

## Photocatalytic degradation of Doxycycline in aqueous solution using Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> catalysts

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**Abstract:** Photocatalytic degradation of Doxycycline in heterogeneous media constituted by nanoparticles of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> was studied. The Bi<sub>2</sub>WO<sub>6</sub> was prepared by hydrothermal method, and the Fe<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> was obtained by mechanical mixing of Bi<sub>2</sub>WO<sub>6</sub> to an amount of Fe<sub>2</sub>O<sub>3</sub> and their photocatalytic activity to degrade doxycycline (Dox) under UV irradiation supported by H<sub>2</sub>O<sub>2</sub> were studied. The H<sub>2</sub>O<sub>2</sub> reacts with photogenerated electrons leading to the production of hydroxyl radicals (OH•). The Fe<sub>2</sub>O<sub>3</sub> acts like a Fenton reagent, accelerating the production of OH•. In the present study Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system demonstrate much higher photocatalytic efficiency to degrade Dox than pure Bi<sub>2</sub>WO<sub>6</sub>.

**Keywords:** Photodegradation; Doxycycline; UV irradiation; Photo-Fenton.

### 1. Introduction

Increasing demand and shortage of clean water sources due to population growth and long-term droughts have become an issue worldwide. It is estimated that millions of people die of severe waterborne diseases annually.

Water is necessary for the survival of all forms of life on our planet. For humans, access to clean and safe water is of fundamental importance for achieving and maintaining acceptable living conditions. One of the greatest achievements of the past century, regarding the protection of public health and the environment, was the development and the wide application of efficient treatment methods for water and wastewaters <sup>1,2</sup>. However, one of the most critical environmental challenges that we have to face in the 21st century is a sustainable supply of clean and safe water because clean water has become an increasingly scarce resource. In view to suppress the worsening of clean water shortage, development of advanced with low-cost and high-efficiency water treatment technologies to treat and reuse wastewater is essential.

In recent years, a broad range of organic pollutants has been identified in the aquatic environment, in concentrations ranging from ng/L to mg/L <sup>1,2</sup>. Despite their low concentration, several effects of these organic pollutants on aquatic organisms have been reported, such as acute and chronic toxicity, endocrine disruption and bioaccumulation.

As Doxycycline (Dox) is from a wide-range antibiotic compound with activity against many species of bacteria is used as a pharmacological agent to treat chronic prostatitis, sinusitis, syphilis, chlamydia, pelvic inflammatory disease, acne, rosacea, and rickettsial infections. However, the doxycycline is commonly detected in the aquatic environment and Wastewater Treatment Plants effluents <sup>2</sup>.

Unfortunately, conventional chemical and biological oxidation treatment methods being employed for water and wastewater usually fail to remove most antibiotics <sup>1-6</sup>. Also, physical treatment methods of water and wastewater, such as adsorption and membrane filtration, transfer these compounds from one phase to another, rather than removing them <sup>1,2,5</sup>. Therefore, for their abatement, advanced treatment methods of water and wastewater are required, in particular in the case that the treated domestic wastewater effluents may be considered for reuse applications <sup>2,7</sup>.

In recent years, several advanced water and wastewater treatment methods have been developed <sup>1,2</sup>. Among them, photocatalysis has received considerable attention as a promising green technology for environmental clean-up.

The development of new photocatalysts is attracting enormous importance. Among them, the Bismuth tungstate (Bi<sub>2</sub>WO<sub>6</sub>) is a typical n-type direct bandgap

semiconductor with a bandgap of 2.75 eV and has prospective applications catalysis <sup>8-10</sup>. In addition, it has been found that Bi<sub>2</sub>WO<sub>6</sub> might act as a stable photocatalyst for the photochemical decomposition of organic contaminants <sup>11</sup>. Additionally, the unique structure of the photocatalyst could enhance its photoreactivity the photoactivity of Bi<sub>2</sub>WO<sub>6</sub>, in which the transfer of electrons to the surface was improved along with the layered network <sup>12,13</sup>. Bi<sub>2</sub>WO<sub>6</sub> exhibit a possible catalytic ability to numerous organic chemicals, and it is mostly synthesized by hydrothermal or solvothermal method.

In order to enhance catalytic efficiency, Bi<sub>2</sub>WO<sub>6</sub> catalyst could be doped with metal or metal oxide, which might trap the photogenerated electrons and restrain the recombination of hole-electron pair <sup>14,15</sup>. H<sub>2</sub>O<sub>2</sub> is a typical oxidative agent and has been often used as ineffective water treatment. As an electron capture agent, H<sub>2</sub>O<sub>2</sub> can also react with photogenerated electrons to produce hydroxyl radicals (OH<sup>•</sup>) as established in eq. (1) <sup>5,16</sup>.



Therefore, when H<sub>2</sub>O<sub>2</sub> is present with Bi<sub>2</sub>WO<sub>6</sub>/Fe<sub>2</sub>O<sub>3</sub> composite, it could interact with the composite and affect the photocatalytic capacity displaying higher photodegradation efficiency.

The present work proposes to dope Bi<sub>2</sub>WO<sub>6</sub> with Fe<sub>2</sub>O<sub>3</sub> to prepare Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub> composite and investigate its efficiency to degrade Doxycycline as an organic pollutant in the presence of H<sub>2</sub>O<sub>2</sub>. In previous work <sup>17</sup>, we have tested the efficiency of the synthesized composite in the degradation of Methyl Orange dye and Phenol as artificial pollutants.

## 2. Materials and Methods

### 2.1. Chemicals and Catalysts preparation

All the chemicals used in this work were analytical grade without further purification.

The Bi<sub>2</sub>WO<sub>6</sub> as synthesized from Bi (NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O according to the published procedure <sup>18</sup>. The iron oxide was prepared <sup>19</sup> by drying Iron III nitrate nonahydrate FeN<sub>3</sub>O<sub>9</sub>.9H<sub>2</sub>O at 120°C for 2h then

submitting the samples to a further calcination treatment at 500°C for 2 hours. The Fe<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> mixed samples were obtained with a mechanical mixing in an agate mortar, by adding 5% of Fe<sub>2</sub>O<sub>3</sub> to Bi<sub>2</sub>WO<sub>6</sub>.

### 2.2. Characterization

The composite structure was analyzed by X-ray diffraction (XRD) using a Rich Seifert 3000 diffractometer with Cu-K.

The UV-visible diffuse reflection spectra (DRS) of the photocatalyst were measured by a Cary 100 (Varian) spectrometer at the range of 250-600 nm using BaSO<sub>4</sub> as a reflectance standard and were converted from UV-visible absorption spectra according to the Kubelka-Munk equation.

### 2.3. Photocatalytic experiments

Photocatalytic activity of the photocatalysts prepared was evaluated by photocatalytic degradation of Dox under UV light irradiation. A reflective enclosure equipped with four circular fluorescent tubes type Philip 15 W with a maximum emission at 365 nm was used as the light source. The solution was placed in a central position in a quartz tube. The initial concentration of Dox in pure water was 4x10<sup>-5</sup> mol/L, and a concentration of 1g/L of the photocatalyst and H<sub>2</sub>O<sub>2</sub> (5%) was stirred.

Before the experiment, the mixed solution (catalyst+Dox) was magnetically stirred in the dark for 20 min to ensure the establishment of an adsorption-desorption equilibrium between the catalyst and Dox. At given times, a definite volume of the suspension was extracted and filtered using a filter (RC 0.45 μm). The Dox in the suspension was determined by measuring the absorbance value at approximately 275 nm using a carry 300 spectrophotometer.

Photolysis of Dox under UV and in the absence of catalysts was carried out under the same conditions experimental used in this work. The photocatalytic degradation mechanism is shown in Fig.1.

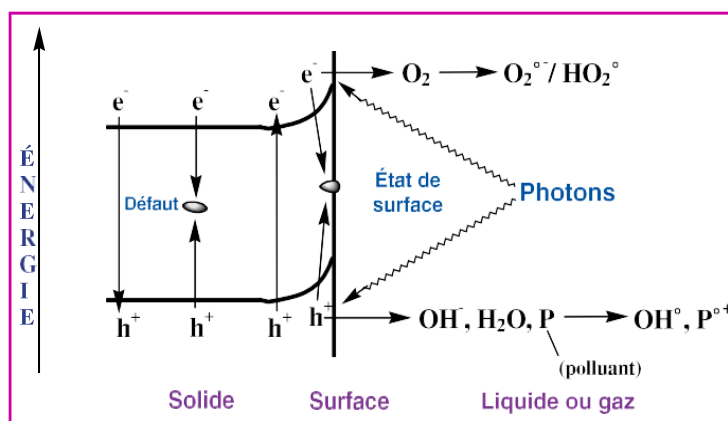


Figure 1. Mecanism of photocatalysis degradation

### 3. Results and discussion

#### 3.1. Materials characterization

The crystal structure of the prepared catalysts was investigated by XRD, and the results are shown in Fig.2. The  $\text{Bi}_2\text{WO}_6$  presented russellite phase (JCPDS

card: 39-0256). For  $\text{Fe}_2\text{O}_3$  the diffraction peaks corresponded to the standard  $\text{Fe}_2\text{O}_3$  (JCPDS card: 65-3107), in the  $\text{Bi}_2\text{WO}_6\text{-Fe}_2\text{O}_3$  (5%) samples the peaks showed just the russellite structure corresponding to the presence of  $\text{Bi}_2\text{WO}_6$ .

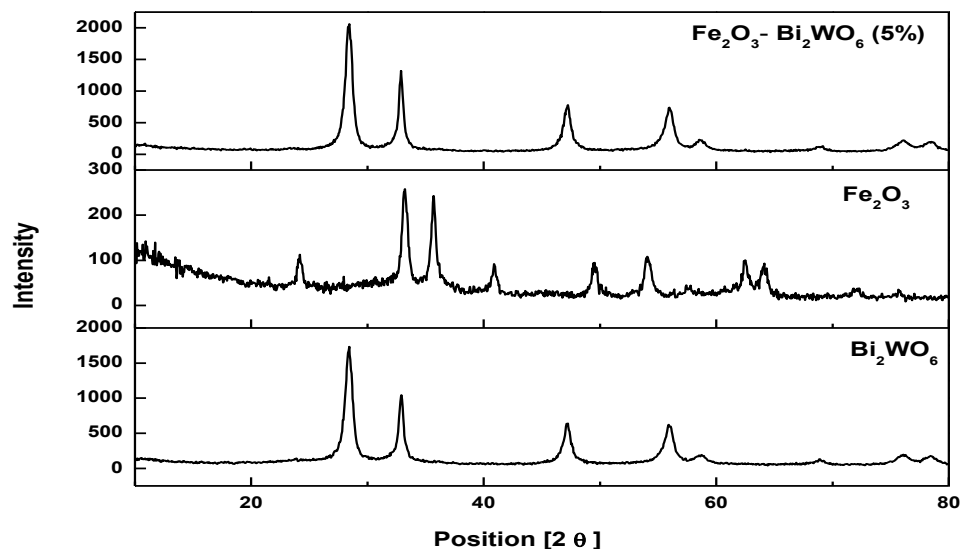


Figure 2. The XRD patterns of the catalysts prepared

The Light absorption of the catalysts and the migration of light-induced electrons and holes of the samples were measured by UV-vis diffuse reflectance spectra (DRS). The absorption spectra were transformed from DRS according to the Kubelka-Munk equation. Fig.3. shows spectrums of the prepared catalysts.

The pure  $\text{Bi}_2\text{WO}_6$  absorbs in the array from UV light to a visible light region less than 450 nm the band-gap was estimated to be 2,7eV which is similar to the value in the literature<sup>19</sup>. The  $\text{Fe}_2\text{O}_3$  absorbs in the entire UV-visible range, with a band-gap of 3, 02 eV. After composited with  $\text{Bi}_2\text{WO}_6$ , the light absorption of the  $\text{Bi}_2\text{WO}_6\text{-Fe}_2\text{O}_3$  composites increased in the visible range.

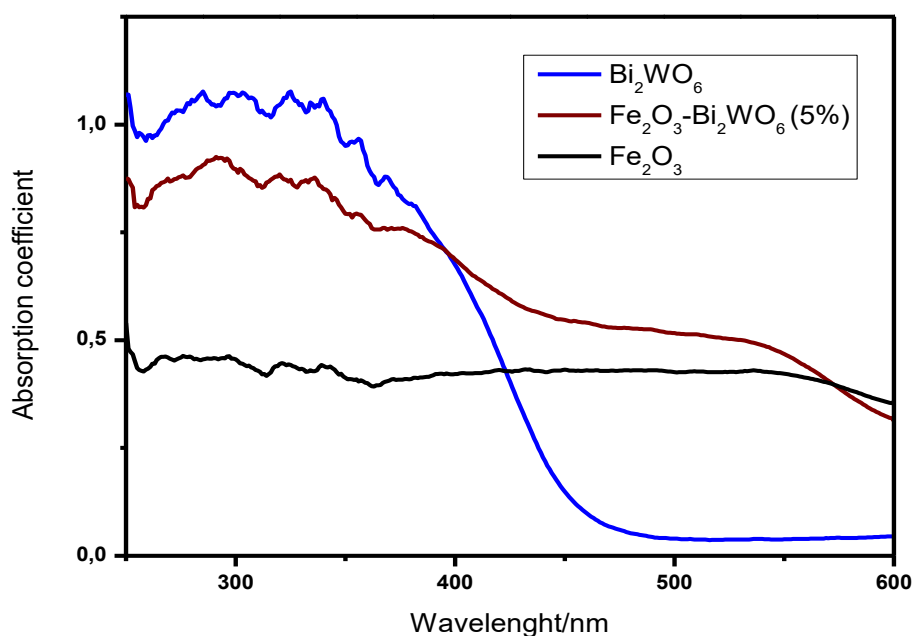


Figure 3. UV-vis diffuse reflectance spectra of the prepared photocatalysts

### 3.2. Photocatalytic activity

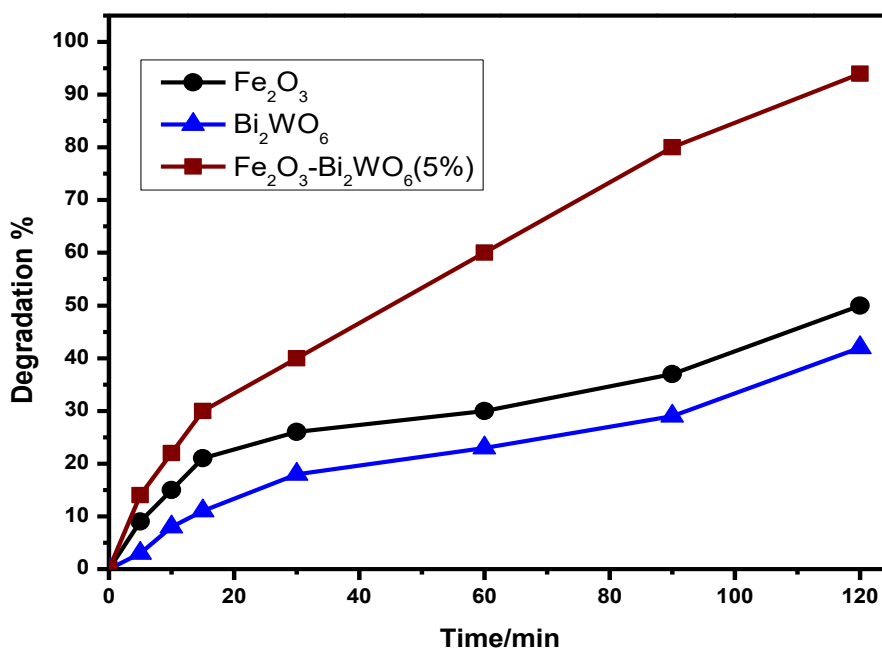
The photocatalytic activity of the catalysts prepared was evaluated by the photodegradation of doxycycline.

Preliminary experiments were carried out in order to verify that Dox was removed by the various heterogeneous photoassisted processes under UV illumination, investigating the effect of H<sub>2</sub>O<sub>2</sub> on Dox under UV. It was observed that in the absence of the photocatalyst, no reduce in Dox concentration was found under UV illumination. Therefore photolysis did not occur. Likewise, no significant difference in

the initial concentration of Dox was found, in the dark and the presence of H<sub>2</sub>O<sub>2</sub>.

UV irradiation over aqueous Dox/ Fe<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> dispersions leads to reduce the absorption intensity. With the increase of irradiation time, the feature absorption band at 275 nm for Dox gets smaller gradually, and the absorbance of the band at 275 nm decreases from 2,582 to 0, 19.

The degradation ratio, defined as  $[1 - (C/C_0)] \times 100\%$ , can evaluate the extent of the degradation of the Dox. As shown in Fig.4, the absorbance peak disappeared after 120 min for Fe<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub>.

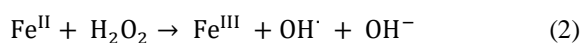


**Figure 4.** Photocatalytic removal of Dox with Fe<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>WO<sub>6</sub> and Fe<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> composites as photocatalyst in the presence of H<sub>2</sub>O<sub>2</sub> (5 %)

As reported in previous studies<sup>20-23</sup>, H<sub>2</sub>O<sub>2</sub> promoted the photocatalytic capability of Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> to degrade organic pollutant.

Though the mechanisms remain ambiguous, it is known that H<sub>2</sub>O<sub>2</sub> allow the photogenerated electron to produce OH<sup>·</sup>, which is a potent oxidative species to degrade organic chemicals<sup>24-26</sup>. As an electron capture agent, H<sub>2</sub>O<sub>2</sub> can also react with photogenerated electrons to produce hydroxyl radicals (OH<sup>·</sup>) as established in eq. (1).

In the system with Fe<sub>2</sub>O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>, an amount of OH<sup>·</sup> was produced through Fenton reaction as shown in eq. (2), and as results, the photodegradation of Dox was higher than pure Fe<sub>2</sub>O<sub>3</sub>.



In the presence of H<sub>2</sub>O<sub>2</sub>, the photogenerated electrons of Bi<sub>2</sub>WO<sub>6</sub> could react with H<sub>2</sub>O<sub>2</sub> to produce OH<sup>·</sup> as eq. (1), the photodegradation of Dox was much higher than pure Bi<sub>2</sub>WO<sub>6</sub>, meaning that OH<sup>·</sup> played an essential part in the photodegradation.

In the Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub> system, the amount of OH<sup>·</sup> produced could be attributed to the heterogeneous Fenton reaction in the surface of Fe<sub>2</sub>O<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> just as eq.(2) and the coupling effect taking place at the interfaces of Fe<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>WO<sub>6</sub>, leading to a higher production of OH<sup>·</sup> compared to pure Bi<sub>2</sub>WO<sub>6</sub> in the presence of H<sub>2</sub>O<sub>2</sub>.

It was established that Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> presented higher photocatalytic productivity to degrade Dox than Bi<sub>2</sub>WO<sub>6</sub>/H<sub>2</sub>O<sub>2</sub>. These could be explained by the additional OH<sup>·</sup> produced in the Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system in comparison to that in the Bi<sub>2</sub>WO<sub>6</sub>/H<sub>2</sub>O<sub>2</sub> system during 120 min irradiation.

In previous work<sup>17</sup>, we found that the Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> presented higher photocatalytic activity in the removal of Methyl Orange and Phenol used as artificial pollutant.

### 4. Conclusion

Doping Bi<sub>2</sub>WO<sub>6</sub> with Fe<sub>2</sub>O<sub>3</sub> improved the photocatalytic capacity to degrade Dox in the

presence of H<sub>2</sub>O<sub>2</sub>. The OH<sup>-</sup> generated by the H<sub>2</sub>O<sub>2</sub> added is crucial to the process of degradation. The Fe<sub>2</sub>O<sub>3</sub> operated as a Fenton-like reagent, accelerating the production of OH<sup>-</sup>, increasing the photodegradation efficiency to Dox in the presence of H<sub>2</sub>O<sub>2</sub> under UV light irradiation.

The Fenton process requires acidic condition (pH around 3); the Bi<sub>2</sub>WO<sub>6</sub>-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system could overcome this inconvenience and be applicable for broad pH conditions of wastewater.

## References

- 1- F. Lin, D. E. Wang, Z. X. Jiang, Y. Ma, J. Li, R. G. Li, C. Li, Photocatalytic oxidation of thiophene on BiVO<sub>4</sub> with dual co-catalysts Pt and RuO<sub>2</sub> under visible light irradiation using molecular oxygen as oxidant, *Energy Environ. Sci.*, **2012**, 5, 6400–6406.
- 2- R. Franking, L. S. Li, M. A. Lukowski, F. Meng, Y. Z. Tan, R. J. Hammers, S. Jin, Facile post-growth doping of nanostructured hematite photoanodes for enhanced photo- electrochemical water oxidation, *Energy Environ. Sci.*, **2013**, 6, 500–512.
- 3- X. Wen, G. Niu, L. Zhang, C. Liang, G. Zeng, A novel Ag<sub>2</sub>O/CeO<sub>2</sub> heterojunction photocatalysts for photocatalytic degradation of enrofloxacin: possible degradation pathways, mineralization activity and an in-depth mechanism insight, *Applied Catalysis B: Environmental*, **2018**, 221, 701-714.
- 4- J. Chen, X. Hua, C. Mao, H. Niu, J. Song, Synthesis of monodisperse pancake-like Bi<sub>2</sub>WO<sub>6</sub> with prominent photocatalytic performances, *Research on Chemical Intermediates*, **2018**, 44, 2251-2259.
- 5- V. Sonkusare, R. G. Chaudhary, S. Ganesh, A. Rai, D. Juneja, Microwave-mediated synthesis, photocatalytic degradation and antibacterial activity of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> micro flowers/novel  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> microspindles, *Nano-Structures & Nano-Objects*, **2018**, 13, 121-131.
- 6- J. Zhou, F. Gong, H. Wang, Y. Xiao, F. Li, W. Mai, 3D mace-like hierarchical ZnO nano-architecture constructed with microcode bundles and porous single-crystalline nanosheets for acetone sensors with enhanced performances, *Materials Science and Engineering: B*, **2017**, 225, 68-74.
- 7- M. Tang, Y. Niu, J. Huang, C. Ming Li, Self-Assembled Flower-like ZnMoO<sub>4</sub>/Graphene Composite Materials as Anode in Lithium-Ion Batteries, *Chemistry Select.*, **2017**, 2, 2144-2149.
- 8- Y. Park, K. J. McDonald, K.S. Choi, Progress in bismuth vanadate photoanodes for use in solar water oxidation, *Chem. Soc. Rev.*, **2013**, 42, 2321–2337.
- 9- Q. Lou, J. Zeng, L. Zheng, Z. Man, W. Wang, A. Kassiba, E. D. Politova, G. Li, Influence of defects on the photocatalytic behavior of La<sup>3+</sup> ions doped SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> ferroelectric materials, *Journal of Applied Physics*, **2019**, 125, 154101.
- 10- S. K. Pilli, T. E. Furtak, L. D. Brown, T. G. Deutsch, J. A. Turner, A. M. Herring, Cobalt-phosphate (Co-Pi) catalyst modified Mo-doped BiVO<sub>4</sub> photoelectrodes for solar water oxidation, *Energy Environ. Sci.*, 2011, 4, 5028–5034.
- 11- L. Zhang, W. Wang, L. Zhou, H. Xu, Bi<sub>2</sub>WO<sub>6</sub> Nano- and Microstructures: Shape Control and Associated Visible-Light-Driven Photocatalytic Activities, *Small*, **2007**, 3, 1618-1625.
- 12- W. Ma, L. Zhang, N. Qian, P. Xiong, X. Zhao, W. Lu, Size-Controlled Synthesis of BiPO<sub>4</sub> Nanostructures and Their Photocatalytic Performances, *Arabian Journal for Science and Engineering*, **2014**, 39, 6721–6725.
- 13- C. Zhang, Y. Zhu, Synthesis of Square Bi<sub>2</sub>WO<sub>6</sub> Nanoplates as High-Activity Visible-Light-Driven Photocatalysts, *Chem. Mater.*, **2005**, 17, 3537-3545.
- 14- Z. Du, R. Guo, J. Lan, S. Jiang, C. Cheng, L. Zhao, L. Peng, Preparation and photocatalytic activity of bismuth tungstate coated polyester fabric, *Fibers and Polymers*, **2017**, 18, 2212–2218.
- 15- D. Ma, S. Wang, P. Cai, J. Jiang, D. Yang, S. Huang, Self-assembled Three-dimensional Hierarchical BiVO<sub>4</sub> Microspheres from Nanoplates: Malic Acid-assisted Hydrothermal Synthesis and Photocatalytic Activities, *Chemistry Letters*, **2009**, 38, 962-963.
- 16- Z. Sun, J. Guo, S. Zhu, J. Ma, Y. Liao, D. Zhang, High photocatalytic performance by engineering Bi<sub>2</sub>WO<sub>6</sub> nanoneedles onto graphene sheets, *RSC Adv.*, **2014**, 4, 27963-27970.
- 17- C. J. Pérez, J. A. Navío, M. C. Hidalgo, A. Bouziani, M. E. Azzouzi, Mixed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> oxides for photoassisted hetero-Fenton degradation of Methyl Orange and Phenol, *Journal of Photochemistry and Photobiology A: Chemistry*, **2017**, 332, 521-533.
- 18- M. Gui, W. Zhang, Q. Su, C. Chen, Preparation and visible light photocatalytic activity of Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> heterojunction photocatalysts, *Journal of Solid State Chemistry*, **2011**, 184, 1977-1982.
- 19- H. Chun, Q. Zhang, J. Yang, Z. Xu, D. Shu, C. Shan, L. Zhu, W. Liao, Y. Xiong, Visible-Light-Induced Activity of AgI-BiOI Composites for Removal of Organic Contaminants from Water and Wastewater, *Sustainable Nanotechnology and the Environment: Advances and Achievements*. American Chemical Society, **2013**, 277-290.
- 20- H. Shi, B. Zou, Z. Li, M. Lu, W. Wang, Direct observation of oxygen-vacancy formation and structural changes in Bi<sub>2</sub>WO<sub>6</sub> nanoflakes induced by electron irradiation, *Beilstein Journal of Nanotechnology*, **2019**, 10, 1434-1442.
- 21- R. Tian, D. Liu, J. Wang, J. Zhou, E. X. Piao, Z. Sun, Three-dimensional BiOI/TiO<sub>2</sub>

- heterostructures with photocatalytic activity under visible light irradiation, *Journal of Porous Materials*, **2018**, 25, 1805-1812.
- 22-J. Yang, X. Wang, X. Zhao, Jun Dai, and Sh. Mo. Synthesis of Uniform Bi<sub>2</sub>WO<sub>6</sub>-Reduced Graphene Oxide Nanocomposites with Significantly Enhanced Photocatalytic Reduction Activity. *The Journal of Physical Chemistry C* 2015, 119 (6), 3068-3078. DOI: 10.1021/jp510041x. 23- P. Chen, H. Wang, H. Liu, Z. Ni, J. Li, Y. Zhou, F. Dong, Directional electron delivery and enhanced reactants activation enable efficient photocatalytic air purification on amorphous carbon nitride Co-Functionalized with O/La, *Appl. Catal. B Environ.*, **2019**, 242, 19–30.
- 24-J. Li, X. Dong, Y. Sun, W. Cen, F. Dong, Facet-dependent interfacial charge separation and transfer in plasmonic photocatalysts, *Appl. Catal. B Environ.*, **2018**, 226, 269–277.
- 25-H. W. Chen, J. Y. Li, M. Liu, X. Y. Liu, Y. X. Zhang, F. Dong, Synthesis of Bi<sub>2</sub>WO<sub>6</sub> with gradient oxygen vacancies for highly photocatalytic NO oxidation and mechanism study, *Chem. Eng. J.*, **2019**, 361, 129–138.
- 26-F. Dong, Y. Zhang, S. Zhang, Photocatalysis for Environmental Applications, *Frontiers in Chemistry*, **2019**, 7, 303.