

**Synthesis and Application of Phosphate Based
Solar-light-driven Composite Photocatalysts**

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4.1 Concluding remarks

This thesis developed two kinds of photocatalyst by different methods for the application of wastewater treatment, photodynamic therapy and water splitting.

Chapter 1 described the development and modification of photocatalysts. Besides, their applications and prospects were systemically introduced.

Chapter 2 described the synthesis, characterization and application of P/Ag/Ag₂O/Ag₃PO₄/TiO₂. This composite was prepared by sol-gel method, and followed by characterizations. It showed higher UV-vis spectra, high electron-hole separation and higher photocatalytic activity for Rh B degradation and photodynamic therapy for cancer cells, compared with pure TiO₂.

Chapter 3 described the synthesis, characterization and application of Ag/Ag₂O/BiPO₄/Bi₂WO₆. This composite was successfully synthesized by hydrothermal method. The influences of ratio of Bi to Ag, calcination temperature, calcination time and PO₄³⁻ content were investigated on photocatalytic performance for Rh B degradation. Optimized Ag/Ag₂O/BiPO₄/Bi₂WO₆ composite showed higher UV-vis spectra, lower PL intensity and higher photocatalytic activity, compared with Bi₂WO₆, BiPO₄/Bi₂WO₆ and Ag/Ag₂O/Bi₂WO₆.

In summary, P/Ag/Ag₂O/Ag₃PO₄/TiO₂ and Ag/Ag₂O/BiPO₄/Bi₂WO₆ were successfully synthesized and showed extremely high photocatalytic activity and stability. Co-doping with those particles could largely inhibit the crystal grain growth, increase the specific surface area and decrease

its original band gap. Moreover, formed heterostructure with consistent stability benefits the charge transfer within the hybrid structure and largely reduces the recombination of photoinduced electron-hole pairs. The synergistic effect of these factors contributes to the excellent photocatalytic performance of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ and Ag/Ag₂O/BiPO₄/Bi₂WO₆. On the basis of their efficient photocatalytic ability and stability under simulated solar light, as-prepared phosphate based composite photocatalyst shows promise for practical applications in environmental purification of organic pollutants, water splitting, photodynamic therapy and even disinfection of bacteria in future. In conclusion, fabricating phosphate based composite photocatalysts was a successful strategy for developing efficient solar-light-driven photocatalysts, as the structures of PO₄³⁻ in those composite could act as the reusable active sites for chemical reactions.

4.2 Future prospects

In further research, in order to systemically investigate the photocytotoxicity for cancer cells, other cancer cells, such as MG63 could be studied by using P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst. To further improve the stability and biocompatibility, PEG and BSA could be used to modify P/Ag/Ag₂O/Ag₃PO₄/TiO₂ particles. Besides, P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst could be applied for bacterial disinfection, due to its enhanced photocatalytic activity.

In addition, Ag/Ag₂O/BiPO₄/Bi₂WO₆ would be further systemically investigated for the hydrogen and oxygen generation. The influence of different solvent, dosage, time, and light intensity should be discussed on the photocatalytic water splitting. Also, the possibility of photocatalytic water splitting by P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst need to be further studied,

in comparison with Ag/Ag₂O/BiPO₄/Bi₂WO₆ photocatalyst.

References

- [1] A.L. Linsebigler, G. Lu, J.T. Yates Jr, Photocatalysis on TiO₂ surfaces: Principles, mechanisms, and selected results, *Chemical reviews*, 95 (1995) 735-758.
- [2] S.U. Khan, M. Al-Shahry, W.B. Ingler, Efficient photochemical water splitting by a chemically modified n-TiO₂, *science*, 297 (2002) 2243-2245.
- [3] W. Choi, A. Termin, M.R. Hoffmann, The role of metal ion dopants in quantum-sized TiO₂: Correlation between photoreactivity and charge carrier recombination dynamics, *The Journal of Physical Chemistry*, 98 (1994) 13669-13679.
- [4] H. Irie, Y. Watanabe, K. Hashimoto, Carbon-doped anatase TiO₂ powders as a visible-light sensitive photocatalyst, *Chemistry Letters*, 32 (2003) 772-773.
- [5] Z. Hou, Y. Zhang, K. Deng, Y. Chen, X. Li, X. Deng, Z. Cheng, H. Lian, C. Li, J. Lin, UV-emitting upconversion-based TiO₂ photosensitizing nanoplatform: Near-infrared light mediated in vivo photodynamic therapy via mitochondria-involved apoptosis pathway, *ACS nano*, 9 (2015) 2584-2599.
- [6] W.W. Yu, L. Qu, W. Guo, X. Peng, Experimental determination of the extinction coefficient of CdTe, CdSe, and CdS nanocrystals, *Chemistry of Materials*, 15 (2003) 2854-2860.
- [7] Z.A. Peng, X. Peng, Formation of high-quality CdTe, CdSe, and CdS nanocrystals using CdO as precursor, *Journal of the American Chemical Society*, 123 (2001) 183-184.
- [8] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, 19.9% - efficient ZnO/CdS/CuInGaSe₂ solar cell with 81.2% fill factor, *Progress in Photovoltaics*:

Research and Applications, 16 (2008) 235-239.

[9] C. Santato, M. Odziemkowski, M. Ulmann, J. Augustynski, Crystallographically oriented mesoporous WO_3 films: Synthesis, characterization, and applications, *Journal of the American Chemical Society*, 123 (2001) 10639-10649.

[10] S.H. Lee, R. Deshpande, P.A. Parilla, K.M. Jones, B. To, A.H. Mahan, A.C. Dillon, Crystalline WO_3 nanoparticles for highly improved electrochromic applications, *Advanced Materials*, 18 (2006) 763-766.

[11] X.-L. Li, T.-J. Lou, X.-M. Sun, Y.-D. Li, Highly sensitive WO_3 hollow-sphere gas sensors, *Inorganic Chemistry*, 43 (2004) 5442-5449.

[12] J. Su, L. Guo, N. Bao, C.A. Grimes, Nanostructured $\text{WO}_3/\text{BiVO}_4$ heterojunction films for efficient photoelectrochemical water splitting, *Nano letters*, 11 (2011) 1928-1933.

[13] S. Yan, Z. Li, Z. Zou, Photodegradation performance of g- C_3N_4 fabricated by directly heating melamine, *Langmuir*, 25 (2009) 10397-10401.

[14] Q. Xiang, J. Yu, M. Jaroniec, Preparation and enhanced visible-light photocatalytic H_2 -production activity of graphene/ C_3N_4 composites, *The Journal of Physical Chemistry C*, 115 (2011) 7355-7363.

[15] M. Groenewolt, M. Antonietti, Synthesis of g - C_3N_4 Nanoparticles in Mesoporous Silica Host Matrices, *Advanced Materials*, 17 (2005) 1789-1792.

[16] S. Yan, Z. Li, Z. Zou, Photodegradation of rhodamine B and methyl orange over boron-doped g- C_3N_4 under visible light irradiation, *Langmuir*, 26 (2010) 3894-3901.

[17] X. Chen, J. Zhang, X. Fu, M. Antonietti, X. Wang, Fe-g- C_3N_4 -catalyzed oxidation of benzene to

phenol using hydrogen peroxide and visible light, *Journal of the American Chemical Society*, 131 (2009) 11658-11659.

[18] X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan, Y. Xie, Enhanced photoresponsive ultrathin graphitic-phase C_3N_4 nanosheets for bioimaging, *Journal of the American Chemical Society*, 135 (2012) 18-21.

[19] J. Tang, Z. Zou, J. Ye, Photocatalytic decomposition of organic contaminants by Bi_2WO_6 under visible light irradiation, *Catalysis Letters*, 92 (2004) 53-56.

[20] H. Fu, C. Pan, W. Yao, Y. Zhu, Visible-light-induced degradation of rhodamine B by nanosized Bi_2WO_6 , *The Journal of Physical Chemistry B*, 109 (2005) 22432-22439.

[21] C. Zhang, Y. Zhu, Synthesis of square Bi_2WO_6 nanoplates as high-activity visible-light-driven photocatalysts, *Chemistry of Materials*, 17 (2005) 3537-3545.

[22] L. Zhang, W. Wang, L. Zhou, H. Xu, Bi_2WO_6 nano - and microstructures: shape control and associated visible - light - driven photocatalytic activities, *Small*, 3 (2007) 1618-1625.

[23] Y. Bi, S. Ouyang, N. Umezawa, J. Cao, J. Ye, Facet effect of single-crystalline Ag_3PO_4 sub-microcrystals on photocatalytic properties, *Journal of the American Chemical Society*, 133 (2011) 6490-6492.

[24] X. Yang, H. Cui, Y. Li, J. Qin, R. Zhang, H. Tang, Fabrication of Ag_3PO_4 -graphene composites with highly efficient and stable visible light photocatalytic performance, *Acs Catalysis*, 3 (2013) 363-369.

[25] Y. Bi, H. Hu, S. Ouyang, Z. Jiao, G. Lu, J. Ye, Selective growth of Ag_3PO_4 submicro-cubes on Ag nanowires to fabricate necklace-like heterostructures for photocatalytic applications, *Journal of*

Materials Chemistry, 22 (2012) 14847-14850.

[26] H. Wang, Y. Bai, J. Yang, X. Lang, J. Li, L. Guo, A facile way to rejuvenate Ag_3PO_4 as a recyclable highly efficient photocatalyst, Chemistry—A European Journal, 18 (2012) 5524-5529.

[27] M. Ge, N. Zhu, Y. Zhao, J. Li, L. Liu, Sunlight-assisted degradation of dye pollutants in Ag_3PO_4 suspension, Industrial & Engineering Chemistry Research, 51 (2012) 5167-5173.

[28] W. Wang, B. Cheng, J. Yu, G. Liu, W. Fan, Visible - Light Photocatalytic Activity and Deactivation Mechanism of Ag_3PO_4 Spherical Particles, Chemistry—An Asian Journal, 7 (2012) 1902-1908.

[29] C. Pan, J. Xu, Y. Wang, D. Li, Y. Zhu, Dramatic Activity of $\text{C}_3\text{N}_4/\text{BiPO}_4$ Photocatalyst with Core/Shell Structure Formed by Self - Assembly, Advanced Functional Materials, 22 (2012) 1518-1524.

[30] C. Pan, Y. Zhu, New type of BiPO_4 oxy-acid salt photocatalyst with high photocatalytic activity on degradation of dye, Environmental Science & Technology, 44 (2010) 5570-5574.

[31] C. Pan, Y. Zhu, Size-controlled synthesis of BiPO_4 nanocrystals for enhanced photocatalytic performance, Journal of Materials Chemistry, 21 (2011) 4235-4241.

[32] H. Xu, Y. Xu, H. Li, J. Xia, J. Xiong, S. Yin, C. Huang, H. Wan, Synthesis, characterization and photocatalytic property of $\text{AgBr}/\text{BiPO}_4$ heterojunction photocatalyst, Dalton Transactions, 41 (2012) 3387-3394.

[33] G. Li, Y. Ding, Y. Zhang, Z. Lu, H. Sun, R. Chen, Microwave synthesis of BiPO_4 nanostructures and their morphology-dependent photocatalytic performances, Journal of Colloid and Interface Science, 363 (2011) 497-503.

- [34] A. Kudo, Y. Miseki, Heterogeneous photocatalyst materials for water splitting, *Chemical Society Reviews*, 38 (2009) 253-278.
- [35] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light, *Nature Materials*, 8 (2009) 76-80.
- [36] P. Wang, B. Huang, X. Qin, X. Zhang, Y. Dai, J. Wei, M.H. Whangbo, Ag@ AgCl: A highly efficient and stable photocatalyst active under visible light, *Angewandte Chemie International Edition*, 47 (2008) 7931-7933.
- [37] T. Arai, M. Yanagida, Y. Konishi, Y. Iwasaki, H. Sugihara, K. Sayama, Efficient complete oxidation of acetaldehyde into CO₂ over CuBi₂O₄/WO₃ composite photocatalyst under visible and UV light irradiation, *The Journal of Physical Chemistry C*, 111 (2007) 7574-7577.
- [38] K. Iwashina, A. Kudo, Rh-doped SrTiO₃ photocatalyst electrode showing cathodic photocurrent for water splitting under visible-light irradiation, *Journal of the American Chemical Society*, 133 (2011) 13272-13275.
- [39] M. Miyauchi, M. Takashio, H. Tobimatsu, Photocatalytic activity of SrTiO₃ codoped with nitrogen and lanthanum under visible light illumination, *Langmuir*, 20 (2004) 232-236.
- [40] D. Wang, J. Ye, T. Kako, T. Kimura, Photophysical and photocatalytic properties of SrTiO₃ doped with Cr cations on different sites, *The Journal of Physical Chemistry B*, 110 (2006) 15824-15830.
- [41] C.J. Lin, Y.H. Yu, Y.H. Liou, Free-standing TiO₂ nanotube array films sensitized with CdS as highly active solar light-driven photocatalysts, *Applied Catalysis B: Environmental*, 93 (2009)

119-125.

[42] Y. Huang, W. Ho, S. Lee, L. Zhang, G. Li, J.C. Yu, Effect of carbon doping on the mesoporous structure of nanocrystalline titanium dioxide and its solar-light-driven photocatalytic degradation of NO_x, *Langmuir*, 24 (2008) 3510-3516.

[43] N.S. Chaudhari, A.P. Bhirud, R.S. Sonawane, L.K. Nikam, S.S. Warule, V.H. Rane, B.B. Kale, Ecofriendly hydrogen production from abundant hydrogen sulfide using solar light-driven hierarchical nanostructured ZnIn₂S₄ photocatalyst, *Green Chemistry*, 13 (2011) 2500-2506.

[44] S.K. Apte, S.N. Garaje, R.D. Bolade, J.D. Ambekar, M.V. Kulkarni, S.D. Naik, S.W. Gosavi, J.O. Baeg, B.B. Kale, Hierarchical nanostructures of CdIn₂S₄ via hydrothermal and microwave methods: efficient solar-light-driven photocatalysts, *Journal of Materials Chemistry*, 20 (2010) 6095-6102.

[45] Y. Cui, J. Briscoe, S. Dunn, Effect of Ferroelectricity on Solar-Light-Driven Photocatalytic Activity of BaTiO₃ Influence on the Carrier Separation and Stern Layer Formation, *Chemistry of Materials*, 25 (2013) 4215-4223.

[46] M.M. Caldwell, Solar UV irradiation and the growth and development of higher plants, *Photophysiology*, 6 (1971) 131-177.

[47] W. Choi, A. Termin, M.R. Hoffmann, Effects of Metal - Ion Dopants on the Photocatalytic Reactivity of Quantum - Sized TiO₂ Particles, *Angewandte Chemie International Edition in English*, 33 (1994) 1091-1092.

[48] W.J. Jo, J.W. Jang, K.j. Kong, H.J. Kang, J.Y. Kim, H. Jun, K. Parmar, J.S. Lee, Phosphate doping into monoclinic BiVO₄ for enhanced photoelectrochemical water oxidation activity, *Angewandte Chemie International Edition*, 51 (2012) 3147-3151.

- [49] X. Chen, C. Burda, The electronic origin of the visible-light absorption properties of C-, N- and S-doped TiO₂ nanomaterials, *Journal of the American Chemical Society*, 130 (2008) 5018-5019.
- [50] P. Yang, C. Lu, N. Hua, Y. Du, Titanium dioxide nanoparticles co-doped with Fe³⁺ and Eu³⁺ ions for photocatalysis, *Materials Letters*, 57 (2002) 794-801.
- [51] J. Liqiang, F. Honggang, W. Baiqi, W. Dejun, X. Baifu, L. Shudan, S. Jiazhong, Effects of Sn dopant on the photoinduced charge property and photocatalytic activity of TiO₂ nanoparticles, *Applied Catalysis B: Environmental*, 62 (2006) 282-291.
- [52] Y. Sasaki, A. Iwase, H. Kato, A. Kudo, The effect of co-catalyst for Z-scheme photocatalysis systems with an Fe³⁺/Fe²⁺ electron mediator on overall water splitting under visible light irradiation, *Journal of Catalysis*, 259 (2008) 133-137.
- [53] S.S. Rayalu, D. Jose, M.V. Joshi, P.A. Mangrulkar, K. Shrestha, K. Klabunde, Photocatalytic water splitting on Au/TiO₂ nanocomposites synthesized through various routes: enhancement in photocatalytic activity due to SPR effect, *Applied Catalysis B: Environmental*, 142 (2013) 684-693.
- [54] T. Hirakawa, P.V. Kamat, Charge separation and catalytic activity of Ag@TiO₂ core-shell composite clusters under UV-irradiation, *Journal of the American Chemical Society*, 127 (2005) 3928-3934.
- [55] Y. Zhou, Q. Zhang, Y. Lin, E. Antonova, W. Bensch, G.R. Patzke, One-step hydrothermal synthesis of hierarchical Ag/Bi₂WO₆ composites: in situ growth monitoring and photocatalytic activity studies, *Science China Chemistry*, 56 (2013) 435-442.
- [56] W. Yao, B. Zhang, C. Huang, C. Ma, X. Song, Q. Xu, Synthesis and characterization of high efficiency and stable Ag₃PO₄/TiO₂ visible light photocatalyst for the degradation of methylene blue

and rhodamine B solutions, *Journal of Materials Chemistry*, 22 (2012) 4050-4055.

[57] Y. Xiaodan, W. Qingyin, J. Shicheng, G. Yihang, Nanoscale ZnS/TiO₂ composites: preparation, characterization, and visible-light photocatalytic activity, *Materials Characterization*, 57 (2006) 333-341.

[58] M. Lu, G. Yuan, Z. Wang, Y. Wang, J. Guo, Synthesis of BiPO₄/Bi₂S₃ Heterojunction with Enhanced Photocatalytic Activity under Visible-Light Irradiation, *Nanoscale research letters*, 10 (2015) 1-7.

[59] M. Xie, X. Fu, L. Jing, P. Luan, Y. Feng, H. Fu, Long - Lived, Visible - Light - Excited Charge Carriers of TiO₂/BiVO₄ Nanocomposites and their Unexpected Photoactivity for Water Splitting, *Advanced Energy Materials*, 4 (2014) 1300995-1301000.

[60] M.-Q. Yang, Y.-J. Xu, Selective photoredox using graphene-based composite photocatalysts, *Physical Chemistry Chemical Physics*, 15 (2013) 19102-19118.

[61] H. Kato, M. Hori, R. Kouta, Y. Shimodaira, A. Kudo, Construction of Z-scheme type heterogeneous photocatalysis systems for water splitting into H₂ and O₂ under visible light irradiation, *Chemistry Letters*, 33 (2004) 1348-1349.

[62] H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, All-solid-state Z-scheme in CdS–Au–TiO₂ three-component nanojunction system, *Nature Materials*, 5 (2006) 782-786.

[63] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, A new photocatalytic water splitting system under visible light irradiation mimicking a Z-scheme mechanism in photosynthesis, *Journal of Photochemistry and Photobiology A: Chemistry*, 148 (2002) 71-77.

[64] J.A. Schwarz, C. Contescu, A. Contescu, Methods for preparation of catalytic materials,

Chemical Reviews, 95 (1995) 477-510.

[65] E. Ohshima, H. Ogino, I. Niikura, K. Maeda, M. Sato, M. Ito, T. Fukuda, Growth of the 2-in-size bulk ZnO single crystals by the hydrothermal method, *Journal of Crystal Growth*, 260 (2004) 166-170.

[66] K. Miyazawa, Y. Kuwasaki, A. Obayashi, M. Kuwabara, C 60 nanowhiskers formed by the liquid-liquid interfacial precipitation method, *Journal of Materials Research*, 17 (2002) 83-88.

[67] H.W. Nasution, E. Purnama, S. Kosela, J. Gunlazuardi, Photocatalytic reduction of CO₂ on copper-doped titania catalysts prepared by improved-impregnation method, *Catalysis Communications*, 6 (2005) 313-319.

[68] T. Miyazawa, S. Koso, K. Kunimori, K. Tomishige, Development of a Ru/C catalyst for glycerol hydrogenolysis in combination with an ion-exchange resin, *Applied Catalysis A: General*, 318 (2007) 244-251.

[69] J. Kong, A.M. Cassell, H. Dai, Chemical vapor deposition of methane for single-walled carbon nanotubes, *Chemical Physics Letters*, 292 (1998) 567-574.

[70] M. Zhang, G. Sheng, J. Fu, T. An, X. Wang, X. Hu, Novel preparation of nanosized ZnO-SnO₂ with high photocatalytic activity by homogeneous co-precipitation method, *Materials Letters*, 59 (2005) 3641-3644.

[71] C. Ao, S. Lee, Indoor air purification by photocatalyst TiO₂ immobilized on an activated carbon filter installed in an air cleaner, *Chemical Engineering Science*, 60 (2005) 103-109.

[72] S. Wang, H. Ang, M.O. Tade, Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art, *Environment International*, 33 (2007) 694-705.

- [73] R. Bakalova, H. Ohba, Z. Zhelev, T. Nagase, R. Jose, M. Ishikawa, Y. Baba, Quantum dot anti-CD conjugates: Are they potential photosensitizers or potentiators of classical photosensitizing agents in photodynamic therapy of cancer?, *Nano Letters*, 4 (2004) 1567-1573.
- [74] H. Kato, K. Asakura, A. Kudo, Highly efficient water splitting into H₂ and O₂ over lanthanum-doped NaTaO₃ photocatalysts with high crystallinity and surface nanostructure, *Journal of the American Chemical Society*, 125 (2003) 3082-3089.
- [75] U. Von Gunten, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, *Water Research*, 37 (2003) 1443-1467.
- [76] O.I. Aruoma, B. Halliwell, B.M. Hoey, J. Butler, The antioxidant action of N-acetylcysteine: Its reaction with hydrogen peroxide, hydroxyl radical, superoxide, and hypochlorous acid, *Free Radical Biology and Medicine*, 6 (1989) 593-597.
- [77] A. Henglein, C. Kormann, Scavenging of OH radicals produced in the sonolysis of water, *International Journal of Radiation Biology and Related Studies in Physics, Chemistry and Medicine*, 48 (1985) 251-258.
- [78] Q. Yang, H. Choi, Y. Chen, D.D. Dionysiou, Heterogeneous activation of peroxymonosulfate by supported cobalt catalysts for the degradation of 2, 4-dichlorophenol in water: The effect of support, cobalt precursor, and UV radiation, *Applied Catalysis B: Environmental*, 77 (2008) 300-307.
- [79] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chemical Reviews*, 95 (1995) 69-96.
- [80] N. Panwar, S. Kaushik, S. Kothari, Role of renewable energy sources in environmental protection: A review, *Renewable and Sustainable Energy Reviews*, 15 (2011) 1513-1524.

- [81] I. Dincer, Renewable energy and sustainable development: a crucial review, *Renewable and Sustainable Energy Reviews*, 4 (2000) 157-175.
- [82] S. Mekhilef, R. Saidur, A. Safari, A review on solar energy use in industries, *Renewable and Sustainable Energy Reviews*, 15 (2011) 1777-1790.
- [83] X. Li, Diversification and localization of energy systems for sustainable development and energy security, *Energy Policy*, 33 (2005) 2237-2243.
- [84] M. Ni, M.K. Leung, D.Y. Leung, K. Sumathy, A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production, *Renewable and Sustainable Energy Reviews*, 11 (2007) 401-425.
- [85] K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, Photocatalyst releasing hydrogen from water, *Nature*, 440 (2006) 295-295.
- [86] A.J. Bard, M.A. Fox, Artificial photosynthesis: solar splitting of water to hydrogen and oxygen, *Accounts of Chemical Research*, 28 (1995) 141-145.
- [87] A. Steinfeld, Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions, *International Journal of Hydrogen Energy*, 27 (2002) 611-619.
- [88] S. Abanades, G. Flamant, Thermochemical hydrogen production from a two-step solar-driven water-splitting cycle based on cerium oxides, *Solar Energy*, 80 (2006) 1611-1623.
- [89] L. Zhang, C. Baumanis, L. Robben, T. Kandiel, D. Bahnemann, Bi_2WO_6 Inverse Opals: Facile Fabrication and Efficient Visible - Light - Driven Photocatalytic and Photoelectrochemical Water - Splitting Activity, *Small*, 7 (2011) 2714-2720.
- [90] P. Birnblecombe, *Pollution: causes, effects and control* 3rd edition, Occupational and

environmental medicine, 54 (1997) 287.

[91] H. Stan, T. Heberer, Pharmaceuticals in the aquatic environment: Water analysis, *Analisis*, 25 (1997) M20-M23.

[92] V. Poots, G. McKay, J. Healy, Removal of basic dye from effluent using wood as an adsorbent, *Journal (Water Pollution Control Federation)*, 50 (1978) 926-935.

[93] D.J. Van Donsel, E.E. Geldreich, N.A. Clarke, Seasonal variations in survival of indicator bacteria in soil and their contribution to storm-water pollution, *Applied Microbiology*, 15 (1967) 1362-1370.

[94] J.J. Borrego, M.A. Morifiño, A. de Vicente, R. Córmax, P. Romero, Coliphages as an indicator of faecal pollution in water. Its relationship with indicator and pathogenic microorganisms, *Water Research*, 21 (1987) 1473-1480.

[95] A. Fujishima, Photosensitized electrolytic oxidation on semiconducting n-type TiO₂ electrode, *Kogyo Kagaku Zasshi*, 72 (1969) 108-113.

[96] A. Fujishima, Electrochemical photolysis of water at a semiconductor electrode, *Nature*, 238 (1972) 37-38.

[97] H. Irie, Y. Watanabe, K. Hashimoto, Nitrogen-concentration dependence on photocatalytic activity of TiO_{2-x}N_x powders, *The Journal of Physical Chemistry B*, 107 (2003) 5483-5486.

[98] G. Yang, Z. Jiang, H. Shi, T. Xiao, Z. Yan, Preparation of highly visible-light active N-doped TiO₂ photocatalyst, *Journal of Materials Chemistry*, 20 (2010) 5301-5309.

[99] J.H. Park, S. Kim, A.J. Bard, Novel carbon-doped TiO₂ nanotube arrays with high aspect ratios for efficient solar water splitting, *Nano Letters*, 6 (2006) 24-28.

- [100] J.C. Yu, L. Zhang, Z. Zheng, J. Zhao, Synthesis and characterization of phosphated mesoporous titanium dioxide with high photocatalytic activity, *Chemistry of Materials*, 15 (2003) 2280-2286.
- [101] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, Preparation of S-doped TiO₂ photocatalysts and their photocatalytic activities under visible light, *Applied Catalysis A: General*, 265 (2004) 115-121.
- [102] J. Okumu, C. Dahmen, A. Sprafke, M. Luysberg, G. Von Plessen, M. Wuttig, Photochromic silver nanoparticles fabricated by sputter deposition, *Journal of Applied Physics*, 97 (2005) 094305.
- [103] R. van de Krol, Y. Liang, J. Schoonman, Solar hydrogen production with nanostructured metal oxides, *Journal of Materials Chemistry*, 18 (2008) 2311-2320.
- [104] B.D. Alexander, P.J. Kulesza, I. Rutkowska, R. Solarska, J. Augustynski, Metal oxide photoanodes for solar hydrogen production, *Journal of Materials Chemistry*, 18 (2008) 2298-2303.
- [105] T. Umebayashi, T. Yamaki, S. Tanaka, K. Asai, Visible Light-Induced Degradation of Methylene Blue on S-doped TiO₂, *Chemistry Letters*, 32 (2003) 330-331.
- [106] X.-Y. Zhang, H.-P. Li, X.-L. Cui, Y. Lin, Graphene/TiO₂ nanocomposites: Synthesis, characterization and application in hydrogen evolution from water photocatalytic splitting, *Journal of Materials Chemistry*, 20 (2010) 2801-2806.
- [107] A. Romanyuk, P. Oelhafen, Formation and electronic structure of TiO₂-Ag interface, *Solar Energy Materials and Solar Cells*, 91 (2007) 1051-1054.
- [108] S.S. Mandal, A.J. Bhattacharyya, Electrochemical sensing and photocatalysis using Ag-TiO₂ microwires, *Journal of Chemical Sciences*, 124 (2012) 969-978.
- [109] D. Wang, Z.-H. Zhou, H. Yang, K.-B. Shen, Y. Huang, S. Shen, Preparation of TiO₂ loaded with

crystalline nano Ag by a one-step low-temperature hydrothermal method, *Journal of Materials Chemistry*, 22 (2012) 16306-16311.

[110] S. Linic, P. Christopher, D.B. Ingram, Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy, *Nature Materials*, 10 (2011) 911-921.

[111] K. Awazu, M. Fujimaki, C. Rockstuhl, J. Tominaga, H. Murakami, Y. Ohki, N. Yoshida, T. Watanabe, A plasmonic photocatalyst consisting of silver nanoparticles embedded in titanium dioxide, *Journal of the American Chemical Society*, 130 (2008) 1676-1680.

[112] P. Christopher, D.B. Ingram, S. Linic, Enhancing photochemical activity of semiconductor nanoparticles with optically active Ag nanostructures: photochemistry mediated by Ag surface plasmons, *The Journal of Physical Chemistry C*, 114 (2010) 9173-9177.

[113] Y. Tian, T. Tatsuma, Mechanisms and applications of plasmon-induced charge separation at TiO₂ films loaded with gold nanoparticles, *Journal of the American Chemical Society*, 127 (2005) 7632-7637.

[114] G. Tian, Y. Chen, H.-L. Bao, X. Meng, K. Pan, W. Zhou, C. Tian, J.-Q. Wang, H. Fu, Controlled synthesis of thorny anatase TiO₂ tubes for construction of Ag-AgBr/TiO₂ composites as highly efficient simulated solar-light photocatalyst, *Journal of Materials Chemistry*, 22 (2012) 2081-2088.

[115] S.B. Rawal, S. Do Sung, W.I. Lee, Novel Ag₃PO₄/TiO₂ composites for efficient decomposition of gaseous 2-propanol under visible-light irradiation, *Catalysis Communications*, 17 (2012) 131-135.

[116] N.O. Gopal, H.-H. Lo, T.-F. Ke, C.-H. Lee, C.-C. Chou, J.-D. Wu, S.-C. Sheu, S.-C. Ke, Visible light active phosphorus-doped TiO₂ nanoparticles: An EPR evidence for the enhanced charge separation, *The Journal of Physical Chemistry C*, 116 (2012) 16191-16197.

- [117] L. Lin, W. Lin, Y. Zhu, B. Zhao, Y. Xie, Phosphor-doped titania-a novel photocatalyst active in visible light, *Chemistry Letters*, 34 (2005) 284-285.
- [118] X. Wang, S. Li, H. Yu, J. Yu, S. Liu, Ag₂O as a new visible - light photocatalyst: Self - stability and high photocatalytic activity, *Chemistry–A European Journal*, 17 (2011) 7777-7780.
- [119] Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, An orthophosphate semiconductor with photooxidation properties under visible-light irradiation, *Nature Materials*, 9 (2010) 559-564.
- [120] B. Cao, P. Dong, S. Cao, Y. Wang, BiOCl/Ag₃PO₄ composites with highly enhanced ultraviolet and visible light photocatalytic performances, *Journal of the American Ceramic Society*, 96 (2013) 544-548.
- [121] X. Guan, L. Guo, Cocatalytic effect of SrTiO₃ on Ag₃PO₄ toward enhanced photocatalytic water oxidation, *ACS Catalysis*, 4 (2014) 3020-3026.
- [122] S. Kumar, T. Surendar, A. Baruah, V. Shanker, Synthesis of a novel and stable g-C₃N₄-Ag₃PO₄ hybrid nanocomposite photocatalyst and study of the photocatalytic activity under visible light irradiation, *Journal of Materials Chemistry A*, 1 (2013) 5333-5340.
- [123] H. Katsumata, T. Sakai, T. Suzuki, S. Kaneco, Highly efficient photocatalytic activity of g-C₃N₄/Ag₃PO₄ hybrid photocatalysts through Z-scheme photocatalytic mechanism under visible light, *Industrial & Engineering Chemistry Research*, 53 (2014) 8018-8025.
- [124] J. Guo, S. Ouyang, H. Zhou, T. Kako, J. Ye, Ag₃PO₄/In (OH)₃ composite photocatalysts with adjustable surface-electric property for efficient photodegradation of organic dyes under simulated solar-light irradiation, *The Journal of Physical Chemistry C*, 117 (2013) 17716-17724.

- [125] P. Amornpitoksuk, S. Suwanboon, Photocatalytic decolorization of methylene blue dye by $\text{Ag}_3\text{PO}_4\text{-AgX}$ ($\text{X} = \text{Cl}^-$, Br^- and I^-) under visible light, *Advanced Powder Technology*, 25 (2014) 1026-1030.
- [126] J. Cao, B. Luo, H. Lin, B. Xu, S. Chen, Visible light photocatalytic activity enhancement and mechanism of $\text{AgBr/Ag}_3\text{PO}_4$ hybrids for degradation of methyl orange, *Journal of Hazardous Materials*, 217 (2012) 107-115.
- [127] Z. Chen, W. Wang, Z. Zhang, X. Fang, High-efficiency visible-light-driven $\text{Ag}_3\text{PO}_4/\text{AgI}$ photocatalysts: Z-scheme photocatalytic mechanism for their enhanced photocatalytic activity, *The Journal of Physical Chemistry C*, 117 (2013) 19346-19352.
- [128] W. Teng, X. Li, Q. Zhao, J. Zhao, D. Zhang, In situ capture of active species and oxidation mechanism of RhB and MB dyes over sunlight-driven $\text{Ag/Ag}_3\text{PO}_4$ plasmonic nanocatalyst, *Applied Catalysis B: Environmental*, 125 (2012) 538-545.
- [129] S. Taylor, M. Mehta, A. Samokhvalov, Production of Hydrogen by Glycerol Photoreforming Using Binary Nitrogen-Metal-Promoted N-M-TiO₂ Photocatalysts, *ChemPhysChem*, 15 (2014) 942-949.
- [130] J. Lu, F. Su, Z. Huang, C. Zhang, Y. Liu, X. Ma, J. Gong, N-doped Ag/TiO_2 hollow spheres for highly efficient photocatalysis under visible-light irradiation, *Rsc Advances*, 3 (2013) 720-724.
- [131] K. Gupta, R. Singh, A. Pandey, A. Pandey, Photocatalytic antibacterial performance of TiO_2 and Ag-doped TiO_2 against *S. aureus.*, *P. aeruginosa* and *E. coli*, *Beilstein Journal of Nanotechnology*, 4 (2013) 345-351.
- [132] K.M. Reddy, S.V. Manorama, A.R. Reddy, Bandgap studies on anatase titanium dioxide

nanoparticles, *Materials Chemistry and Physics*, 78 (2003) 239-245.

[133] S. Dai, Y. Wu, T. Sakai, Z. Du, H. Sakai, M. Abe, Preparation of highly crystalline TiO₂ nanostructures by acid-assisted hydrothermal treatment of hexagonal-structured nanocrystalline titania/cetyltrimethylammonium bromide nanoskeleton, *Nanoscale Research Letters*, 5 (2010) 1829.

[134] Y. Zheng, L. Zheng, Y. Zhan, X. Lin, Q. Zheng, K. Wei, Ag/ZnO heterostructure nanocrystals: Synthesis, characterization, and photocatalysis, *Inorganic Chemistry*, 46 (2007) 6980-6986.

[135] A. Imanishi, E. Tsuji, Y. Nakato, Dependence of the work function of TiO₂ (rutile) on crystal faces, studied by a scanning auger microprobe, *The Journal of Physical Chemistry C*, 111 (2007) 2128-2132.

[136] T. Yan, H. Zhang, Y. Liu, W. Guan, J. Long, W. Li, Fabrication of robust M/Ag₃PO₄ (M = Pt, Pd, Au) Schottky-type heterostructures for improved visible-light photocatalysis, *RSC Advances*, 4 (2014) 37220–37230.

[137] V.M. Daskalaki, M. Antoniadou, G. Li Puma, D.I. Kondarides, P. Lianos, Solar light-responsive Pt/CdS/TiO₂ photocatalysts for hydrogen production and simultaneous degradation of inorganic or organic sacrificial agents in wastewater, *Environmental Science & Technology*, 44 (2010) 7200-7205.

[138] Y.N. Yang, Q. Zhu, D.W. Li, X.H. Hu, Degradation of Rhodamine B by Highly Efficient Photocatalyst TiO₂-Ag/Ag⁺ under Simulated Sunlight Irradiation, *Advanced Materials Research*, 1051 (2014) 112-116.

[139] Y. Lei, L.-D. Zhang, G.-W. Meng, G.-H. Li, X. Zhang, C. Liang, W. Chen, S. Wang, Preparation and photoluminescence of highly ordered TiO₂ nanowire arrays, *Applied Physics Letters*, 78 (2001) 1125-1127.

- [140] Y.-H. Chang, C.-M. Liu, C. Chen, H.-E. Cheng, The effect of geometric structure on photoluminescence characteristics of 1-D TiO₂ nanotubes and 2-D TiO₂ films fabricated by atomic layer deposition, *Journal of The Electrochemical Society*, 159 (2012) D401-D405.
- [141] C.D. Jaeger, A.J. Bard, Spin trapping and electron spin resonance detection of radical intermediates in the photodecomposition of water at titanium dioxide particulate systems, *Journal of Physical Chemistry*, 83 (1979) 3146-3152.
- [142] Y.A. Ilan, G. Czapski, D. Meisel, The one-electron transfer redox potentials of free radicals. I. The oxygen/superoxide system, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 430 (1976) 209-224.
- [143] B.G. Kwon, Characterization of the hydroperoxyl/superoxide anion radical (HO₂/O₂⁻) formed from the photolysis of immobilized TiO₂ in a continuous flow, *Journal of Photochemistry and Photobiology A: Chemistry*, 199 (2008) 112-118.
- [144] T. Tatsuma, S.-I. Tachibana, A. Fujishima, Remote oxidation of organic compounds by UV-irradiated TiO₂ via the gas phase, *The Journal of Physical Chemistry B*, 105 (2001) 6987-6992.
- [145] B.H. Bielski, D.E. Cabelli, R.L. Arudi, A.B. Ross, Reactivity of HO₂/O₂⁻ radicals in aqueous solution, *Journal of Physical and Chemical Reference Data*, 14 (1985) 1041-1100.
- [146] M. Shang, W. Wang, H. Xu, New Bi₂WO₆ nanocages with high visible-light-driven photocatalytic activities prepared in refluxing EG, *Crystal Growth and Design*, 9 (2008) 991-996.
- [147] L. Zhang, W. Wang, Z. Chen, L. Zhou, H. Xu, W. Zhu, Fabrication of flower-like Bi₂WO₆ superstructures as high performance visible-light driven photocatalysts, *Journal of Materials Chemistry*, 17 (2007) 2526-2532.

- [148] Y. Zhou, Y. Zhang, M. Lin, J. Long, Z. Zhang, H. Lin, J.C.-S. Wu, X. Wang, Monolayered Bi_2WO_6 nanosheets mimicking heterojunction interface with open surfaces for photocatalysis, *Nature Communications*, 6 (2015).
- [149] J. Tian, Y. Sang, G. Yu, H. Jiang, X. Mu, H. Liu, A Bi_2WO_6 - based hybrid photocatalyst with broad spectrum photocatalytic properties under UV, visible, and near - infrared irradiation, *Advanced Materials*, 25 (2013) 5075-5080.
- [150] Y. Tian, B. Chang, J. Lu, J. Fu, F. Xi, X. Dong, Hydrothermal synthesis of graphitic carbon nitride- Bi_2WO_6 heterojunctions with enhanced visible light photocatalytic activities, *ACS Applied Materials & Interfaces*, 5 (2013) 7079-7085.
- [151] C. Pan, D. Li, X. Ma, Y. Chen, Y. Zhu, Effects of distortion of PO_4 tetrahedron on the photocatalytic performances of BiPO_4 , *Catalysis Science & Technology*, 1 (2011) 1399-1405.
- [152] Y.-F. Lin, H.-W. Chang, S.-Y. Lu, C. Liu, Preparation, characterization, and electrophysical properties of nanostructured BiPO_4 and Bi_2Se_3 derived from a structurally characterized, single-source precursor $\text{Bi}[\text{Se}_2\text{P}(\text{O}_i\text{Pr})_2]_3$, *The Journal of Physical Chemistry C*, 111 (2007) 18538-18544.
- [153] Y. Lv, Y. Zhu, Y. Zhu, Enhanced photocatalytic performance for the BiPO_{4-x} nanorod induced by surface oxygen vacancy, *The Journal of Physical Chemistry C*, 117 (2013) 18520-18528.
- [154] Z. Li, S. Yang, J. Zhou, D. Li, X. Zhou, C. Ge, Y. Fang, Novel mesoporous g- C_3N_4 and BiPO_4 nanorods hybrid architectures and their enhanced visible-light-driven photocatalytic performances, *Chemical Engineering Journal*, 241 (2014) 344-351.
- [155] Y. Lv, Y. Liu, Y. Zhu, Y. Zhu, Surface oxygen vacancy induced photocatalytic performance

- enhancement of a BiPO₄ nanorod, *Journal of Materials Chemistry A*, 2 (2014) 1174-1182.
- [156] Y. Li, J. Liu, X. Huang, J. Yu, Carbon-modified Bi₂WO₆ nanostructures with improved photocatalytic activity under visible light, *Dalton Transactions*, 39 (2010) 3420-3425.
- [157] P. Zhang, J. Zhang, A. Xie, S. Li, J. Song, Y. Shen, Hierarchical flower-like Bi₂WO₆ hollow microspheres: Facile synthesis and excellent catalytic performance, *Rsc Advances*, 5 (2015) 23080-23085.
- [158] D. Wang, G. Xue, Y. Zhen, F. Fu, D. Li, Monodispersed Ag nanoparticles loaded on the surface of spherical Bi₂WO₆ nanoarchitectures with enhanced photocatalytic activities, *Journal of Materials Chemistry*, 22 (2012) 4751-4758.
- [159] Z. Sun, J. Guo, S. Zhu, L. Mao, J. Ma, D. Zhang, A high-performance Bi₂WO₆-graphene photocatalyst for visible light-induced H₂ and O₂ generation, *Nanoscale*, 6 (2014) 2186-2193.
- [160] S. Sun, W. Wang, D. Jiang, L. Zhang, X. Li, Y. Zheng, Q. An, Bi₂WO₆ quantum dot-intercalated ultrathin montmorillonite nanostructure and its enhanced photocatalytic performance, *Nano Research*, 7 (2014) 1497-1506.
- [161] D. Wang, T. Hisatomi, T. Takata, C. Pan, M. Katayama, J. Kubota, K. Domen, Core/shell photocatalyst with spatially separated Co - catalysts for efficient reduction and oxidation of water, *Angewandte Chemie International Edition*, 52 (2013) 11252-11256.
- [162] B. Kiss, C. Didier, T. Johnson, T.D. Manning, M.S. Dyer, A.J. Cowan, J.B. Claridge, J.R. Darwent, M.J. Rosseinsky, Photocatalytic water oxidation by a pyrochlore oxide upon irradiation with visible light: Rhodium substitution into Yttrium Titanate, *Angewandte Chemie International Edition*, 53 (2014) 14480-14484.

[163] F. Zhang, A. Yamakata, K. Maeda, Y. Moriya, T. Takata, J. Kubota, K. Teshima, S. Oishi, K. Domen, Cobalt-modified porous single-crystalline LaTiO_2N for highly efficient water oxidation under visible light, *Journal of the American Chemical Society*, 134 (2012) 8348-8351.

List of publications and awards

Publications:

1. Xiaohong Hu, Qi Zhu, Xinlong Wang, Naoki Kawazoe and Yingnan Yang, Nonmetal-metal-semiconductor-promoted P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst with superior photocatalytic activity and stability, *J. Mater. Chem. A*, 3 (2015) 17858-17865. IF: 8.262
2. Xiaohong Hu, Zhibin Gu, Qi Zhu, Nan Zhang, Dawei Li and Yingnan Yang, Wastewater treatment by sonophotocatalysis using PEG modified TiO₂ film in a circular photocatalytic-ultrasonic system, *Ultrasonics Sonochemistry*, 36 (2017) 301-308. IF: 4.556
3. Qi Zhu¹, Xiaohong Hu¹, Mishma S. Stanislaus, Nan Zhang, Ruida Xiao, Na Liu and Yingnan Yang, A novel P/Ag/Ag₂O/Ag₃PO₄/TiO₂ composite film for water purification and antibacterial application under solar light irradiation (¹ These authors contributed equally to this work.), *Science of the Total Environment*, 577 (2017) 236-244. IF: 3.976
4. Xinlong Wang, Xiaohong Hu, Jingchao Li, Adriana C. Mulero Russe, Naoki Kawazoe, Yingnan Yang and Guoping Chen, Influence of cell size on cellular uptake of gold nanoparticles, *Biomater. Sci.*, 4 (2016) 970–978. IF: 3.614
5. Xinlong Wang, Xiaohong Hu, Naoki Kawazoe, Yingnan Yang and Guoping Chen, Manipulating cell nanomechanics using micropatterned surfaces, *Advanced Functional Materials*, 26 (2016)7634–7643. IF: 11.38
6. Xinlong Wang, Xiaohong Hu, Ida Dulinska-Molak, Naoki Kawazoe, Yingnan Yang and Guoping Chen, “Discriminating the independent influence of cell adhesion and spreading area on stem cell fate determination using micropatterned surfaces” *Scientific Reports*, 6 (2016) 28708. IF:

5.228

7. Xinlong Wang, Yingjun Yang, Xiaohong Hu, Naoki Kawazoe, Yingnan Yang and Guoping Chen, Morphological and mechanical properties of osteosarcoma microenvironment cells explored by atomic force microscopy, *Analytical Sciences*, 32 (2016) 1172-1182. IF: 1.174

8. Nan Zhang, Silvia Mishma Stanislaus, Xiaohong Hu, Chengyu Zhao, Qi Zhu, Dawei Li and Yingnan Yang Strategy of mitigating ammonium-rich waste inhibition on anaerobic digestion by using illuminated bio-zeolite fixed-bed process, *Bioresource Technology*, 222 (2016) 59-65. IF: 4.932

9. Yingnan Yang, Qi Zhu, Dawei Li and Xiaohong Hu, Degradation of rhodamine B by highly efficient photocatalyst $\text{TiO}_2\text{-Ag/Ag}^+$ under simulated sunlight irradiation, *Advanced Materials Research*, 1051 (2014) 112-116. IF: 0.23

10. Hanying Zheng, Dawei Li, Mishma S. Stanislaus, Nan Zhang, Qi Zhu, Xiaohong Hu and Yingnan Yang, Development of a bio-zeolite fixed-bed bioreactor for mitigating ammonia inhibition of anaerobic digestion with extremely high ammonium concentration livestock waste, *Chemical Engineering Journal*, 280 (2015) 106-114. IF: 5.310

Patent:

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Award:

1. Excellent presentation award, 1st Asia University Symposium on Biomedical Engineering.

December 12th-14th, 2014, Taipei, Taiwan.

2. Best poster design award, International agricultural ESD symposium. November 18th-19th,

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