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Preparation and characterization of new visible-light-driven $BaCo_{0.5}Nb_{0.5}O_3$ photocatalyst

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Abstract

A new type of visible-light-driven photocatalyst $BaCo_{0.5}Nb_{0.5}O_3$ was successfully synthesized via a sol–gel process in this study. After heating the precursors at 1000 °C, a pure perovskite phase was obtained. The particle size and crystallinity of $BaCo_{0.5}Nb_{0.5}O_3$ powders markedly increased with a rise in the calcination temperature. The band gap of $BaCo_{0.5}Nb_{0.5}O_3$ calculated from the UV–visible spectra was found to be less than that of titania. $BaCo_{0.5}Nb_{0.5}O_3$ was demonstrated to have photocatalytic activity under visible light irradiation and this activity significantly depended on the synthesis temperature. The sol–gel derived powders were found to have better photocatalytic activity than the solid-state derived powders because of the reduced particle size and increased surface area.

Keywords: Photocatalyst; $BaCo_{0.5}Nb_{0.5}O_3$; Sol–gel; Perovskite

1. Introduction

In recent years, photocatalysts have been extensively used for the degradation of various kinds of pollutants. Since the discovery of the water splitting ability of TiO_2 under UV light irradiation by Fujishima and Honda [1], the photocatalytic activity of TiO_2 has been widely investigated. TiO_2 is active under UV light illumination; however, it can not absorb visible light because of its large band gap (~3.2 eV). To broaden the application of TiO_2, various types of transition metal ions have been added into TiO_2 in trials. It was reported that doping transition metal ions into TiO_2 can shift the absorption edge to the visible light region [2,3]. However, the presence of foreign metal ions is generally detrimental to the degradation of organic species in the aqueous system [4–8]. On the other hand, a new series of photocatalysts $MCo_{1/3}Nb_{2/3}O_3$ (M = Ca, Sr, and Ba) have been studied recently [9]. These compounds have a complex ABO_3-type perovskite structure in which the B sites are randomly occupied by cobalt ions and niobium ions in a charge-balanced manner. It is suggested that the valence bands and conduction bands in these compounds are composed of the cobalt-ion 3d states and niobium-ion 4d states, respectively [9]. Other kinds of perovskite compounds were also found to have potential photocatalytic activities [10–12].

In this study, we developed a new type of photocatalyst $BaCo_{0.5}Nb_{0.5}O_3$. The sol–gel route incorporating polymerizing agents was adopted to synthesize $BaCo_{0.5}Nb_{0.5}O_3$ powders. The optical properties of the prepared powders were investigated. The effects of heating temperature on the morphology of the formed particles were studied. The photocatalytic activities of the powders prepared via the sol–gel processes were also evaluated.

2. Experimental

$BaCo_{0.5}Nb_{0.5}O_3$ was prepared via a sol–gel method. Citric acid and ethylene glycol were used as the polymerizing agents in this process. Barium-ion solution, cobalt-ion solution, and niobium-ion solution were prepared by dissolving reagent-grade barium nitrate, cobalt nitrate hexahydrate, and niobium nitrate in distilled water. These solutions were first mixed together to form an aqueous solution, followed by adding citric acid monohydrate. The molar ratio of barium ion:cobalt ion: niobium ion:citric acid was set to be 1:0.5:0.5:6. After stirring the mixed solution for 1 h, ethylene glycol with the mole 1.5

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times that of citric acid was added into the above solution. The solution was later heated at 250 °C for 1.5 h to remove water, and further heated at 350 °C to induce the polymerization reactions. In order to remove any residual organics, the polymeric precursors were further heated at 500 °C for 30 min to form the precursor powders.

The above formed powders were calcined from 600 to 1200 °C for 2 h to produce the polycrystalline powders. The apparent color of the prepared powders was brown. The phases in the powders were examined via X-ray diffraction (XRD) analysis using an X-ray diffractometer (MAC Science MXP3) by CuKα radiation. The diffuse reflectance spectra were recorded employing a UV–vis spectrophotometer (Hitachi U-3410). The optical-grade $BaSO_4$ powder was used as reference. Methylene blue solution was used to evaluate the photocatalytic activities of the prepared powders. A 30 W FL lamp was employed as the light source, and a 400 nm glass filter was utilized to cut off light with wavelength shorter than 400 nm. The morphology and particle size of the prepared samples were examined via a transmission electron microscope (TEM).

3. Results and discussion

Fig. 1 depicts the X-ray diffraction patterns of the sol–gel derived $BaCo_{0.5}Nb_{0.5}O_3$ powders calcined at various temperatures. After heating at 600 °C for 2 h, a small amount of perovskite phase was found to coexist with $BaCO_3$ and Nb_2O_5. With a rise in the heating temperature, the amount of perovskite phase also increased. When the calcination temperature reached 1000 °C, single-phased $BaCo_{0.5}Nb_{0.5}O_3$ was obtained and all the diffraction peaks were assigned to $BaCo_{0.5}Nb_{0.5}O_3$ perovskite structure with a space group of $Pm\bar{3}m$. $BaCo_{0.5}Nb_{0.5}O_3$ was found to be iso-structural to $BaCo_{0.5}Ta_{0.5}O_3$ because they had similar X-ray diffraction patterns. The lattice parameter of $BaCo_{0.5}Nb_{0.5}O_3$ was calculated to be 4.078 Å. As the annealing temperature rose up to 1200 °C, the crystallinity of $BaCo_{0.5}Nb_{0.5}O_3$ was further enhanced.

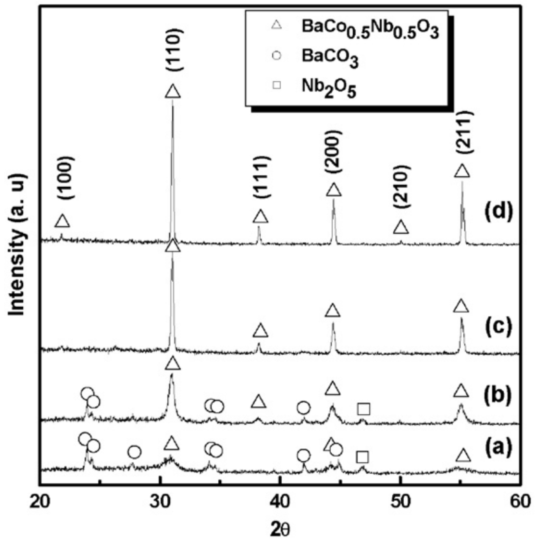

Fig. 1. XRD patterns of the sol–gel derived precursors of $BaC_{0.5}Nb_{0.5}O_3$ powders heated at (a) 600 °C, (b) 800 °C, (c) 1000 °C and (d) 1200 °C for 2 h.

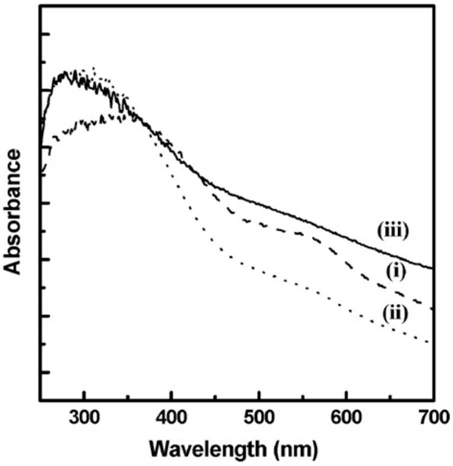

Fig. 2. UV–vis diffuse reflectance spectra of the sol–gel derived precursors of $BaC_{0.5}Nb_{0.5}O_3$ heated at (i) 1200 °C, (ii) 1000 °C and (iii) 800 °C.

The optical properties of the prepared $BaCo_{0.5}Nb_{0.5}O_3$ perovskite powders were investigated. The UV–vis diffuse reflectance spectra of the prepared $BaCo_{0.5}Nb_{0.5}O_3$ powders are illustrated in Fig. 2. The scanning wavelengths ranged from 250 to 700 nm. It is demonstrated in the spectra that all the prepared samples absorbed light in the visible light region. The obvious absorption near 400 nm is considered to result from the absorption of the intrinsic band gap. The value of the intrinsic band-gap energy of $BaCo_{0.5}Nb_{0.5}O_3$ heated at 1000 °C was calculated according to the following equation [13]:

$$\alpha h\nu = 2.7\times 10^5 (2m_r/m)^{3/2}(f/\eta)(\hbar\nu - E_g) \qquad (1)$$

where α represents the absorption coefficient, $\hbar\nu$ the absorption energy of photon ($E = \hbar\nu$), m_r the reduced mass of the electron and hole, and E_g the energy of band gap. The band gap of $BaCo_{0.5}Nb_{0.5}O_3$ was estimated to be 2.26 eV, which is much smaller than that of TiO_2 (3.2 eV). It is indicated from these results that $BaCo_{0.5}Nb_{0.5}O_3$ can absorb visible light. The theoretical calculations of the electronic structure of $BaCo_{1/3}Nb_{2/3}O_3$ and the graphical representation

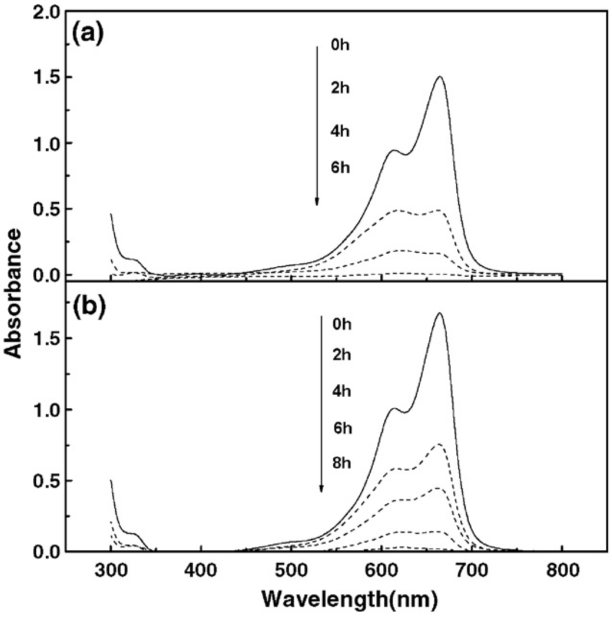

Fig. 3. UV–vis spectra of methylene blue degraded by the sol–gel derived precursors of $BaCo_{0.5}Nb_{0.5}O_3$ heated at (a) 1000 °C and (b) 1200 °C.

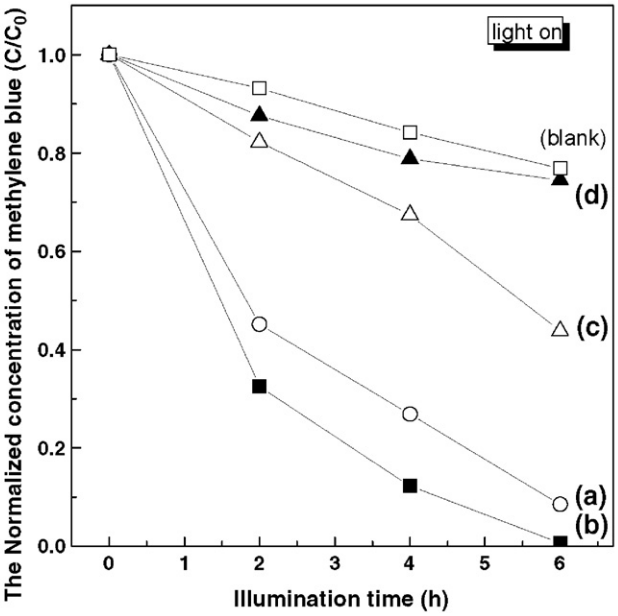

Fig. 4. Degradation of methylene blue under visible light by the sol–gel derived precursors of $BaCo_{0.5}Nb_{0.5}O_3$ heated at (a) 1200 °C, (b) 1000 °C, (c) 800 °C and (d) the powders prepared via solid-state reaction at 1200 °C.

of the energy levels were reported by Yin et al. [9]. The lattice parameter and the band gap of $BaCo_{0.5}Nb_{0.5}O_3$ are similar to those of $BaCo_{1/3}Nb_{2/3}O_3$. In addition, both of these two materials have the same perovskite structure. Therefore, it is reasonable to believe that these two materials have similar band structure. The band structure of $BaCo_{1/3}Nb_{2/3}O_3$ should be composed of the Co^{3+} 3d level and Nb^{5+} 4d level. The visible light absorption of this compound could be due to the electronic excitations from the Co^{3+} (t_{2g}) state to the Nb^{5+} (4d) state.

The photocatalytic activities of the prepared powders under visible light (>400 nm) irradiation were evaluated based on the decomposition behavior of methylene blue. Fig. 3 illustrates the UV–vis spectra of methylene blue degraded by $BaCo_{0.5}Nb_{0.5}O_3$ powders derived after 1000 and 1200 °C heating. The maximum absorbance of methylene blue solutions decreased markedly with a prolongation in the illumination time as shown in Fig. 3(a) and (b), indicating that the prepared samples decomposed methylene blue under visible light. During the illumination process, the maximum absorption peaks in the UV–vis spectra were found to shift towards the shorter wavelength region revealing the formation of *N*-demethylated intermediates during the decomposition process [14].

Fig. 4 illustrates the variation in the concentration of methylene blue solutions decomposed by the prepared photocatalysts under visible light irradiation. It was found that the photocatalytic activity of the solid-state derived powders was markedly lower than that of the samples synthesized via the sol–gel process. C_0 and C represent the initial and resultant concentrations of methylene blue solution, respectively. The values of normalized concentration C/C_0 after 6 h-illumination of visible light were around 0.438, 0.006, and 0.080 when the sol–gel derived $BaCo_{0.5}Nb_{0.5}O_3$ powders heated at 800, 1000, and 1200 °C were used, respectively. It is indicated that the sol–gel derived powders heated at 1000 °C exhibited the highest activity. It only took 6 h of illumination to nearly decompose methylene blue completely.

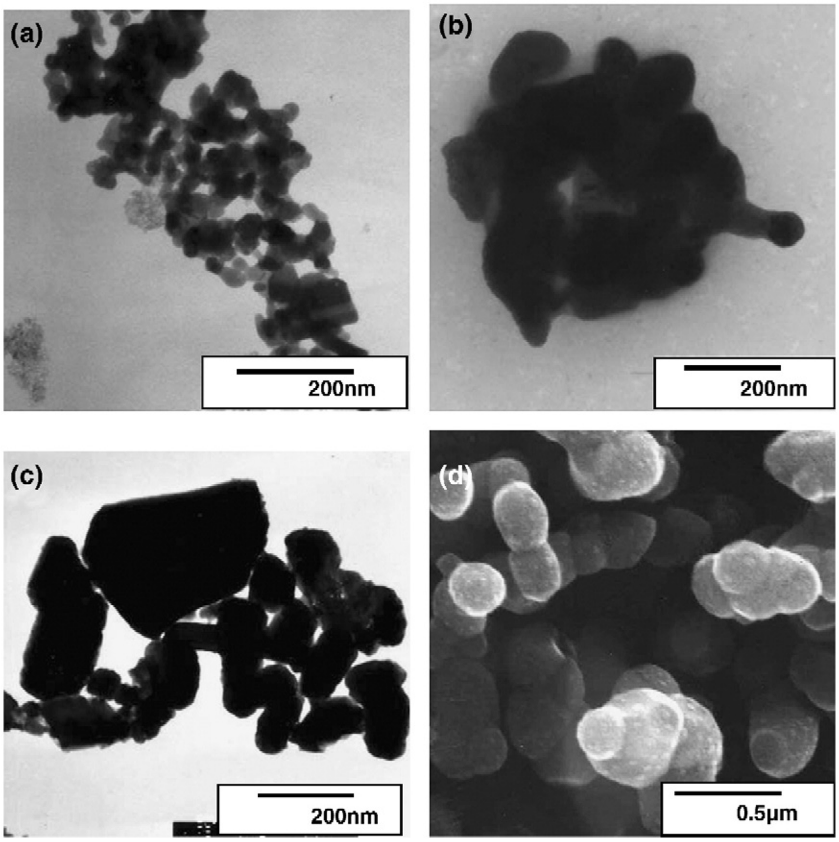

Fig. 5. TEM photographs for the sol–gel derived precursors of $BaCo_{0.5}Nb_{0.5}O_3$ heated at (a) 800 °C, (b) 1000 °C and (c) 1200 °C. (d) SEM photograph for the powders prepared via solid-state reaction at 1200 °C.

The morphology and microstructures of the prepared $BaCo_{0.5}Nb_{0.5}O_3$ powders were investigated. Fig. 5(a), (b), and (c) shows the TEM micrographs of the samples prepared via the sol–gel process at various temperatures. The particle size of the powders heated at 800, 1000 and 1200 °C was around 20, 100 and 140 nm, respectively, indicating an enlargement of the particle size of $BaCo_{0.5}Nb_{0.5}O_3$ powders with increasing heating temperature. Due to this coarsening effect, the particle size of the 1000 °C-heated sample was larger than that of the sample heated at 800 °C. It is considered that high temperature promoted the agglomeration of the sample particles and thereby the formation of the secondary particles. The grain growth of $BaCo_{0.5}Nb_{0.5}O_3$ powders was even more apparent as the calcination temperature was increased to 1200 °C. The TEM micrographs demonstrate that calcination temperature affected the morphology and particle size of the obtained powders. Fig. 5(d) shows the SEM microstructures of $BaCo_{0.5}Nb_{0.5}O_3$ powders prepared via the solid-state process after 1200 °C heating. As compared to the sol–gel process, the powders synthesized via the solid-state method have a larger average particle size of around 0.3 μm. The result indicates that the solid-state derived photocatalysts have relatively small specific surface area, rendering insufficient photocatalytic activity of these prepared powders.

$BaCo_{0.5}Nb_{0.5}O_3$ compound shows photocatalytic activity under visible light irradiation because it requires less energy than TiO_2 to produce the electron (e^-) and hole (h^+) pair due to its smaller band gap. The crystallinity of the prepared samples dominates their photocatalytic activity. When the sol–gel derived powders were heated at elevated temperatures, the photocatalytic activity of the powders with enhanced crystallinity was improved. However, after heating at 1200 °C, the enlarged particles resulted in a decrease on the surface area, thereby deteriorating the photocatalytic activity. This indicates that the photocatalytic activity of $BaCo_{0.5}Nb_{0.5}O_3$ depends on particle size as well as on crystallinity.

4. Conclusions

New photocatalyst $BaCo_{0.5}Nb_{0.5}O_3$ powders with a complex perovskite structure were successfully synthesized using the sol–gel method in this study. This perovskite-structured material was confirmed to have photocatalytic activity under visible light irradiation. Pure-phased $BaCo_{0.5}Nb_{0.5}O_3$ was formed after heating the sol–gel derived precursors at 1000 °C. It was demonstrated that the sol–gel derived $BaCo_{0.5}Nb_{0.5}O_3$ powders exhibited greater photocatalytic activities in comparison with the solid-state derived powders. The heating conditions had significant effects on the morphology and particle size of the prepared powders. The 1000 °C-heated $BaCo_{0.5}Nb_{0.5}O_3$ powders exhibited the highest photocatalytic activity among all the prepared powders because of the well-crystallized structure and small particle size.

References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[2] J.C. Xu, Y.L. Shi, J.E. Huang, B. Wang, H.L. Li, J. Mol. Catal., A Chem. 219 (2004) 351.
[3] A.J. Bard, J. Electrochem. Soc. 10 (1979) 59.
[4] A. Fuerte, M.D. Hernandez-Alonso, A. Martinez-Arias, M. Fernandes-Garcia, J.C. Conesa, J. Soria, Chem. Commun. 24 (2001) 2718.
[5] H. Yamashita, Y. Ichihashi, M. Takeuchi, S. Kishiguchi, M. Anpo, J. Synchrotron Radiat. 6 (1999) 451.
[6] M.R. Hoffmann, T.S. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[7] D. Dvoranova, V. Brezova, M. Mazur, M.A. Malati, Appl. Catal., B Environ. 37 (2002) 91.
[8] S. Klosek, D. Raftery, J. Phys. Chem., B 105 (2001) 2815.
[9] J. Yin, Z. Zou, J. Ye, J. Phys. Chem., B 107 (2003) 4936.
[10] W.F. Yao, H. Wang, X.H. Xu, S.X. Shang, Y. Hou, Y. Zhang, M. Wang, Mater. Lett. 12 (2003) 1899.
[11] Z. Xinhua, Z. Jianmin, Z. Shunhua, L. Zhiguo, M. Naiben, H. Dietrich, J. Cryst. Growth 284 (2005) 486.
[12] D.I. Woodward, I.M. Reaney, Acta Crystallogr. Sect. B-Struct. Sci. 61 (2005) 387.
[13] I. Kosacki, V. Petrovsky, H.U. Anderson, Appl. Phys. Lett. 74 (1999) 341.
[14] M. Windholz, The Merk Index, 10th edMerck & Co., Rahway, 1983.