{3−} and O^{2−} anions are nearly the same, oxygen sites in the TiO₂ lattice are easily substituted by nitrogen atoms with increasing oxygen–titanium coordination number during the shock loading process [20]. Substitutional N-doping was achieved during the very short time of shock wave action eventually realizing high concentration of nitrogen doping and the maximum concentration of nitrogen was 13.45 at.%.

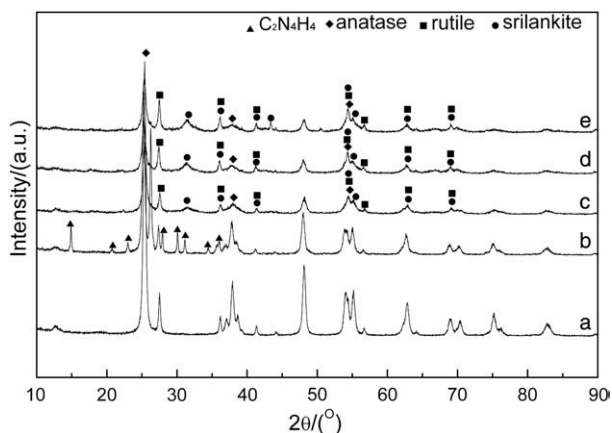


Fig. 1. XRD patterns of shock-recovered samples. Unshocked P25 TiO₂ (a), shock-recovered P25 + C₂N₄H₄ (10%) samples at 1.20 km/s (b), 1.90 km/s (c), 2.25 km/s (d) and 2.52 km/s (e).

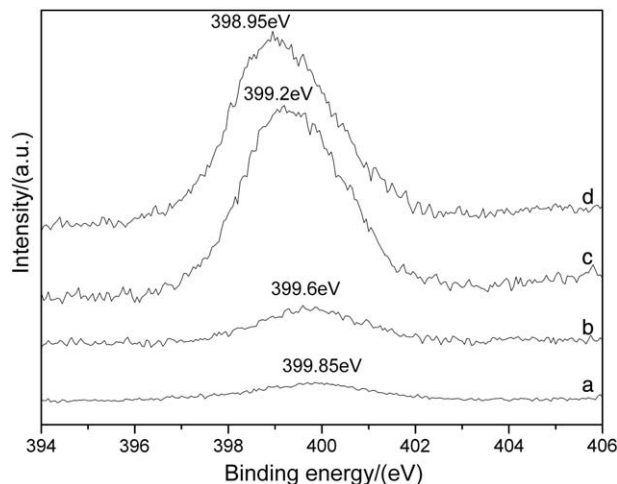


Fig. 2. XPS spectra of N for shock-recovered P25 + C₂N₄H₄ (10%) samples at 1.20 km/s (a), 1.90 km/s (b), 2.25 km/s (c) and 2.52 km/s (d).

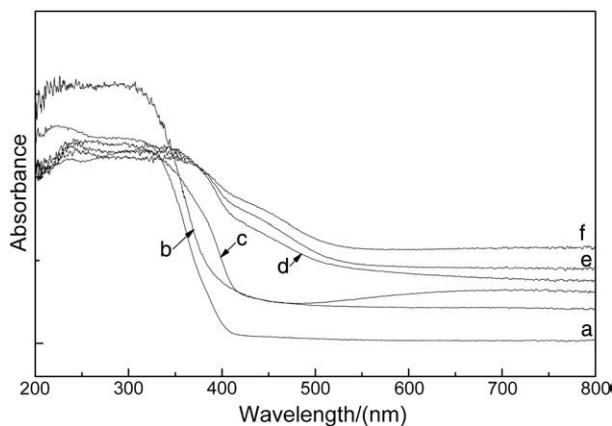


Fig. 3. UV-Vis spectra of shock-recovered samples. Unshocked P25 TiO₂ (a), shocked P25 TiO₂ at 2.25 km/s (b), shock-recovered P25 + C₂N₄H₄ (10%) samples at 1.20 km/s (c), 1.90 km/s (d), 2.25 km/s (e) and 2.52 km/s (f).

The UV-Vis diffusive reflectance spectra of unshocked P25 TiO₂ and shock-recovered P25 + C₂N₄H₄ (10%) samples were shown in Fig. 3. It can be seen clearly that the samples of doped TiO₂ by shock wave have exhibited obvious red shifts to the absorption edge of about 730 nm compared with that of 400 nm of unshocked P25 TiO₂. Furthermore, the horizontal adsorption of all the shock doping samples exhibited obvious enhancement in the whole visible-light region, corresponding to the color changes from white to gray black after shock treatment. It may be correlated with the defects, Ti³⁺ and color centers created by oxygen vacancy and dislocation under shock wave action [21]. Compared with shocked P25 TiO₂, the high concentration nitrogen-doped (9–14 at.%) TiO₂ by shock wave showed noticeable light absorption ability in the visible-light region (500 nm < λ < 800 nm) mainly due to the shock induced substitutional doping of N and the subsequent energy gap narrowing. Shock doping enhances the absorbance of TiO₂ in visible-light region much greater than the conventional methods.

4. Conclusions

In summary, high concentration N-doped TiO₂ was assembled by shock induced chemical reaction of nitrogen dopant dicyandiamide.

The nitrogen atoms exchange with matrix oxygen atoms of TiO₂ during the rapid shock induced pressure-phase transition process from anatase to srilankite high-pressure phase. The maximum concentration of nitrogen of doped TiO₂ by shock loading at 2.52 km/s is 13.45 at.% much higher than that of current reports and the absorption edge is extended to 730 nm corresponding to the energy gap of 1.73 eV. The present experimental results suggest that shock doping might be a novel preparation route for TiO₂ semiconductor with N or other element doping of high concentration.

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