Enhanced Visible-light-driven Photocatalytic Activity of Multiferroic KBiFe$_2$O$_5$ by Adjusting pH Value

LI Jian$^1$, ZHANG Gang-Hua$^2$, FAN Li-Kun$^2$, HUANG Guo-Quan$^1$, GAO Zhi-Peng$^3$, ZENG Tao$^{1,2}$

(1. College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, China; 2. Shanghai Key Laboratory of Engineeering Materials Application and Evaluation, Shanghai Research Institute of Materials, Shanghai 200437, China; 3. National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang 621900, China)

Abstract: Multiferroic KBiFe$_2$O$_5$ was successfully prepared by a facile hydrothermal method. Its phase purity and morphology were investigated by powder X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The visible-light absorption was confirmed by UV-Vis diffuse reaction spectroscopy (UV-Vis DRS). Effect of pH value on visible-light-driven photocatalytic properties of KBiFe$_2$O$_5$ was evaluated by degrading rhodamine B (RhB) and methyl orange (MO). It can be found that lower pH value contributed to smaller average particle size. The D$_{50}$ of the sample at pH 7 is about 10 times larger than that at pH 2. Acid condition is beneficial to the dispersion of KBiFe$_2$O$_5$ nanoparticles, which leads to an enhanced photocatalytic performance. Photocatalytic activity of KBiFe$_2$O$_5$ is significantly improved by decreasing pH value of the solution, which is attributed to the promoted dispersion of catalyst particles in the suspension and the enhanced adsorption of dye molecules on the catalyst surface.

Key words: KBiFe$_2$O$_5$; photocatalyst; visible-light irradiation; pH value

Traditional metal oxides or metal sulfides semiconductors, such as TiO$_2$[1-3], ZnO[4-5] and ZnS[6-7], have received considerable attentions due to their potential application for the degradation of organic contaminants and hydrogen generation from water[8-9]. However, due to the finite absorbance of the UV-light (~5% of the sunlight) and the fast recombination of the photogenerated carriers[10], the large band gap $E_g$ (>3 eV) and low conversion efficiency limit their practical application. Actually, the spontaneous polarization of ferroelectric materials can act as a homogeneous inner electric field which is beneficial to separating the photogenerated carriers[11-12]. Nevertheless, the $E_g$ of most reported ferroelectric photocatalysts, such as BiFeO$_3$ (2.6 eV)[13] and Bi$_2$WO$_6$ (2.72 eV)[14], are still insufficient to absorb the entire solar spectrum. Therefore, many efforts have been devoted to promoting the photocatalytic performances of ferroelectric materials recently[15-18]. The optimal band-gap range for excellent light-absorbing materials is about 1.0 eV - 1.8 eV based on the energy distribution of the solar spectrum[19]. Most recently, several ferroelectrics have been reported with narrow $E_g$ around 1.5 eV, such as KBiFe$_2$O$_5$[20] and [KNbO$_3$]$_{1-x}$[BaNi$_2$O$_{2/3}$][21]. Contrast to the enhanced light absorption and promoted photoelectric response, few studies have given deep insight into their photocatalytic performance so far.

Commonly, the photocatalytic performances of the most photocatalysts have been demonstrated to be highly pH-dependent[22]. Under acidic condition, the enhanced photocatalytic activities have been achieved in several ferroelectric materials, such as BiFeO$_3$[23] and Bi$_2$WO$_6$[24]. It has been proposed that the concentration of H$^+$ on the catalyst surface at different pH values would affect the dispersion of catalyst particles and the absorption of dye molecules on catalyst surface, and thus influence the photocatalytic activity[23-25]. But there is no report on the effect of pH value on the photocatalytic properties of such ferroelectrics with narrow $E_g$. Although the primary photocatalytic activity of multiferroic KBiFe$_2$O$_5$ has been reported, the photocatalytic efficiency is still less than satisfactory. Therefore, enhanced photocatalytic performances can also be expected in these narrow-band-gap ferroelectrics by adjusting the pH value.

In this work, KBiFe$_2$O$_5$ has been employed as a candidate to investigate the role of pH value on the photocatalytic properties of the ferroelectric materials with
Because of the mild reaction conditions and simple apparatus, hydrothermal synthesis has been utilized to synthesize the pure phase KBiFe₂O₅. The visible-light-driven photocatalytic properties under different pH values have been investigated by degrading the rhodamine B (RhB) and methyl orange (MO) dyes. The photocatalytic efficiency of KBiFe₂O₅ can be significantly improved by increasing the initial acidity of dye solution.

1 Experimental

As a typical preparation method of KBiFe₂O₅, 7.5 mL Bi(NO₃)₃·5H₂O (0.2 mol/L) and 15 mL Fe(NO₃)₃·9H₂O (0.2 mol/L) were initially mixed in a beaker, then 50 g KOH was directly added into the mixture with constantly magnetic stirring. When the reaction mixture was cooled to room temperature in the air, it was then transferred into a 50 mL Teflon-lined stainless steel autoclave with 70% filling and heat-treated at 220 °C for 48 h. After the autoclave was cooled and depressurized, the product was collected and washed with deionized water and dried at 80 °C in air.

The purity and crystallinity of KBiFe₂O₅ were characterized by X-ray diffractometer (XRD) on Bruker D8 advance diffractometer operating with Cu Kα radiation. The crystal and morphology were checked by field emission scanning electron microscopy (FE-SEM). The optical absorption was measured using a UV-3100 Shimadzu ultraviolet-visible-infrared spectrophotometer. Photocatalytic performance was evaluated by degrading RhB and MO at various pH under visible-light-irradiation using a 500 W Xe lamp with a cut off filter for λ ≥ 420 nm. The reaction temperature was kept at room temperature by cooling water to prevent any thermal catalytic effect. The distance between the liquid surface and the light source was about 10 cm. For photocatalytic experiments, the crystalline KBiFe₂O₅ was first grinded into nanoparticles around 100 nm–200 nm (as shown in Fig. 2(b)) through high speed ball milling, so as to improve its specific surface area for photocatalytic activity. The diffuse reflectance spectra of KBiFe₂O₅ and the extrapolated band gap are shown in Fig. 2(c) and (d). Based on the Kubelka-Munk (K-M) function[27], the band-gap of as-prepared KBiFe₂O₅ can be determined as 1.63 eV, which is consistent with the data reported previously[20].

To reveal the effect of pH value on the photocatalytic performance of KBiFe₂O₅, the photocatalytic decompositions of RhB and MO have been carried out at different pH values.

1. Experimental

As a typical preparation method of KBiFe₂O₅, 7.5 mL Bi(NO₃)₃·5H₂O (0.2 mol/L) and 15 mL Fe(NO₃)₃·9H₂O (0.2 mol/L) were initially mixed in a beaker, then 50 g KOH was directly added into the mixture with constantly magnetic stirring. When the reaction mixture was cooled to room temperature in the air, it was then transferred into a 50 mL Teflon-lined stainless steel autoclave with 70% filling and heat-treated at 220 °C for 48 h. After the autoclave was cooled and depressurized, the product was collected and washed with deionized water and dried at 80 °C in air.

The purity and crystallinity of KBiFe₂O₅ were characterized by X-ray diffractometer (XRD) on Bruker D8 advance diffractometer operating with Cu Kα radiation. The crystal and morphology were checked by field emission scanning electron microscopy (FE-SEM). The optical absorption was measured using a UV-3100 Shimadzu ultraviolet-visible-infrared spectrophotometer. Photocatalytic performance was evaluated by degrading RhB and MO at various pH under visible-light-irradiation using a 500 W Xe lamp with a cut off filter for λ ≥ 420 nm. The reaction temperature was kept at room temperature by cooling water to prevent any thermal catalytic effect. The distance between the liquid surface and the light source was about 10 cm. For photocatalytic experiments, the crystalline KBiFe₂O₅ was first grinded into nanoparticles around 100 nm–200 nm (as shown in Fig. 2(b)) through high speed ball milling, so as to improve its specific surface area for photocatalytic activity. The diffuse reflectance spectra of KBiFe₂O₅ and the extrapolated band gap are shown in Fig. 2(c) and (d). Based on the Kubelka-Munk (K-M) function[27], the band-gap of as-prepared KBiFe₂O₅ can be determined as 1.63 eV, which is consistent with the data reported previously[20].

To reveal the effect of pH value on the photocatalytic performance of KBiFe₂O₅, the photocatalytic decompositions of RhB and MO have been carried out at different pH values.

The photocatalytic capability of KBiFe₂O₅ powders was evaluated by degradation rate (D) of dye solution and the reaction kinetics of dye degradation, which was quantitatively described on the basis of a pseudo-first-order reaction model. These parameters can be calculated from the following equations[26]:

\[ D(\%) = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\% \]  
\[ \ln \frac{C_t}{C_0} = kt \]

Where D(%) was the degradation rate of dye solution at time t, C₀ and Cₜ were the concentrations of dye solution at time t₀ and t respectively, A₀ and Aₜ were the absorbance of dye solution at time t₀ and t respectively. According to the Eq. (2), a plot of −ln(Cₜ/C₀) versus t will yield a slope of apparent rate constant (k, min⁻¹).

2 Results and discussion

The XRD patterns of as-grown KBiFe₂O₅ powders (Fig. 1) can be indexed to the orthorhombic space group P2₁cn with cell parameters a = 0.7988(2) nm, b = 1.1819(2) nm, c = 0.5734(1) nm, which is identical to the simulated one using single-crystal data[20]. The excellent crystallinity of the sample has been confirmed by FE-SEM images as shown in Fig. 2(a). FE-SEM photograph shows clearly the material to be made up of rod-like single crystals, around 25 μm in width and 100 μm–200 μm in length. For photocatalytic experiments, the crystalline K BiFe₂O₅ was first grinded into nano particles around 100 nm–200 nm (as shown in Fig. 2(b)) through high speed ball milling, so as to improve its specific surface area for photocatalytic activity. The diffuse reflectance spectra of KBiFe₂O₅ and the extrapolated band gap are shown in Fig. 2(c) and (d). Based on the Kubelka-Munk (K-M) function[27], the band-gap of as-prepared KBiFe₂O₅ can be determined as 1.63 eV, which is consistent with the data reported previously[20].

To reveal the effect of pH value on the photocatalytic performance of KBiFe₂O₅, the photocatalytic decompositions of RhB and MO have been carried out at different pH values.

![Fig. 1 XRD patterns of as-grown KBiFe₂O₅ and after degradation at pH 2](image-url)
Fig. 2 FE-SEM image (a, b), diffuse reflection spectrum (c), and $(F(R)hv)^2$ against hv (d) of KBiFe$_2$O$_5$

The effect of pH on the dispersion of KBiFe$_2$O$_5$ particles in the suspension was verified through granularity analysis using laser particle size analyzer. The average particle sizes ($D_{50}$) of KBiFe$_2$O$_5$ at different pH value were listed in Table 1. It can be found that lower pH value contributed to smaller average particle size. The $D_{50}$ of the sample at pH=7 is about 10 times larger than that at pH=2, which is attributed to the agglomeration of the nanoparticles caused by the effect of Vander Waals force in the suspension with higher pH value. Thus, the acid
Fig. 3  Degradation rates of RhB (a) and MO (b) using KBiFe$_2$O$_5$ at different pH values, and absorption changes of RhB (c) and MO (d) solution in photocatalytic process at pH 2

Fig. 4  Corresponding reaction rate constant $k$ for the photocatalytic degradation of RhB (a) and MO (b) by KBiFe$_2$O$_5$ at various pH value, and circulating runs in the photocatalytic degradation of RhB (c) and MO (d) at pH 2
condition is beneficial to the dispersion of KBiFe₂O₅ nanoparticles, which leads to an enhanced photocatalytic performance.

3 Conclusions

In conclusion, multiferroic KBiFe₂O₅ has been successfully prepared by a facile hydrothermal method. The phase purity and morphology were investigated by XRD and FE-SEM. The visible-light absorption was confirmed by UV-Vis spectroscopy. The visible-light-driven photocatalytic performances for degrading RhB and MO can be extremely promoted by decreasing pH value. This finding may provide a new route to improve the photo-degradation efficiency of ferroelectric photocatalyst by adjusting the pH value of dye solutions.

References:

[1] CHOI H, SHIN D, YEO B C, et al. Simultaneously controllable doping sites and the activity of a W-N codoped TiO₂ photocatalyst. ACS Catal., 2016, 6(5): 2745–2753.

[2] CHOI H, SOFRANKO A C, DIONYSIOU D D. Nanocrystalline TiO₂ photocatalytic membranes with a hierarchical mesoporous multilayer structure: synthesis, characterization, and multifunction. Adv. Funct. Mater., 2006, 16: 1067–1074.

[3] LIN JING-CHENG, TANG XIAO, CHU WAN-YI. Synthesis and photocatalysis property of ultra-small TiO₂ nanoclusters in aqueous media. J. Inorg. Mater., 2017, 32(8): 863–869.

[4] NG K H, CHENG C K. Photo-polishing of POMe into CH₃-lean biogas over the UV-responsive ZnO photocatalyst. Chem. Eng. J., 2016, 300: 127–138.

[5] AKHAVAN O. Graphene nanomesh by ZnO nanorod photocatalysts. ACS nano, 2010, 4(7): 4174–4180.

[6] HSU MU-HSIANG, CHANG CHI-JUNG, WENG HAU-TING. Efficient H₂ production using Ag₉S-coupled ZnO@ZnS core–shell nanorods decorated metal wire mesh as an immobilized hierarchical photocatalyst. ACS Sustain. Chem. Eng., 2016, 4: 1381–1391.

[7] XUE CHAO, AN HUA, YAN XIAO-QING, et al. Spatial charge separation and transfer in ultrathin CdInS₂/rGO nanosheet arrays decorated by ZnS quantum dots for efficient visible-light-driven hydrogen evolution. Nano Energy, 2017, 39: 513–523.

[8] CHEN SHAN-SHAN, TAKATA T, DOMEN K. Particulate photocatalysts for overall water splitting. Nature Rev. Matal., 2017, 2(10): 17050–1–17.

[9] FAN YING-YING, MA WEI-GUANG, HAN DONG-XUE, et al. Convenient recycling of 3D AgX graphene aerogels (X = Br, Cl) for efficient photocatalytic degradation of water pollutants. Adv. Mater., 2015, 27: 3767–3773.

[10] ZHANG NING, CHEN DA, NIU FENG, et al. Enhanced visible light photocatalytic activity of Gd doped BiFeO₃ nanoparticles and mechanism insight. Sci. Rep., 2016, 6: 26467–1–11.

[11] LI SHUN, LIN YUAN-HUA, ZHANG BO-PING, et al. Controlled fabrication of BiFeO₃ uniform microcrystals and their magnetic and photocatalytic behaviors. J. Phys. Chem. C, 2010, 114: 2903–2908.

[12] ZHANG GANG-HUA, LIU FENG-LIANG, GU TING-TING, et al. Enhanced ferroelectric and visible-light photoelectric properties in multiferroic KBiFe₂O₅ via pressure-induced phase transition. Adv. Electron. Mater., 2017, 3(3): 1600498–1–8.

[13] RAMIREZ F, JR E M, SOUZA J A, et al. Comprehensive theoretical and experimental study of electrical transport mechanism on BiFeO₃ multiferroic nanoparticles. J. Alloy and Compd., 2017, 720: 47–53.

[14] ZHANG PENG, TENG XIAO-XU, FENG XIAN-HUA, et al. Preparation of Bi₁₋ₓWO₃ photocatalyst by high-energy ball milled Bi₁₋ₓWO₃ mixture. Ceram. Int., 2016, 42: 16749–16757.

[15] ZENG TAO, LOU QI-WEI, BAI YANG, et al. Enhanced visible-light-driven photocatalytic Activity of Multiferroic KBiFe₂O₅ by Adjusting pH Value. J. Inorg. Mater., 2014, 23(28): 220–226.

[16] SU R, SHEN Y, LI L, et al. Silver-modified nanosized ferroelectrics as a novel photocatalyst. Small, 2015, 11(2): 202–207.

[17] MOHAN S, SUBRAMANIAN B, BHAIUMIK I, et al. Nanocrystalline Bi₁₋ₓGdₓFeO₃ multiferroic photocatalyst on its sunlight driven photocatalytic activity. RSC Adv., 2014, 4: 16871–16878.

[18] GUO JIA, ZHU YI, ZHANG YUAN-MING, et al. Hydrothermal synthesis and visible-light photocatalytic properties of BiWO₄ with different structures and morphologies. J. Inorg. Mater., 2012, 27(1): 26–32.

[19] WÜRZFEL P, WÜRZFEL U. Physics of Solar Cells. Weinheim : Wiley, 2009.

[20] ZHANG GAN-TING, WU HUI, LI GUO-BAO. New high Tc multiferroics KBiFe₂O₅ with narrow band gap and promising photovoltaic effect. Sci. Rep., 2013, 3: 1265–1–8.

[21] GRINBERG I, WEST D V, TORRES M, et al. Enhanced visible-light-absorbing ferroelectric and photovoltaic materials. Nature, 2013, 503(7477): 509–512.

[22] RANJIBARI A, MOKHTARANI N. Post treatment of composting leachate using ZnO nanoparticles immobilized on moving media. Appl. Catal. B: Environ., 2017, 220: 211–221.

[23] WANG XIONG, LIN YING, DING XIFENG, et al. Enhanced visible-light-response photocatalytic activity of bismuth ferrite nanoparticles. J. Alloy and Compd., 2011, 509: 6585–6588.

[24] ZHOU YING, ZHANG XIAO-JING, ZHAO ZI-YAN, et al. Effects of pH on the visible-light induced photocatalytic and photoelectrochemical performances of hierarchical Bi₁₋ₓWO₃ microspheres. Superlattice Microst., 2014, 72: 238–244.

[25] YAO WEI-FENG, XU XIAO-HONG, et al. Photocatalytic property of perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials. Small, 2013, 9(8): 1334–1338.

[26] SUN YUE, LI JIA-WEN, LI ZHONG-HUA, et al. Design of highly ordered Ag-SrTiO₃ nanotube arrays for photocatalytic degradation of methyl orange. J. Solid State Chem., 2011, 184: 1924–1930.

[27] ZENG TAO, BAI YANG, LI HAO, et al. Fabrication of barium titanate nanophotocatalysts with gridding structures and photocatalytic activities. J. Inorg. Mater., 2015, 30(12): 1334–1338.
不同 pH 下 KBiFe₂O₅ 可见光催化性能研究

李健 1, 张刚华 2, 范立坤 2, 黄国全 1, 高志鹏 3, 曾涛 1,2

(1. 上海电力学院 环境与化学工程学院, 上海 200090; 2. 上海材料研究所 上海市工程材料应用与评价重点实验室, 上海 200437; 3. 中国工程物理研究院 流体物理研究所, 冲击波和爆轰物理国家重点实验室, 绵阳 621900)

摘 要: 采用温和的水热法制备了多铁 KBiFe₂O₅ 粉体。利用 X 射线衍射(XRD)和场发射扫描电子显微镜(FE-SEM)等手段对样品的纯度及形貌进行了表征。利用紫外-可见漫反射(UV-Vis DRS)测试了样品的光吸收性能。通过降解罗丹明 B(RhB)和甲基橙(MO)研究了染料溶液 pH 值对 KBiFe₂O₅ 可见光催化性能的影响。结果显示, KBiFe₂O₅ 的可见光催化性能随着溶液 pH 值的下降而显著提升, 这是由于溶液中的催化剂在酸性条件下具有更好的分散性, 并且染料分子更容易吸附到催化剂表面, 从而提高催化效率。

关 键 词: KBiFe₂O₅; 光催化剂; 可见光照射; pH

中图分类号: X703 文献标识码: A