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Photocatalytic degradation of Doxycycline in aqueous solution using Fe_2O_3 andFe_2O_3-Bi_2WO_6 catalysts

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Abstract: Photocatalytic degradation of Doxycycline in heterogeneous media constituted by nanoparticles of Fe_2O_3 and Fe_2O_3-Bi_2WO_6 was studied. The Bi_2WO_6 was prepared by hydrothermal method, and the Fe_2O_3-Bi_2WO_6 was obtained by mechanical mixing of Bi_2WO_6 to an amount of Fe_2O_3 and their photocatalytic activity to degrade doxycycline (Dox) under UV irradiation supported by H_2O_2 were studied. The H_2O_2 reacts with photogenerated electrons leading to the production of hydroxyl radicals ($OH^\bullet$). The Fe_2O_3 acts like a Fenton reagent, accelerating the production of $OH^\bullet$. In the present study Bi_2WO_6-Fe_2O_3/ H_2O_2 system demonstrate much higher photocatalytic efficiency to degrade Dox than pure Bi_2WO_6.

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 [1,2]. 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[1,2]. 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 [2].

Unfortunately, conventional chemical and biological oxidation treatment methods being employed for water and wastewater usually fail to remove most antibiotics [1-6]. 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 [1,2,5]. 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 [2,7].

In recent years, several advanced water and wastewater treatment methods have been developed [1,2]. 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_2WO_6) is a typical n-type direct bandgap

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semiconductor with a bandgap of 2.75 eV and has prospective applications catalysis [8-10]. In addition, it has been found that Bi_2WO_6 might act as a stable photocatalyst for the photochemical decomposition of organic contaminants [11]. Additionally, the unique structure of the photocatalyst could enhance its photoreactivity the photoactivity of Bi_2WO_6, in which the transfer of electrons to the surface was improved along with the layered network [12,13]. Bi_2WO_6 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_2WO_6 catalyst could be doped with metal or metal oxide, which might trap the photogenerated electrons and restrain the recombination of hole-electron pair [14,15]. H_2O_2 is a typical oxidative agent and has been often used as ineffective water treatment. As an electron capture agent, H_2O_2 can also react with photogenerated electrons to produce hydroxyl radicals ($OH^•$) as established in eq. (1) [5,16].

$$H_2O_2 + e^-_{CB} \rightarrow OH^{\cdot} + OH^- \quad (1)$$

Therefore, when H_2O_2 is present with Bi_2WO_6/Fe_2O_3 composite, it could interact with the composite and affect the photocatalytic capacity displaying higher photodegradation efficiency.

The present work proposes to dope Bi_2WO_6 with Fe_2O_3 to prepare Bi_2WO_6-Fe_2O_3 composite and investigate its efficiency to degrade Doxycycline as an organic pollutant in the presence of H_2O_2. In previous work [17], we have tested the efficiency of the synthesized composite in the degradation of Methyl Orange day 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_2WO_6 as synthesized from Bi $(NO_3)_3.5H_2O$ according to the published procedure [18]. The iron oxide was prepared [19] by drying Iron III nitrate nonahydrate $FeN_3O_9.9H_2O$ at 120°C for 2h then submitting the samples to a further calcination treatment at 500°C for 2 hours. The Fe_2O_3-Bi_2WO_6 mixed samples were obtained with a mechanical mixing in an agate mortar, by adding 5% of Fe_2O_3 to Bi_2WO_6.

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 $BaSO_4$ 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 $4x10^{-5}$ mol/L, and a concentration of 1g/L of the photocatalyst and H_2O_2 (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 spectro-photometer.

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.

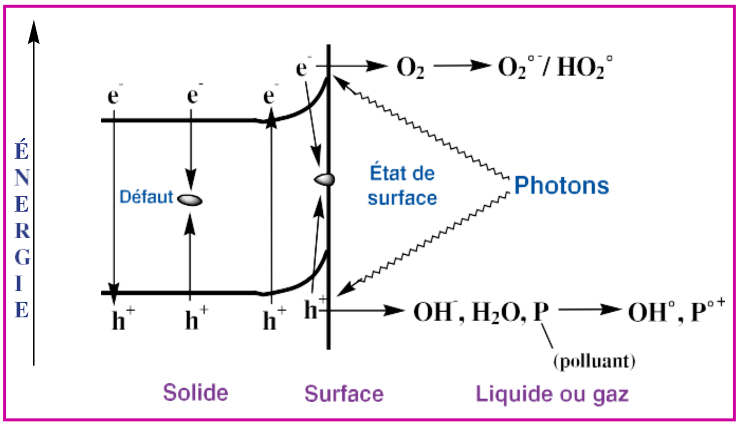

Figure 1. Mecanism of photocatalysis degradation

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 Bi_2WO_6 presented russellite phase (JCPDS card: 39-0256). For Fe_2O_3 the diffraction peaks corresponded to the standard Fe_2O_3 (JCPDS card: 65-3107), in the Bi_2WO_6-Fe_2O_3 (5%) samples the peaks showed just the russellite structure corresponding to the presence of Bi_2WO_6.

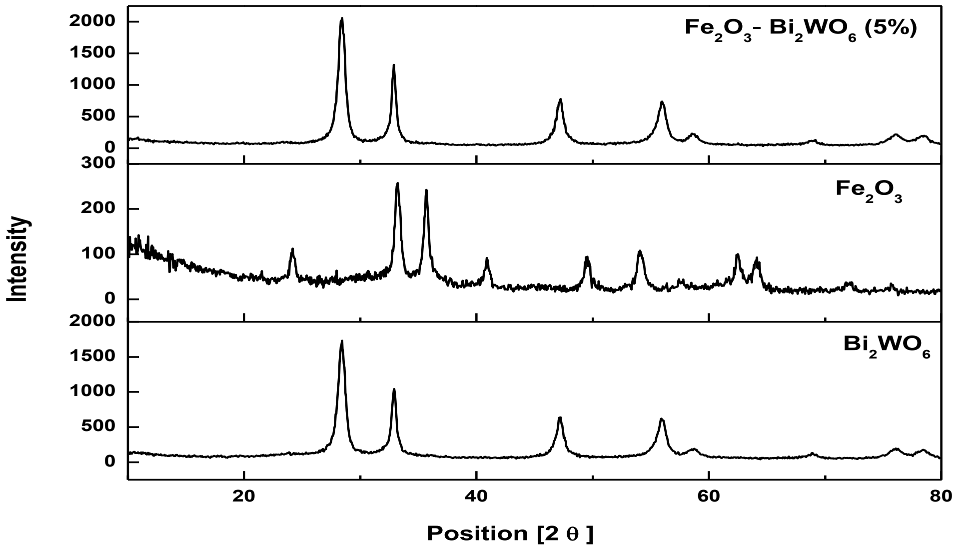

Figure 2. The XRD patterns of the catalysts prepared

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 Bi_2WO_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 [19]. The Fe_2O_3 absorbs in the entire UV-visible range, with a band-gap of 3, 02 eV. After composited with Bi_2WO_6, the light absorption of the Bi_2WO_6-Fe_2O_3 composites increased in the visible range.

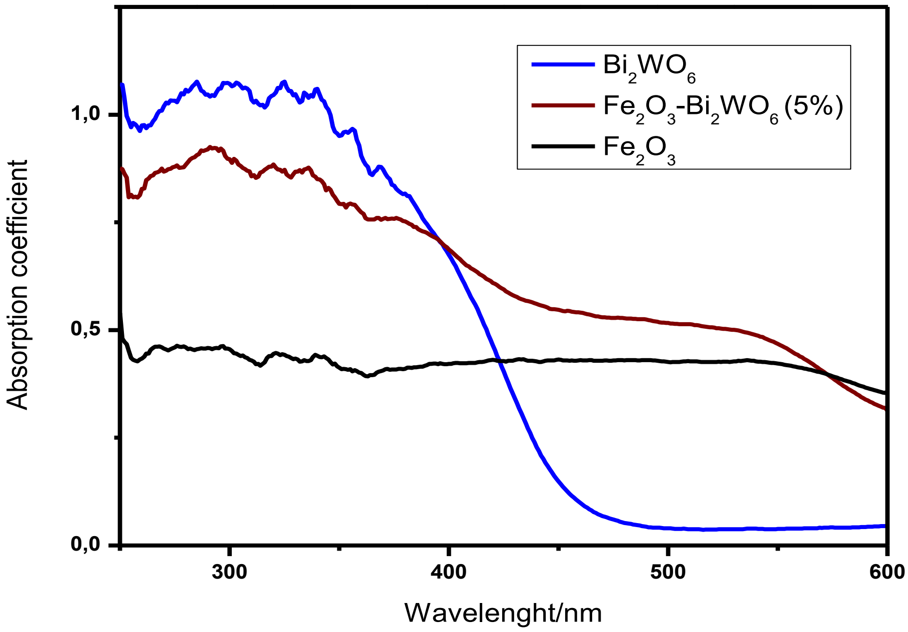

Figure 3. UV-vis diffuse reflectance spectra of the prepared photocatalysts

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_2O_2 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_2O_2.

UV irradiation over aqueous Dox/ Fe_2O_3-Bi_2WO_6 dispersions leads to reduce the absorption intensity. With the increase of irradiation time, the feature absorption band at 275 nm for Doxgets 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_2O_3-Bi_2WO_6.

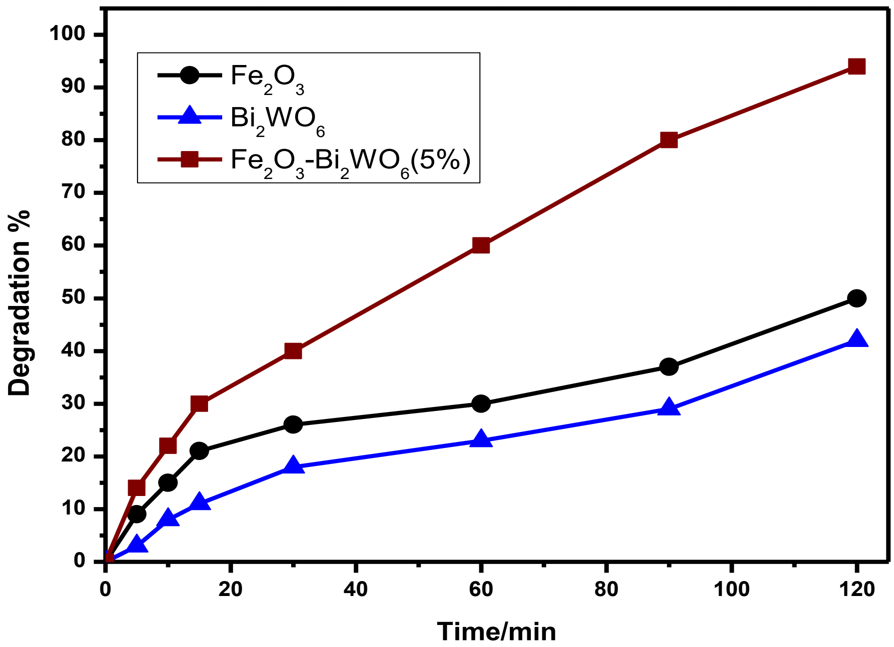

Figure 4. Photocatalytic removal of Dox with Fe_2O_3, Bi_2WO_6 and Fe_2O_3-Bi_2WO_6composites as photocatalyst in the presence of H_2O_2 (5 %)

As reported in previous studies [20-23], H_2O_2 promoted the photocatalytic capability of Bi_2WO_6-Fe_2O_3 and Fe_2O_3 to degrade organic pollutant.

Though the mechanisms remain ambiguous, it is known that H_2O_2 allow the photogenerated electron to produce OH·, which is a potent oxidative species to degrade organic chemicals [24-26]. As an electron capture agent, H_2O_2 can also react with photogenerated electrons to produce hydroxyl radicals (OH·) as established in eq. (1).

In the system with Fe_2O_3/ H_2O_2, an amount of OH· was produced through Fenton reaction as shown in eq. (2), and as results, the photodegradation of Dox was higher than pure Fe_2O_3.

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + OH^{\cdot} + OH^{-} \qquad (2)$$

In the presence of H_2O_2, the photogenerated electrons of Bi_2WO_6 could react with H_2O_2 to produce $OH^{\cdot}$ as eq. (1), the photodegradation of Dox was much higher than pure Bi_2WO_6, meaning that $OH^{\cdot}$ played an essential part in the photodegradation.

In the Bi_2WO_6-Fe_2O_3 system**,** the amount of $OH^{\cdot}$ produced could be attributed to the heterogeneous Fenton reaction in the surface of Fe_2O_3 with H_2O_2 just as eq.(2) and the coupling effect taking place at the interfaces of Fe_2O_3 and Bi_2WO_6, leading to a higher production of $OH^{\cdot}$ compared to pure Bi_2WO_6 in the presence of H_2O_2.

It was established that Bi_2WO_6-Fe_2O_3/H_2O_2 presented higher photocatalytic productivity to degrade Dox than Bi_2WO_6/H_2O_2. These could be explained by the additional $OH^{\cdot}$ produced in the Bi_2WO_6-Fe_2O_3/H_2O_2 system in comparison to that in the Bi_2WO_6/H_2O_2 system during 120 min irradiation.

In previous work [17], we found that the Bi_2WO_6-Fe_2O_3/H_2O_2 presented higher photocatalytic activity in the removal of Methyl Orange and Phenol used as artificial pollutatants.

4. Conclusion

Doping Bi_2WO_6 with Fe_2O_3 improved the photocatalytic capacity to degrade Dox in the presence of H_2O_2. The $OH^.$ generated by the H_2O_2 added is crucial to the process of degradation. The Fe_2O_3 operated as a Fenton-like reagent, accelerating the production of $OH^.$, increasing the photodegradation efficiency to Dox in the presence of H_2O_2 under UV light irradiation.

The Fenton process requires acidic condition (pH around 3); the Bi_2WO_6-Fe_2O_3/H_2O_2 system could overcome this inconveniency 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 $BiVO_4$ with dual co-catalysts Pt and RuO_2 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_2O/CeO_2 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_2WO_6 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 α -Bi_2O_3 micro flowers/novel γ -Bi_2O_3 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 $ZnMoO_4$ /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^{3+} ions doped $SrBi_2Nb_2O_9$ 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 $BiVO_4$ photoelectrodes for solar water oxidation, Energy Environ Sci., 2011, 4, 5028–5034.

11- L. Zhang, W. Wang, L. Zhou, H. Xu, Bi_2WO_6 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 $BiPO_4$ Nanostructures and Their Photocatalytic Performances, Arabian Journal for Science and Engineering, **2014**, 39, 6721–6725.

13- C. Zhang, Y. Zhu, Synthesis of Square Bi_2WO_6 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 $BiVO_4$ 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_2WO_6 nanoneedles onto graphene sheets, RSC Adv., **2014**, 4, 27963-27970.

17- C. J. Páez, J. A. Navío, M. C, Hidalgo, A. Bouziani, M. E. Azzouzi, Mixed α-Fe_2O_3/Bi_2WO_6 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_2O_3/Bi_2WO_6 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_2WO_6 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_2

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 Bi2WO6-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_2WO_6 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.