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EFFECTS OF SHOCK DOPING ON THE ENERGY GAP OF TiO_2

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Abstract. In this paper, nitrogen-doped titania was achieved by detonation-driven flyer impacting on the mixtures of TiO_2 and different nitrogen precursors. XRD, UV-Vis and XPS spectra were employed to characterize the phase composition, N doping concentration and energy gap of recovered samples. N doping concentration can be effectively regulated by choosing different doping nitrogen resources, changing initial content of doping nitrogen resources and flyer velocity in order to regulate the energy gap of TiO_2. The maximum concentration of nitrogen of doped TiO_2 by shock loading at 3.37 km/s is 13.45 at%. The results show that anatase transforms to rutile and srilankite appears at a higher flyer velocity (1.9-2.52km/s), the concentration of doped nitrogen in the recovered samples increases with increasing flyer velocity, the maximum concentration of nitrogen is 13.45 at%. The edge adsorption wavelength of nitrogen-doped titania induced by shock wave is shifted from 435nm to 730 nm and the corresponding energy gap is reduced from 2.85 eV to 1.73 eV.

Introduction

TiO_2 semiconductor that has oxidative capacity, chemical stability and low cost advantages is widely applied in the solar energy conversion and environmental remediation and is consider to be a most effective photo-functional material [1-2]. But the main drawback of TiO_2 for photocatalysis is that its energy gap is rather large, the energy gap of three common phases of TiO_2 such as rutile, anatase and brookite is 3.03eV, 3.2eV and 3.4eV respectively. Thus titania is only active in the ultraviolet region (λ<420 nm) accounting for less than 5% of the natural solar light. Therefore, a large effort has been made to prepare element-doped TiO_2 in order to enhance visible-light absorption and reduce energy gap. Element doping consists of metal doping, nonmetal doping [3] and multi-element codoping, doped elements are usually transition metal ions such as Fe, Cr, and V, etc. and non-metal anion such as N, C, S and F and so on. Element-doped TiO_2 has been prepared by many different ways such as sputtering, powder nitriding, ion implantation, chemical vapor deposition, hydrolysis, spray thermal decomposition and so on [4-10]. Present several doping methods are hard to achieve high N-doping concentration and therefore difficult to greatly enhance the absorbance of TiO_2 in visible region and reduce the energy gap. 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 [11]. Yakovyna et al. [12] 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 [13]. 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 reduce the energy gap. In this paper, powder mixture of little dopant and titanium dioxide were impacted by detonation-driven high velocity flyer, under instantaneous high shock temperature and pressure, the visible-light absorption and energy gap of nitrogen-doped titania induced by shock wave were regulated by choosing different doping nitrogen resources, changing initial content of doping nitrogen resources and flyer velocity.

Experimental

P25 TiO_2 (Degussa Co., Germany) was chosen as a precursor, nitrogen-rich substances such as dicyandiamide (DCD, $C_2N_4H_4$), hexamethylene tetramine (HMT, $C_6N_4H_{12}$) and sodium amide ($NaNH_2$) were used as doping nitrogen resources. The sample was the mixture of P25 TiO_2 and doping nitrogen resources. The steel flyer was propelled to a high velocity ranging from 1 to 3.5 km/s which can be regulated by control the flyer thickness and the height of main charge by detonation of the main charge of nitromethane (CH_3NO_2), initiated by booster charge of 8701 explosive. The steel flyer impacted the container with the samples subjecting to shock wave compression. The experimental conditions are shown in Table 1. The approximate calculation on the shock pressure and temperature in Table 1 can be described elsewhere in detail [14]. The details of shock doping method and shock loading apparatus were described in Ref. 15.

The recovered container was cut open by a lathe. The phase compositions of the recovered samples were determined on an X-ray diffractometer (XRD) (Rigaku D/MAX-2500) using Cu Kα radiation (λ=0.15406 nm) at 40 kV work voltage and 200 mA work current. Nitrogen doping was analyzed by X-ray photoelectron spectrometry (XPS) (Thermo ESCA LAB 250). The light absorption spectra of the samples were determined using a UV-vis diffuse reflectance spectrophotometer (Shimadzu UV-vis 250 IPC) [16-18]. Before the XPS and XRD characterization, recovered samples were washed by water for three times in order to remove the excess nitrogen resources.

Table 1. Experimental conditions and result. A: P25+$C_2N_4H_4$ (1%), B: P25+$C_2N_4H_4$ (5%), C: P25+$C_2N_4H_4$ (10%), D: P25+$NaNH_2$(10%); E: P25+HMT(10%)

Samples	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 (%)
P25						400	3.10	0	85.3	14.7	0
P25	1.77	0.45	2.25	13.8	1809	440	2.82	0	43.0	49.2	7.8
A	1.76	0.45	2.25	13.0	1809	605	2.05	2.07	59.9	32.4	7.7
B	1.88	0.52	2.25	13.0	1809	662	1.87	4.26	62.8	23.4	13.8
C	1.59	0.47	1.9	9.50	1280	698	1.78	9.22	67.7	21.0	11.3
C	1.64	0.50	2.25	13.0	1809	710	1.75	11.28	50.7	27.5	21.8
C	1.61	0.48	2.52	15.5	2045	730	1.73	13.45	46.9	30.1	23.0
D	1.40	0.42	2.52	14.0	2045	436	2.84	1.52	64.9	13.4	21.7
E	2.38	0.73	2.52	18.4	2045	436	2.84	1.91	54.2	17.5	28.3

Results and discussion

XRD analysis

The phase contents of recovered samples can be calculated from the integrated intensities of anatase (101), rutile (110), and srilankite (111) peaks according to the following formulas [19]:

$$W_A = k_A A_A / (k_A A_A + A_R + k_S A_S) \tag{1}$$

$$W_R = A_R / (k_A A_A + A_R + k_S A_S) \tag{2}$$

$$W_S = k_S A_S / (k_A A_A + A_R + k_S A_S) \tag{3}$$

where W_A, W_R, and W_S represent the weight fractions of anatase, rutile, and srilankite, respectively. The results of the calculation are shown in Table 1.

XPS studies

X-ray photoelectron spectroscopy (XPS) was used to obtain semiquantitative data on chemical element compositions of the recovered samples. The nitrogen concentrations of shock recovered C serial samples were 9.22 at%, 11.28 at% and 13.45 at% respectively as given in Table 1. It is found that the doping concentration of nitrogen is strongly correlated with the conversion yield from anatase to rutile and srilankite. 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 [20-21]. The srilankite high-pressure phase can only be short-range order in microsecond times under shock conditions and the oxygen-titanium coordination number varies from point to point [21]. As the radius of N^{3-} and O^{2-} anions are nearly the same, oxygen sites in the TiO_2 lattice are easily substituted by nitrogen atoms with increasing oxygen-titanium coordination number during the shock loading process [22-24]. Ti-O matrix atoms in titania lattice occurred a short distance displacement and newly ligand exchange meanwhile nitrogen species formed by shock induced chemical reaction of dicyandiamide exchanged with non-steady-state matrix oxygen atoms of TiO_2 rapidly [19]. Substitutional N-doping was achieved during the very short time of shock wave action. The nitrogen atoms exchange with matrix oxygen atoms of TiO_2 during the rapid shock induced pressure-phase transition process from anatase to srilankite high-pressure phase and the maximum concentration of nitrogen was 13.45 at%.

UV-vis spectra

The UV-vis diffusive reflectance spectra of unshocked P25 TiO_2 and shock-recovered C serial samples were shown in Fig 1. The energy gaps of these samples were calculated by a following [25]:

$$Eg(eV)=1240 / \lambda(nm) \tag{4}$$

where λ is the wavelength of adsorption edge. The wavelength of adsorption edge of unshocked P25 TiO_2 is 400 nm as shown in Fig. 1 and the corresponding energy gap is 3.10 eV. The adsorption edge of these three shock-recovered C serial samples exhibited obvious red shifts to about 700-730 nm compared with 400 nm of P25 TiO_2 raw material and the corresponding energy gap is 1.78eV, 1.75eV, and 1.73eV separately as given in Table 1. Increasing flyer velocity, the energy gap of shock-recovered C serial samples decreased with the increasing concentration of doped nitrogen. Since the energy gaps of different phases of TiO_2 (anatase 3.2eV, rutile 3.0eV, srilankite 3.4eV) are different, the energy gap also can be influenced by the phase transition during the shock loading process. As shown in Figure 1 (b, c, d), the overlap parts (400-450nm) in the UV-visible diffuse reflectance spectra of these three shock-recovered C samples are caused by formation of rutile phase with low energy gap by shock induced phase transition; the large absorption shoulder between 450nm and 550nm in the UV-visible diffuse reflectance spectra are due to the nitrogen-doping induced by shock wave. Furthermore, the horizontal adsorption in the range of about 550nm to 800nm of all the three shock-recovered C serial samples exhibited obvious enhancement that is regularly ascended with increasing flyer velocity corresponding to the color changes from white to gray black after shock treatment. It may be correlated with the defects, Ti^{3+} and color centers created by oxygen vacancy and dislocation under shock wave action [26].

The UV-vis diffusive reflectance spectra of unshocked P25 TiO_2, shocked P25 TiO_2 and shock-recovered A, B, C serial samples at 2.25 km/s were shown in Fig. 2. The UV-vis diffusive reflectance spectra of shock-recovered A, B, C serial samples (c, d, e) exhibited obvious absorption shoulder (450-550 nm), the absorption shoulder became larger and the corresponding energy gaps were reduced with the increasing initial content of dicyandiamide. The energy gaps of these recovered samples were calculated as given in Table 1.

The UV-vis diffusive reflectance spectra of unshocked P25 TiO_2 and shock-recovered C, D, E serial samples at 2.52 km/s were shown in Fig. 3. Shock-recovered C serial sample exhibited much more obvious red shift than shock-recovered D and E serial samples. Since the percentage of nitrogen atom in the nitrogen-containing molecules of dicyandiamide ($C_2N_4H_4$), sodium amide ($NaNH_2$) and hexamethylene tetramine ($C_6N_4H_{12}$) are 40%, 25% and 18% respectively. Under shock treatment, dicyandiamide ($C_2N_4H_4$) was decomposed into substances with higher concentrations of nitrogen than sodium amide ($NaNH_2$) and hexamethylene tetramine ($C_6N_4H_{12}$), which is conducive to achieve high concentration of nitrogen doping and obvious red shift with corresponding energy gap reduced.

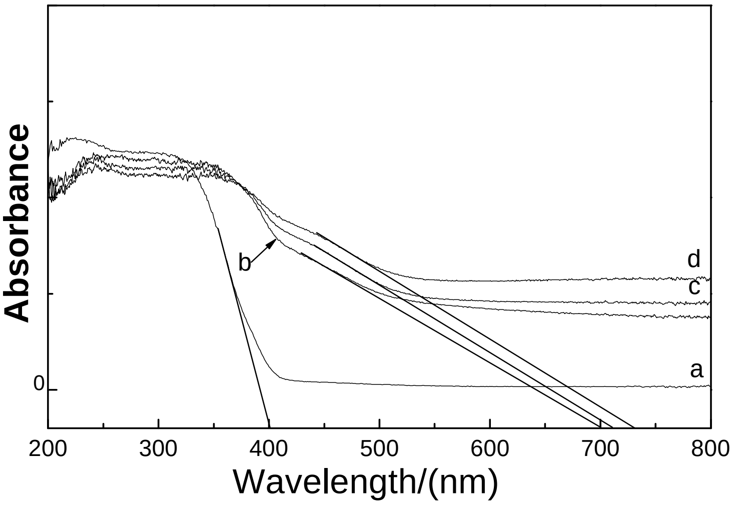

Fig.1 UV-vis spectra of shock-recovered C serial samples at different flyer impacting velocity. P25 TiO_2 raw material (a); shock-recovered C serial samples at 1.90km/s(b) ,2.25km/s(c) and 2.52km/s(d) C: P25+$C_2N_4H_4$ (10%)

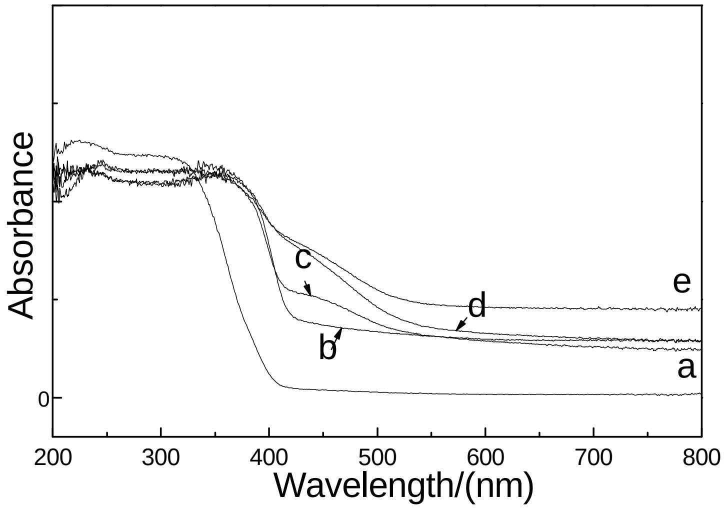

Fig.2 UV-vis spectra of shock-recovered samples with influence of different initial content of dicyandiamide. P25 TiO_2 raw material (a); shocked P25 TiO_2 (b); shock-recovered A, B, C serial samples at 2.25km/s (c, d, e), A: P25+$C_2N_4H_4$ (1%), B: P25+$C_2N_4H_4$ (5%), C: P25+$C_2N_4H_4$ (10%)

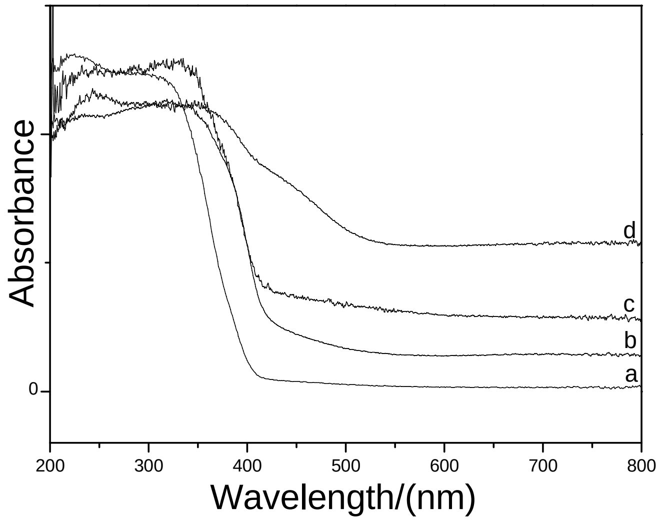

Fig.3 UV-vis spectra of shock-recovered samples with influence of different doping nitrogen resources. P25 TiO_2 raw material (a); shock-recovered E, D, C serial samples at 2.52km/s (b, c, d), C: P25+$C_2N_4H_4$ (10%), D: P25+$NaNH_2$(10%); E: P25+HMT(10%)

Conclusions

In summary, the edge adsorption wavelength of nitrogen-doped titania induced by shock wave can be shifted from 400nm to 730 nm and the corresponding energy gap is reduced from 3.10 eV to 1.73 eV. Increasing flyer velocity, the nitrogen doping concentration and the content of srilankite high-pressure pahse of titania doped by 10% content of $C_2N_4H_4$ increased and the corresponding energy gap decreased; at the same flyer velocity, absorption shoulder became larger and the corresponding energy gaps were reduced with the initial content of dicyandiamide increasing. The absorption edge and energy gap can also be affected by choosing different doping nitrogen resources. Dicyandiamide ($C_2N_4H_4$) is better than hexamethylene tetramine (HMT, $C_6N_4H_{12}$) and sodium amide ($NaNH_2$) to achieve high concentration of nitrogen doping and reduce energy gap. The present experimental results suggest that shock doping might be a novel method to achieve high concentration of element doping and influence the energy gap of titania.

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Explosion, Shock Wave and High-Energy Reaction Phenomena

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