Hydrothermal Synthesis, Structure and Photocatalytic Properties of La/Bi Co-Doped NaTaO₃

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La/Bi co-doped NaTaO₃ nanomaterials for photocatalytic applications have been successfully synthesized by hydrothermal method at low temperature. The obtained materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and UV-Vis molecular absorption spectroscopy. The results showed that the particle sizes of La/Bi co-doped NaTaO₃ were smaller than that of the pure NaTaO₃. La/Bi co-doping has extended optical absorption in the visible light region and then successfully increased photocatalytic activity of the La/Bi-codoped NaTaO₃ that were evaluated by degradation of methylene blue (MB).

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1. Introduction

NaTaO₃ has attracted extensive attention due to its good stability and high photocatalytic activity for water splitting. In a significant development, Kato *et al.* showed that a maximum of 56% quantum efficiency can be obtained by La-doped NaTaO₃ loaded NiO.¹⁾ However, because of its large band gap (~4.0 eV), NaTaO₃ can only work under ultraviolet light, which accounts for 4% of solar energy, resulting in low energy conversion efficiency. Many efforts have been made to extend the light absorption of NaTaO₃ toward visible light region and doping has been proved to be a feasible method to improve its photocatalytic activity.

The previous results have proved that the visible light response in NaTaO₃ is achieved by the doping of elements such as Co, Mn, Cu, Bi, N.²⁻⁸⁾ However, the doping by only one element with different valence makes a charge imbalance, which causes the lattice defects in photocatalysts. The poor photocatalytic activity is result of the recombination of photo-generated electrons and holes at these defect locations. Codoping may be a useful method to reduce the lattice defects and improve the activity of photocatalysts. Recently, Kudo *et al.* have reported that TiO₂ and SrTiO₃ codoped with Sb⁵⁺ and Cr³⁺ showed higher activity than TiO₂ and SrTiO₃ doped with only Cr³⁺. This was ascribed mainly to the reduction of oxygen defects and formation of Cr⁶⁺ ions in the lattice.⁹⁾ The co-doping La, Cr into NaTaO₃ obtained similar results.^{10,11)}

In this paper, we report the hydrothermal synthesis of NaTaO₃ co-doped with lanthanum and bismuth and study the decomposition of methylene blue solution under visible light irradiation.

2. Experimental Procedure

2.1 Process and materials

Ta₂O₅ (Sigma-Aldrich), NaOH (AR), equimolar amounts of La₂O₃ and Bi₂O₃ (Sigma-Aldrich; 0–10% by moles) were used as starting materials. In the typical synthesis procedure, Ta₂O₅, NaOH, La₂O₃, Bi₂O₃ were added first into distilled water. The mixture underwent ultrasonic treatment and transferred to a Teflon cup with steel casing. Hydrothermal process was carried out under optimal conditions of temperature, reaction time and solvent that were examined.¹²⁾ The obtained products were filtered and washed with distilled water, then dried at 80°C in air ambience.

2.2 Characterization

The crystal structure of the obtained samples were investigated by using a D8 ADVANCE-Brucker X-ray diffractograph equipped with Cu K α radiation ($\lambda = 0.15406$ nm). The XRD patterns were measured from 20° to 70° with a scanning step of 0.03°. The surface morphology and characteristics were analyzed by scanning electron microscopy (SEM) on S4800-NIHE. Element compositions of the sample were measured by energy dispersive X-ray spectroscopy (EDS; S4800-NIHE). UV-vis absorption spectra of the powder samples were recorded in Carry 5000 UV spectroscopy.

2.3 Photocatalytic reactions

The photocatalytic performance of the synthesized powders was evaluated by detecting the degradation of methylene blue. In our experiment, an amount of 40 mg of the powder catalyst was suspended in 50 ml of MB solution (30 μ mol/l). The suspension was kept in dark for 60 min to achieve adsorption equilibrium. After that the solution was then irradiated with a 250 W high pressure Hg lamp. The change of MB concentration in the solution was detected by using a spectrophotometer (Agilent 8453).

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3. Results and Discussions

3.1 Powder X-ray diffraction analysis

As reported in our previous paper¹²⁾ NaTaO₃ with Pbnm symmetry has started to form at 80°C and become perfectly formed at 120°C, by the hydrothermal method. Therefore, in this study, all samples were synthesized at the same optimal temperature of 120°C. Figure 1 presents XRD patterns of the pure NaTaO₃ and the samples doped with La/Bi content changed in a range of (0–10% mol). The XRD pattern of the pure sample is well identified to orthorhombic phase of the

NaTaO₃ (Space group No. 62; Pcmn; JCPDS card No. 025-0863). All the XRD patterns of doped samples match well with the reported pattern of NaTaO₃, no impurity phases involving bismuth oxides and/or lanthanum oxides are observed. The sharp shape and high intensity of all the X-ray peaks confirm the high crystallinity and purity of the synthesized material. One can see in inset of Fig. 1, X-ray line shifts to the smaller 2θ angle as concentration of La and Bi increases. This shift of the X-ray lines is a fact to confirm that La and Bi has been doped into lattice of NaTaO₃. Using XpovderVer.2010.01.33PRO we have calculated lattice parameters for all the samples. The obtained results are presented in Table 1.

3.2 Morphology characterization

Figure 2 presents SEM images of the NaTaO₃ (a) and 10% La/Bi codoped NaTaO₃ sample (b). The pure NaTaO₃ particles exhibit the well-defined cubic shaped morphology with the edge size around 200 nm. All the La, Bi doped samples have smaller particle size and their morphology

Fig. 1 XRD pattern of NaTaO₃ and samples doped with La/Bi (0–10% mol).

Table 1 Lattice parameters of the samples.

	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	Space group
Pure NaTaO ₃	0.55078	0.77649	0.54837	Pcmn
La,Bi 1%	0.54956	0.77678	0.54942	
La,Bi 3%	0.54986	0.77729	0.54980	
La,Bi 5%	0.55000	0.77755	0.55001	
La,Bi 10%	0.55039	0.77808	0.55025

Fig. 2 SEM image of NaTaO₃ (a) and SEM-EDS images of 10% La/Bi codoped %-NaTaO₃ sample (b), (c).

Fig. 3 UV-vis absorbance spectra of NaTaO₃ (a) and La/Bi co-doped NaTaO₃ samples with different concentrations (b).

becomes spherical as concentration of doped La and Bi is increased. According to Ref. 5), under Na-rich condition, majority of Bi ions occupy Ta site in structure of NaTaO₃. As known the ionic radius of Bi³⁺ (0.102 nm) is larger than that of Ta⁵⁺ (0.064 nm). Therefore, the replace of Bi³⁺ for Ta⁵⁺ in structure of NaTaO₃ induces an expansion of the unit cell volume as well as simultaneously causes crystalline deformations. The increase of dopant amount causes the increase of crystalline distortion. As the result, the particles are rounded. In addition the elemental composition-analyze was taken by using the energy dispersive spectroscopy (EDS) technique. The EDS result of the 10% La/Bi co-doped NaTaO₃ sample reveals that the La and Bi content in the sample is coincided with the starting amount of La/Bi (Fig. 2(c)).

3.3 Optical properties

Figure 3 presents the UV-vis absorption spectra of the pure NaTaO₃ and La/Bi co-doped NaTaO₃ samples with different concentrations. All the UV-vis absorption spectra were recorded in a wavelength range of (250–600) nm at room temperature. It can be seen from Fig. 3(a) that the pure NaTaO₃ sample has absorption edge around 310 nm. The absorption edge of the co-doped samples has shifted towards the longer wavelength side as the doping concentration increased. Comparing spectra of all the samples (Fig. 3(b)), we easily to conclude that the absorption spectrum of the La-doped samples is similar to that of the pure sample. In contrary the absorption of the Bi-doped and La/Bi co-doped samples exhibits a strong red shift. According to the calculated results in some previous paper,^{13,14)} the orthorhombic phase of NaTaO₃ has a direct band gap. Therefore, energy band gap E_g can calculate from the following equation:

$$\alpha = B \frac{(h\nu - E_g)^{1/2}}{h\nu} \quad (1)$$

Where α is absorption coefficient, B is a constant, h is Planck constant and ν is frequency excitation light.

From the UV-vis absorbance spectra of the samples, we redraw the dependence of $(\alpha h\nu)^2$ in the excitation photon energy and presented in Fig. 4. The linear part of $(\alpha h\nu)^2$ vs. $h\nu$ curve was extrapolated to estimate the E_g of the

Fig. 4 Dependence of $(\alpha h\nu)^2$ in excitation photon energy.

Table 2 Band gap energy of the samples.

Samples	E_g (eV)
Pure NaTaO ₃	4.02
La/Bi 1%	3.98
La/Bi 3%	3.89
La/Bi 5%	3.93
La/Bi 10%	3.79

photocatalysts at the point that $(\alpha h\nu)^2 = 0$. The energy band gap has been evaluated and presented in Table 2.

The red shift and increase of absorption in the visible light region of the samples is an expected factor to improve photocatalytic activity of the material irradiated with the visible light. Regarding the absorption in visible light of Bi doped NaTaO₃ Pushkar²⁾ suggested that occupancy of Bi ions at Ta site would induce Bi 6s mid-gap energy states that are responsible for the absorption. Unusually we recorded a negative value of absorption of the pure NaTaO₃ and La-doped samples (seen in Fig. 3(a) and 3(b)). This abnormal absorption was observed in some reports^{2,5)} but no explain was reported until now. We suppose this abnormal absorption result may be related with a photoluminescence contribution of NaTaO₃ samples.

Fig. 5 Methylene blue relative degradation in solution containing NaTaO₃ catalyst.

3.4 Photocatalytic activity

Photocatalytic activity of the synthesized materials was evaluated by studying degradation of methylene blue. Figure 5 presents the relative change of MB concentration in solution containing NaTaO₃ catalyst. It can be seen from Fig. 5, the MB concentration in solution without NaTaO₃ catalyst decreased only about 5% after 90 min irradiated by a mercury lamp. In a case of the solution containing pure NaTaO₃, MB concentration has been decreased around 82.4% after irradiation for 90 min. The best performance was shown by La/Bi co-doped NaTaO₃ sample. MB in solution is almost completely degraded after irradiation for 90 minutes. Both the Bi-doped NaTaO₃ and La/Bi co-doped samples almost have a same MB degradation rate during first 60 min of irradiation. In the next irradiation time the La/Bi co-doped NaTaO₃ has higher MB degradation rate. This may be due to a reduction of the particle grain size of the La, Bi co-doped NaTaO₃ sample in comparison with the Bi-doped one.

The photocatalytic activity recorded in our case is higher than that reported¹⁵⁾ for the degradation of MB in an aqueous solution containing NaTaO₃ and NaTaO₃ doped with La and Sm prepared by the solid state reaction. It was shown in that report, the MB was completely degraded after irradiated for more than 400 min.

4. Conclusion

In summary, La/Bi co-doped NaTaO₃ materials (0–10% by moles) were successfully fabricated by hydrothermal method. The co-doping reduces the particle size, extends the absorption edge towards longer wavelength. The present results indicate that selective La and Bi occupancy at different cation sites in NaTaO₃ lattice is a useful way to fabricate the expected photocatalytic materials working under visible light.

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