Material Sciences 材料科学, 2017, 7(2), 224-231
Published Online March 2017 in Hans. http://www.hanspub.org/journal/ms
http://dx.doi.org/10.12677/ms.2017.72029

Hans汉斯

Review on Enhancement of $BiFeO_3$ Photocatalytic Property

Liangshuang Miao, Qiang Chen, Pai Li*

School of Materials Science and Engineering, Hubei University, Wuhan Hubei
Email: *paili@foxmail.com

Received: Mar. 18th, 2017; accepted: Mar. 28th, 2017; published: Mar. 31st, 2017

Abstract

We briefly review recent investigations on the enhancing photocatalytic performance of Bismuth ferrite $BiFeO_3$ both experimentally and theoretically. In this review, we mainly put our focus on most recent progress in ways (control of the size and shape of $BiFeO_3$; ions doping and designing BFO_3 nanocomposites) that can improve the photocatalytic properties of $BiFeO_3$. Among them, the most effective method is to form composite materials.

Keywords

$BiFeO_3$, Visible Light, Photocatalytic Property

提高铁酸铋光催化活性的进展研究

苗良爽，陈　强，李　派*

湖北大学材料科学与工程学院，湖北　武汉
Email: *paili@foxmail.com

收稿日期：2017年3月18日；录用日期：2017年3月28日；发布日期：2017年3月31日

摘　要

本文从理论与实验两方面总结了近年来三种提高铁酸铋$BiFeO_3$光催化性能的途径：调控铁酸铋晶粒尺寸和形貌、选择不同掺杂金属元素、设计不同$BiFeO_3$基复合材料。这三种调控手段都能有效提高$BiFeO_3$光催化活性，其中以形成复合材料体系的方法效果最为显著。

*通讯作者。

文章引用: 苗良爽, 陈强, 李派. 提高铁酸铋光催化活性的进展研究[J]. 材料科学, 2017, 7(2): 224-231.
http://dx.doi.org/10.12677/ms.2017.72029

关键词

$BiFeO_3$，可见光，光催化

1. 引言

铁酸铋 $BiFeO_3$ (BFO) [1]是目前唯一的室温多铁性材料，近年来在强关联电磁耦合领域受到物理材料学者们的青睐。此外，相对于传统的二氧化钛基光催化剂，BFO 具有更小的禁带宽度(2.0 eV 左右)，因而 BFO 在可见光范围内具有更好的光催化应用前景。但是较低的光量子效率阻碍了 BFO 基催化剂在可见光催化领域的实际应用。目前，提高 BFO 光催化性能的手段主要有：控制 BFO 的晶粒尺寸和形貌[2] [3] [4]、离子掺杂、设计 BFO 的复合材料[5] [6]等。本文总结归纳了主要的三种提高铁酸铋 BFO 光催化性能的方法，对 BFO 未来的应用提出了展望。

2. 提高铁酸铋光催化性能的三种方式

2.1. 控制铁酸铋的粒径和形貌

光催化剂的光催化性能取决于几个微观结构因素，比如晶粒尺寸、表面化学、形貌和结晶性。这些因素中，小的晶粒尺寸和特殊的形貌是最重要的，因为小的晶粒尺寸有利于形成大的表面区域，而特殊的形貌直接决定晶体完美和缺陷。此外，控制特定材料的尺寸和形貌已被广泛研究，这些因素在决定材料的的磁性、电学性能和光学性能方面扮演很重要的角色。虽然具有尺寸依赖性的铁酸铋的铁磁性和铁电性已经被研究，但是铁酸铋光催化性能的尺寸依赖性的研究还很少。

He 等人已经揭示了减小 BFO 纳米颗粒的尺寸，从而提高了光催化性能的提高[7]。这里的 BFO 纳米颗粒的尺寸是通过溶胶凝胶法中的不同的退火温度和时间来控制。虽然 BFO-550-1 的晶粒尺寸最小，它的催化性能还是不如 BFO-550-2。因为晶粒拥有大的比表面积通常伴有大量的表面缺陷，这些缺陷会导致光生电荷的复合，从而降低了光催化性能。Li 等人[8]也报道了晶粒尺寸对 BFO 纳米结构的光吸收和光催化性能有重大的影响。如今人们在无机材料的控制合成、自组织和规律几何形状方面取得了显著的进步。最近，有不少研究工作是关于通过不同的化学方法合成 BFO 的特定形貌并导致 BFO 对可见光相应的增强和光催化性能的提高。Fei 等人[9]报道了 BFO 片和棒高度择优取向的(111)c 面相对于 BFO 立方的(100)c 面有更高的光催化活性。Li 等人[10]也报道过类似的实验结果，显示 BFO 微球没有催化性能，BFO 微立方表现出很弱的光催化性能，而 BFO 的亚微立方有很高的光催化能力。Huo 等人[11]制备的介孔空心球的 BFO 也有很强的光催化活性。如表 1 所示为最近报道的不同尺寸和形貌的铁酸铋光催化剂的信息总结。

人们通常认为半导体光催化剂的基本原理是光生电子空穴迁移到催化剂表面作为氧化还原反应的来源，与被吸收的物质发生反应，然后导致了污染物的分解。BFO 纳米颗粒作为一种半导体光催化剂，降解有机染料的效率取决于光催化过程中晶粒的整体移动到晶体表面[12]光生电子空穴对的迁移。对纯的半导体光催化剂来说，电子空穴的复合可以分为两种，整体复合和表面复合。在结晶良好的大晶粒中，整体复合处于主导地位，它会随着晶体的尺寸的减小而减小。晶粒尺寸的减小同时会导致大的表面积，增

Table 1. Different size and morphology of bismuth ferrite photocatalyst
表 1. 不同尺寸和形貌的铁酸铋光催化剂

光催化剂	形貌	颗粒尺寸(nm)	制备方法	发表年份	参考文献
$BiFeO_3$	spherical	80~120	Sol-gel	2007	[14]
$BiFeO_3$	spherical	5	hydrothermal	2009	[15]
$BiFeO_3$	submicrocubes	500	hydrothermal	2010	[10]
$BiFeO_3$	pills/ rods	500~1000	hydrothermal	2011	[9]
$BiFeO_3$	Hollow/spheres	100~3000	aerosol-spraying	2011	[11]
$BiFeO_3$	thin films (mesoporous framework)	18	block copolymer	2011	[16]
$BiFeO_3$	nanoparticle	50~60	Sol-gel	2011	[17]
$Bi_2Fe_4O_9$	nanocrystals	14~78	Sol-gel	2011	[18]
$BiFeO_3$	spherical	30,000~50,000	hydrothermal	2012	[19]
$BiFeO_3$	nanofiber	220~480	electrospinning	2013	[20]
$Bi_2Fe_4O_9$	nanoflake	100~1500	hydrothermal	2013	[21]
$Bi_2Fe_4O_9$	defective cube	3000	solvothermal	2014	[22]
$BiFeO_3$	Cubic	1400	hydrothermal	2015	[2]
$BiFeO_3$	cubic inverse opal	270	Sol-gel	2015	[23]

加有效的活性位点[13]。另一方面，光学带隙是晶粒尺寸的函数，而电化学带隙会随着晶粒尺寸的增加而减小。此外，量子尺寸效应在极小的半导体晶粒尺寸下会限制电荷的移动与传输，同时会导致半导体导带和价带能级变成分立能级，使有效带隙变宽。这种情况会增强电子空穴的氧化还原能力，从而提高半导体的光催化活性。

2.2. 选择合适离子掺杂

BFO 的 A 位或 B 位掺杂异质原子(Cr^{3+}，Ti^{4+}，Mn^{3+}，La^{3+}等)对稳定 ABO_3 的钙钛矿结构和改变其性能方面有很重要的影响[24] [25] [26] [27]。Nan 组已经出版了好几篇关于离子掺杂提高铁酸铋光催化性能的报道：BFO 的 A 位掺 La [28]、Ca [29]、Ba [30]和在 A、B 为共掺 Ba/Mn [31]和 Ca/Mn [32]的研究都是通过基于电纺丝的溶胶凝胶法制备，这些离子掺杂对于 BFO 纳米纤维的尺寸、形貌和带隙的影响都很小。铋离子的变化和铁离子的替代由于其他金属离子的掺杂而产生杂相。结果显示由于 Bi 位离子的掺杂相结构从 R3c 空间群向 C222 空间群转变。且离子掺杂有利于光催化性能的提高，在可见光催化剂领域有很大的潜在应用价值。此外，研究表明这种光催化性能并不是随着掺杂浓度增加而单调的增加。当掺杂浓度超过特定值时，BFO 的光催化效率不升反降。文章认为 BFO 光催化性能随着掺杂浓度增加而增加的阶段，是因为自由载流子的增多，也就是光生电子空穴更加有效的分离即电子空穴复合速率的降低；当金属离子掺杂浓度太大时，会改变 BFO 导带的位置，同时带入空位和其它缺陷，从而降低催化剂的性能。Guo 等人[33]也报道了通过快速退火的溶胶凝胶法将 Gd 掺入 BFO 纳米粒子中。在 Gd 的掺杂浓度低于 0.1 时，会显著提高其光催化性能，然而，Gd 的掺杂浓度继续增加时，光催化性能降低。在掺杂浓度为 0.1 时出现的最大光催化值可以解释为此时在菱方和正交相界处出现的最大介电常数，这种现象会增大晶粒和溶液界面处的空间电荷区域面积。如表 2 所示为最近报道的不同元素掺杂的铁酸铋光催化剂的信息总结。

Table 2. Different doping elements of bismuth ferrite photocatalyst
表 2. 不同元素掺杂的铁酸铋光催化剂

光催化剂	掺杂元素	ABO_3结构材料掺杂的位置	掺杂含量(%)	发表年份	参考文献
$BiFeO_3$	Gd	A	10	2010	[36]
$Bi_2Fe_4O_9$	Al	B	50	2012	[37]
$BiFeO_3$	Sr	A	0	2012	[38]
$BiFeO_3$	La	A	10	2012	[39]
$BiFeO_3$	Ca, Mn	A, B	15, 5	2013	[40]
$BiFeO_3$	Ca	A	15	2013	[41]
$BiFeO_3$	Ba,Mn	A,B	15	2013	[42]
$BiFeO_3$	La/Yb	A	5	2013	[43]
$BiFeO_3$	Ba	A	15	2014	[30]
$BiFeO_3$	Ca	A	10	2014	[44]
$BiFeO_3$	Nd	A	20	2015	[45]
$BiFeO_3$	La, Ba/Ca	A	5, 5/5	2015	[46]
$BiFeO_3$	Dy	A	15	2015	[47]

从以上的实验结果可知，掺杂后的铁酸铋光催化活性的提高取决于掺杂离子种类和浓度。金属离子掺杂是作为电子或空穴捕获陷阱来改变电子空穴的复合率从而影响 BFO 的光催化性能。通常铁酸铋的光催化效率与掺杂浓度通常呈抛物线的关系。最初随着掺杂浓度的增加导致有效的陷阱位点的减少，光催化效率提高。之后带隙中金属离子杂质能级的出现使带隙能量红移，杂质能级和导带或者价带间由于电荷的转移出现可见光的吸收[34]。电子空穴复合率随着掺杂浓度增加以指数方式增加，从而降低了光催化性能。因此，光催化活性最佳值的出现可以解释为上述两种效应的竞争平衡值。此外，光催化最佳值的出现也可能是因为界面处出现最大介电常数和空间电荷区域面积的增大的缘故[35]。半导体和另外相(例如液体、气体或金属)的接触会导致电荷重新分布和形成双电子层[13]。在界面处可移动的载流子的迁移或者表面电载流子的陷阱产生了空间电荷层。这也为成分过渡处光催化性能最佳掺杂浓度提供最合理的解释。

2.3. 设计铁酸铋基复合材料

此外，很多研究通过控制合成 BFO 的复合材料来提高其光催化活性。Luo 和 Maggard 报道了 $SrTiO_3$ 包裹 BFO 的纳米结构在可见光照射下可以分解水产生氢气和表现出增强的光催化性能[48]。另一方面，此复合材料系统提供了一种独特有竞争力的方法使具有可见光活性的 $SrTiO_3$ 复合材料光催化系统有了更宽的应用范围。Li 等人[49]也报道锐钛矿二氧化钛包裹 BFO 的纳米复合材料很强的可见光光催化性能。Guo 等人[50]通过溶胶凝胶法合成的 BFO 纳米颗粒和 γ-Fe_2O_3 寄生相复合材料，发现其光催化性能得到了很大的提高。此外，也有报道通过微波水热法的到纯的 $Bi_{25}FeO_{40}$、BFO 和 $Bi_{25}FeO_{40}$-BFO 混合物，发现 $Bi_{25}FeO_{40}$-BFO 混合物的光催化性能得到了大幅的提高，这种结构可以解释为混晶效应[51]。有意思的是，Li 等人[52]通过快捷的水热反应法得到了 BFO-石墨烯的纳米复合材料。复合材料的光催化速率是纯 BFO 的六倍，石墨烯的引入可以改变带隙和与 BFO 形成共价作用。最近，Liu 等人[53]制备的 BFO/C 的核壳结构的光催化性能也得到了大幅提高，这里碳层的引入提高了 BFO 的光吸收和对染料的吸附作用。同时有利于光生电子空穴的分离，从而提高了光催化性能。如表 3 所示为最近报道的不同化合物复合铁酸铋光催化剂的信息总结。

Table 3. Different bismuth ferrite based composites photocatalyst
表 3. 不同复合材料体系铁酸铋基光催化剂

复合光催化剂	复合结构	光催化应用	制备方法	发表年份	参考文献
$SrTiO_3$- $BiFeO_3$	coating	water splitting	hydrothermal	2006	[6]
$BiFeO_3$/TiO2	core-shell	photodegradation	hydrothermal	2009	[38]
$BiFeO_3$/SWCNTs	coating	reduction of CO_2	sol-gel	2009	[8]
$BiFeO_3$/γ-Fe_2O_3	heterojunction	photodegradation	sol–gel	2011	[39]
$BiFeO_3$/$Bi_{25}FeO_{40}$	heterojunction	photodegradation	hydrothermal	2012	[2]
$BiFeO_3$–$(Na_{0.5}Bi_{0.5})TiO_3$	coating	photodegradation	sol–gel	2012	[45] [46]
$BiFeO_3$–graphene	coating	photodegradation	hydrothermal	2013/2014	[3] [11] [47]
$BiFeO_3$@carbon	core-shell	photodegradation	electrospining	2013	[40]
$BiFeO_3$/(γ)-Fe_2O_3	heterojunction	photodegradation	sol–gel	2013	[48]
$Bi_{25}FeO_{40}$-graphene	coating	photodegradation	hydrothermal	2013	[12]
$Bi_2Fe_4O_9$-graphene	coating	photodegradation	hydrothermal	2014/2015	[49] [50] [51]
Pt/$BiFeO_3$	cover	photodegradation	hydrothermal	2015	[52]
g-C_3N_4/$BiFeO_3$	coating	photodegradation	deposition–precipitation	2015	[53]
$BiFeO_3$@carbon -microspheres	heterojunction	photodegradation	hydrothermal	2015	[54]
Ag, Au @ $BiFeO_3$	coating	photodegradation	Templates method and thermal evaporation	2015	[55]
Au/ $BiFeO_3$	cover	photodegradation	sol–gel	2015	[56]
$BiFeO_3$/N-graphene	coating	photodegradation	hydrothermal	2016	[57]

与传统材料相比，复合纳米材料有几个优势，比如量子尺寸效应，纳米尺寸的半导体颗粒拥有较高的氧化还原能力，同时提高带隙能量，这些都有助于提高催化剂的活性[54]。此外，纳米复合材料可以分为两类，一类是两种不同的半导体的复合，另一种是半导体和非半导体的复合，另一方面两种半导体的接触时，他们对应的不同的导带和价带的能级结构可以作为一种很有潜力的提高电荷分离，提高载流子寿命，增加界面电荷迁移的效率[55]。半导体界面高效的电子转移被认为是敏化剂和 BFO 的复合形成，BFO 的导带位置必须在敏化剂的对应的导带之上。在可见光的照射下，只有敏化剂被激发，产生的电子被激发到 BFO 的导带。如果敏化剂的价带在 BFO 的价带之下，产生的空穴就不会移动到 BFO 的价带。当系统在可见光照射下时，两种半导体都被激发，电子从敏化剂移动到 BFO，这样加上 BFO 自身激发的电子，BFO 导带获得的电子浓度变高。BFO 价带产生的空穴转移到敏化剂的价带上，导致敏化剂和电解液界面的空穴浓度增加。事实上当敏化剂的浓度升高时，降解率并不会变化。当半导体接触时，粒子间会发生电荷转移。提高溶液中敏化剂的量会产生两种影响。产生自由电子数的增加和离子间碰撞几率的增加。这两种影响有利于降解效率的提高。然而，一种矛盾的现象会被观察到：当敏化剂的量达到一个临界值的时候，由于陷阱的作用，载流子会被耗尽[56] [57]。另一方面，对于 BFO 和石墨烯或者碳材料的复合材料系统，在光催化过程中，引入的碳和石墨烯将提供一种网状结构来收集和转移 BFO 价带产生的电子，这样会减少光生电子空穴的复合速率，使更多的留下来的空穴参与氧化反应，从而降解有机染料[53]。附着的碳和石墨烯层有利于 BFO 纳米复合材料的光子的吸收，这些光子会参与光催化反应，从而提高光催化性能。

3. 展望

本文总结了目前提高 BFO 光催化性能的最主要的三种途径：控制铁酸铋的颗粒大小和形貌、离子掺杂和设计铁酸铋复合材料，并详细介绍了这三种改善途径的理论机制。目前，BFO 的光催化活性已经能应用与处理废水中的有机污染物，但在光解制氢以及 CO_2 燃料方面研究尚浅。我们期待 BFO 在能源领域与环境领域内能有更好的建树。

致　谢

感谢国家自然科学基金(51202062，51572073，61274010)湖北省自然科学基金(2015CFA038, 2015CFB265)资助。

参考文献 (References)

[1] Catalan, G. and Scott, J.F. (2009) Physics and Applications of Bismuth Ferrite. *Advanced Materials*, **21**, 2463-2485. https://doi.org/10.1002/adma.200802849

[2] Gao, T., Chen, Z., Niu, F., Zhou, D., Huang, Q., Zhu, Y., Qin, L., Sun, X. and Huang, Y. (2015) Shape-Controlled Preparation of Bismuth Ferrite by Hydrothermal Method and Their Visible-Light Degradation Properties. *Journal of Alloys and Compounds*, **648**, 564-570.

[3] Wang, X., Lin, Y., Ding, X. and Jiang, J. (2011) Enhanced Visible-Light-Response Photocatalytic Activity of Bismuth Ferrite Nanoparticles. *Journal of Alloys and Compounds*, **509**, 6585-6588.

[4] Tan, G.Q., Zheng, Y.Q. and Miao, H.Y. (2012) Controllable Microwave Hydrothermal Synthesis of Bismuth Ferrites and Photocatalytic Characterization. *Journal of the American Ceramic Society*, **95**, 280-289. https://doi.org/10.1111/j.1551-2916.2011.04775.x

[5] Zhu, A., Zhao, Q., Li, X. and Shi, Y. (2014) $BiFeO_3/TiO_2$ Nanotube Arrays Composite Electrode: Construction, Characterization, and Enhanced Photo Electrochemical Properties. *ACS Applied Materials & Interfaces*, **6**, 671-679. https://doi.org/10.1021/am404774z

[6] Niu, F., Chen, D., Qin, L., Gao, T., Zhang, N., Wang, S., Chen, Z., Wang, J., Sun, X. and Huang, Y. (2015) Synthesis of Pt/BiFeO3 Heterostructured Photocatalysts for Highly Efficient Visible-Light Photocatalytic Performances. *Solar Energy Materials and Solar Cells*, **143**, 386-396.

[7] He, J., Guo, R.Q., Fang, L., Dong, W., Zheng, F.G. and Shen, M.R. (2013) Characterization and Visible Light Photocatalytic Mechanism of Size-Controlled $BiFeO_3$ Nanoparticles. *Materials Research Bulletin*, **48**, 3017-3024.

[8] Li, S., Lin, Y.H., Zhang, B.P., Nan, C.W. and Wang, Y. (2009) Photocatalytic and Magnetic Behaviors Observed in Nanostructured $BiFeO_3$ Particles. *Journal of Applied Physics*, **105**, Article ID: 056105. https://doi.org/10.1063/1.3080131

[9] Fei, L., Yuan, J., Hu, Y., Wu, C., Wang, J. and Wang, Y. (2011) Visible Light Responsive Perovskite BiFeO3 Pills and Rods with Dominant {111}c Facets. *Crystal Growth & Design*, **11**, 1049-1053. https://doi.org/10.1021/cg101144s

[10] Li, S., Lin, Y.H., Zhang B.P., Wang, Y. and Nan, C.W. (2010) Controlled Fabrication of BiFeO3 Uniform Microcrystals and Their Magnetic and Photocatalytic Behaviors. *The Journal of Physical Chemistry C*, **114**, 2903-2908. https://doi.org/10.1021/jp910401u

[11] Huo, Y., Miao, M., Zhang, Y., Zhu, J. and Li, H. (2011) Aerosol-Spraying Preparation of a Mesoporous Hollow Spherical $BiFeO_3$ Visible Photocatalyst with Enhanced Activity and Durability. *Chemical Communications*, **47**, 2089-2091. https://doi.org/10.1039/C0CC04247A

[12] Zhang, Z.B., Wang, C.C., Zakaria, R. and Ying, J.Y. (1998) Role of Particle Size in Nanocrystalline TiO_2-Based Photocatalysts. *The Journal of Physical Chemistry B*, **102**, 10871-10878. https://doi.org/10.1021/jp982948+

[13] Amy, L., Linsebigler, G.L. and Yates, J.T. (1995) Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chemical Reviews*, **95**, 735-758. https://doi.org/10.1021/cr00035a013

[14] Gao, F., Chen, X.Y., Yin, K.B., Dong, S., Ren, Z.F., Yuan, F., Yu, T., Zou, Z.G. and Liu, J.M. (2007) Visible-Light Photocatalytic Properties of Weak Magnetic BiFeO3 Nanoparticles. *Advanced Materials*, **19**, 2889-2892. https://doi.org/10.1002/adma.200602377

[15] Xue, Z., Wang, T. and Chen, B. (2015) Degradation of Tetracycline with $BiFeO_3$ Prepared by a Simple Hydrothermal Method. *Materials*, **8**, 6360-6378. https://doi.org/10.3390/ma8095310

[16] Reitz, C., Suchomski, C., Weidmann, C. and Brezesinski, T. (2011) Block Copolymer-Templated $BiFeO_3$ Nanoarchi-

tectures Composed of Phase-Pure Crystallites Intermingled with a Continuous Mesoporosity: Effective Visible-Light Photocatalysts. *Nano Research*, **4**, 414-424. https://doi.org/10.1007/s12274-011-0096-y

[17] Deng, J., Banerjee, S., Mohapatra, S.K., Smith, Y.R. and Misra, M. (2011) Bismuth Iron Oxide Nanoparticles as Photocatalyst for Solar Hydrogen Generation from Water. *Journal of Fundamentals of Renewable Energy and Applications*, **1**, 1-10.

[18] Zhang, Q., Gong, W., Wang, J., Ning, X., Wang, Z., Zhao, X., Ren, W. and Zhang, Z. (2011) Size-Dependent Magnetic, Photoabsorbing, and Photocatalytic Properties of Single-Crystalline Bi2Fe4O9 Semiconductor Nanocrystals. *Journal of Physical Chemistry C*, **115**, 25241-25246. https://doi.org/10.1021/jp208750n

[19] Wei, J., Li, H., Mao, S., Zhang, C., Xu, Z. and Dkhil, B. (2012) Effect of Particle Morphology on the Photocatalytic Activity of $BiFeO_3$ Microcrystallites. *Journal of Materials Science-Materials in Electronics*, **23**, 1869-1874. https://doi.org/10.1007/s10854-012-0676-y

[20] Wang, W., Li, N., Chi, Y., Li, Y., Yan, W., Li, X. and Shao, C. (2013) Electrospinning of Magnetical Bismuth Ferrite Nanofibers with Photocatalytic Activity. *Ceramics International*, **39**, 3511-3518.

[21] Yang, X., Zhang, Y., Xu, G., Wei, X., Ren, Z., Shen, G. and Han, G. (2013) Phase and Morphology Evolution of Bismuth Ferrites via Hydrothermal Reaction Route. *Materials Research Bulletin*, **48**, 1694-1699.

[22] Liu, Y., Zuo, R. and Qi, S. (2014) Surfactant-Free Solvothermal Synthesis and Optical Characterization of Bi2Fe4O9 in Mixed H2O/EtOH Solvent. *Powder Technology*, **254**, 30-35.

[23] Tan, T.Y., Xie, W., Zhu, G.J., Shan, J., Xu, P.F., Li, L.N. and Wang, J.W. (2015) Fabrication and Photocatalysis of $BiFeO_3$ with Inverse Opal Structure. *Journal of Porous Materials*, **22**, 659-663. https://doi.org/10.1007/s10934-015-9938-4

[24] Palkar, V.R., Kundaliya, D.C. and Malik, S.K. (2003) Effect of Mn Substitution on Magnetoelectric Properties of Bismuth Ferrite System. *Journal of Applied Physics*, **93**, 4337. https://doi.org/10.1063/1.1558992

[25] Wang, Y. and Nan, C.W. (2006) Enhanced Ferroelectricity in Ti-Doped Multiferroic $BiFeO_3$ Thin Films. *Applied Physics Letters*, **89**, Article ID: 052903. https://doi.org/10.1063/1.2222242

[26] Lin, Y.H., Jiang, Q.H., Wang, Y., Nan, C.W., Chen, L. and Yu, J. (2007) Enhancement of Ferromagnetic Properties in $BiFeO_3$ Polycrystalline Ceramic by La Doping. *Applied Physics Letters*, **90**, Article ID: 172507. https://doi.org/10.1063/1.2732182

[27] Hiroshi Naganuma, J.M. and Okamura, S. (2008) Ferroelectric, Electrical and Magnetic Properties of Cr, Mn, Co, Ni, Cu Added Polycrystalline $BiFeO_3$ Film. *Applied Physics Letters*, **93**, Article ID: 052901. https://doi.org/10.1063/1.2965799

[28] Soltani, T. and Entezari, M.H. (2014) Solar-Fenton Catalytic Degradation of Phenolic Compounds by Impure Bismuth Ferrite Nanoparticles Synthesized via Ultrasound. *Chemical Engineering Journal*, **251**, 207-216.

[29] Li, Z., Shen, Y. and Yang, C. (2013) Significant Enhancement in the Visible Light Photocatalytic Properties of $BiFeO_3$-Graphene Nanohybrids. *Journal of Materials Chemistry A*, **1**, 823-829. https://doi.org/10.1039/C2TA00141A

[30] Feng, Y.N., Wang, H.C., Shen, Y., Lin, Y.H. and Nan, C.W. (2014) Magnetic and Photocatalytic Behaviors of Ba-Doped $BiFeO_3$ Nanofibers. *International Journal of Applied Ceramic Technology*, **11**, 676-680. https://doi.org/10.1111/ijac.12205

[31] Luo, J. and Maggard, P.A. (2006) Hydrothermal Synthesis and Photocatalytic Activities of SrTiO3-Coated Fe2O3 and BiFeO3. *Advanced Materials*, **18**, 514-517. https://doi.org/10.1002/adma.200500109

[32] Feng, Y.N., Wang, H.C., Shen, Y., Lin, Y.H. and Nan, C.W. (2013) Magnetic and Photocatalytic Behaviors of Ca Mn Co-Doped $BiFeO_3$ Nanofibres. *Modern Research in Catalysis*, **2**, 1-5. https://doi.org/10.4236/mrc.2013.23A001

[33] Guo, R., Fang, L., Dong, W., Zheng, F.G. and Shen, M.R. (2010) Enhanced Photocatalytic Activity and Ferromagnetism in Gd Doped $BiFeO_3$ Nanoparticles. *The Journal of Physical Chemistry C*, **114**, 21390-21396.

[34] Wonyong Choi, A.T. and Hoffmann, M.R. (1994) The Role of Metal Ion Dopants in Quantum-Sized TiO_2: Correlation between Photoreactivity and Charge Carrier Recombination Dynamics. *The Journal of Physical Chemistry C*, **98**, 13669-13679. https://doi.org/10.1021/j100102a038

[35] Bhardwaj, A., Burbure, N.V., Gamalski, A. and Rohrer, G.S. (2010) Composition Dependence of the Photochemical Reduction of Ag by $Ba_{1-x}Sr_xTiO_3$. *Chemistry of Materials*, **22**, 3527-3534. https://doi.org/10.1021/cm100718t

[36] Wang, X., Mao, W. and Zhang, J. (2015) Facile Fabrication of Highly Efficient G-C3N4/BiFeO3 Nanocomposites with Enhanced Visible Light Photocatalytic Activities. *Journal of colloid and interface science*, **448**, 17-23.

[37] Liu, Z., Wu, B., Yin, D., Zhu, Y. and Wang, L. (2012) Enhanced Photocatalytic Activity in Al-Substituted Bi2Fe4O9 Submicrocrystals. *Journal of Materials Science*, **47**, 6777-6783. https://doi.org/10.1007/s10853-012-6600-2

[38] Wang, B., Wang, S., Gong, L. and Zhou, Z. (2012) Structural, Magnetic and Photocatalytic Properties of Sr2+-Doped

$BiFeO_3$ Nanoparticles Based on an Ultrasonic Irradiation Assisted Self-Combustion Method. *Ceramics International*, **38**, 6643-6649.

[39] Zhang, Z., Liu, H., Lin, Y., Wei, Y., Nan, C.W. and Deng, X. (2012) Influence of La Doping on Magnetic and Optical Properties of Bismuth Ferrite Nanofibers. *Journal of Nanomaterials*, **2012**, Article ID: 238605. https://doi.org/10.1155/2012/238605

[40] Sun. H., Liu. Y. and Zhang. Y. (2014) Synthesis of Bi2Fe4O9/Reduced Graphene Oxide Composite by One-Step Hydrothermal Method and Its High Photocatalytic Performance. *Journal of Materials Science-Materials in Electronics*, **25**, 4212-4218.

[41] Feng, Y.N., Wang, H.C., Luo, Y.D., Shen, Y. and Lin, Y.H. (2013) Ferromagnetic and Photocatalytic Behaviors Observed in Ca-Doped BiFeO3 Nanofibres. *Journal of Applied Physics*, **113**, Article ID: 146101. https://doi.org/10.1063/1.4801796

[42] Wang, H.C., Lin, Y.H., Feng, Y.N. and Shen, Y. (2013) Photocatalytic Behaviors Observed in Ba and Mn Doped BiFeO3 Nanofibers. *Journal of Electroceramics*, **31**, 271-274. https://doi.org/10.1007/s10832-013-9818-8

[43] Wu, C., Wei, J. and Kong, F. (2013) Effect of Rare Earth Dopants on the Morphologies and Photocatalytic Activities of $BiFeO_3$ Microcrystallites. *Journal of Materials Science-Materials in Electronics*, **24**, 1530-1535. https://doi.org/10.1007/s10854-012-0966-4

[44] Zaki, M.I., Ramadan, W., Katrib, A. and Rabee, A.I.M. (2014) Surface Chemical and Photocatalytic Consequences of Ca-Doping of $BiFeO_3$ as Probed by XPS and HO_2 Decomposition Studies. *Applied Surface Science*, **317**, 929-934.

[45] Chen, Z., Wu, Y., Wang, X., Jin, W. and Zhu, C. (2015) Ferromagnetism and Enhanced Photocatalytic Activity in Nd Doped BiFeO3 Nanopowders. *Journal of Materials Science-Materials in Electronics*, **26**, 9929-9940. https://doi.org/10.1007/s10854-015-3669-9

[46] Reddy Vanga, P., Mangalaraja, R.V. and Ashok, M. (2015) Structural, Magnetic and Photocatalytic Properties of La and Alkaline Co-Doped $BiFeO_3$ Nanoparticles. *Materials Science in Semiconductor Processing*, **40**, 796-802.

[47] Sakar, M., Balakumar, S., Saravanan, P. and Bharathkumar, S. (2015) Compliments of Confinements: Substitution and Dimension Induced Magnetic Origin and Band-Bending Mediated Photocatalytic Enhancements in $Bi_{1-x}Dy_xFeO_3$ Particulate and Fiber Nanostructures. *Nanoscale*, **7**, 10667-10679. https://doi.org/10.1039/C5NR01079A

[48] Hu, Z.T., Liu. J. and Yan, X. (2015) Low-Temperature Synthesis of Graphene/Bi2Fe4O9 Composite for Synergistic Adsorption-Photocatalytic Degradation of Hydrophobic Pollutant under Solar Irradiation. *Chemical Engineering Journal*, **262**, 1022-1032.

[49] Li, S., Lin, Y.H., Zhang, B.P., Li, J.F. and Nan, C.W. (2009) $BiFeO_3/TiO_2$ Core-Shell Structured Nanocomposites as Visible-Active Photocatalysts and Their Optical Response Mechanism. *Journal of Applied Physics*, **105**, Article ID: 054310. https://doi.org/10.1063/1.3091286

[50] Guo, R.Q., Fang, L., Dong, W., Zheng, F.G. and Shen, M.R. (2011) Magnetically Separable $BiFeO_3$ Nanoparticles with a γ-Fe_2O_3 Parasitic Phase: Controlled Fabrication and Enhanced Visible-Light Photocatalytic Activity. *Journal of Materials Chemistry*, **21**, 18645-18652. https://doi.org/10.1039/c1jm13072b

[51] Liu, Y. and Zuo, R.Z. (2012) Tunable Morphology and Optical Absorption of Bismuth Ferrite Synthesized by Sol–Gel–Hydrothermal Method. *Journal of Materials Science*: *Materials in Electronics*, **23**, 2276-2281. Https://Doi.Org/10.1007/S10854-012-0816-4

[52] Xian, T., Yang, H. and Di, L.J. (2015) Graphene-Assisted Enhancement of Photocatalytic Activity of Bismuth Ferrite Nanoparticles. *Research on Chemical Intermediates*, **41**, 433-441. https://doi.org/10.1007/s11164-013-1204-2

[53] Liu, Y., Zuo, R.Z. and Qi, S.S. (2013) Controllable Preparation of $BiFeO_3$ Carbon Core/Shell Nanofibers with Enhanced Visible Photocatalytic Activity. *Journal of Molecular Catalysis A*: *Chemical*, **376**, 1-6. https://doi.org/10.1016/j.molcata.2013.04.005

[54] Guo, C., Ge, M., Liu, L., Gao, G., Feng, Y. and Wang, Y. (2009) Directed Synthesis of Mesoporous TiO_2 Microspheres: Catalysts and Their Photocatalysis for Bisphenol a Degradation. *Environmental Science & Technology*, **44**, 419-425. https://doi.org/10.1021/es9019854

[55] Long, M., Cai, W., Cai, J., Zhou, B., Chai, X. and Wu, Y. (2006) Efficient Photocatalytic Degradation of Phenol over $Co_3O_4/BiVO_4$ Composite under Visible Light Irradiation. *The Journal of Physical Chemistry B*, **110**, 20211-20216. https://doi.org/10.1021/jp063441z

[56] Bessekhouad, Y., Robert, D. and Weber, J.V. (2004) $B_{i2}S_3/TiO_2$ and CdS/TiO_2 Heterojunctions as an Available Configuration for Photocatalytic Degradation of Organic Pollutant. *Journal of Photochemistry and Photobiology A*: *Chemistry*, **163**, 569-580.

[57] Bessekhouad, Y., Robert, D. and Weber, J.V. (2005) Photocatalytic Activity of Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ Heterojunctions. *Catalysis Today*, **101**, 315-321.