Photo-Fenton Process over an Fe-Free 3%-CuO/Sr0.76Ce0.16WO4 Photocatalyst under Simulated Sunlight

Mingyan Fu, Jia Yang,* Xiaorui Sun,* Wei Tian, Guihua Yin, Sheng Tian, Mingdan Tan, Hongfu Liu, Xiaofeng Xing, and Huisheng Huang

ABSTRACT: Photo-Fenton is a promising photocatalytic technology that utilizes sunlight. Herein, an Fe-free 3%-CuO/Sr0.76Ce0.16WO4 photocatalyst was synthesized to apply simulated wastewater degradation via a photo-Fenton process under simulated sunlight. The photodegradation efficiency of RhB solution over the 3%-CuO/Sr0.76Ce0.16WO4 photocatalyst is 93.2% in the first 3 h; its photocatalytic efficiency remains at 91.6% even after three cycle experiments. The kinetic constant of the 3%-CuO/Sr0.76Ce0.16WO4 photocatalyst is 0.0127 min⁻¹, which is 2.8-fold that of an intrinsic Sr0.76Ce0.16WO4 sample. The experiment of radical quenching revealed that the photogenerated electrons and holes are transferred to CuO to form hydroxyl radicals. Besides, the photocatalyst was characterized by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), diffused reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS) measurements. It has some reference significance for the design of iron-free photocatalysts.

1. INTRODUCTION

Environmental protection has been facing a huge challenge with the increasing development of industries, i.e., printing and dyeing industry, leather tanning, pharmaceutical industry, petrochemical engineering, and so on. The organic content in wastewater as a harmful byproduct is generated in these industrial processes. It is necessary to remove contaminants via any advantageous method. The Fenton reaction is an effective method for the nonselective decomposition of organic pollutants, which is due to the powerful oxidation ability of hydroxyl radicals. Faheem et al. reported Cu2O-CuFe2O4 microparticles to degrade phenol at a pH of 4 in the presence of H2O2. When the initial pH value of rhodamine 6G is 6.9, a 1 wt % iron-containing TiO2 photocatalyst displays almost complete color removal after 90 min of the photoreaction. The Bi2Ga3.2Fe0.8O9 photocatalyst presents a nearly 100% photodegradation activity of RhB at neutral conditions. The Fe element in the photocatalyst plays the role of an active site to facilitate the production of •OH. However, the possible existence of ferromagnetism may cause the photocatalyst to disperse unevenly in the solution via a magnetic agitator, which is unfavorable for the photocatalytic reaction.

Recently, an iron-free semiconducting material was utilized in the photo-Fenton reaction. A ZnS/SnO2 nanosheet acts in solution, an Fe2O3-decorated TiO2 nanotube shows an excellent methyl orange decomposition performance of 90% in 10 min. When the initial pH value of rhodamine 6G is 6.9, a 1 wt % iron-containing TiO2 photocatalyst displays almost complete color removal after 90 min of the photoreaction. The Bi2Ga3.2Fe0.8O9 photocatalyst presents a nearly 100% photodegradation activity of RhB at neutral conditions. The Fe element in the photocatalyst plays the role of an active site to facilitate the production of •OH. However, the possible existence of ferromagnetism may cause the photocatalyst to disperse unevenly in the solution via a magnetic agitator, which is unfavorable for the photocatalytic reaction.

To eliminate the limitation of the pH value in the Fenton reaction, the photo-Fenton reaction was developed as a selective strategy for the decomposition of organic contaminants. Generally, the Fe element is a key component of the catalyst that is utilized in the photo-Fenton reaction. For instance, without adjusting the pH value of the reaction solution, an Fe2O3-decorated TiO2 nanotube shows an excellent methyl orange decomposition performance of 90% in 10 min. When the initial pH value of rhodamine 6G is 6.9, a 1 wt % iron-containing TiO2 photocatalyst displays almost complete color removal after 90 min of the photoreaction. The Bi2Ga3.2Fe0.8O9 photocatalyst presents a nearly 100% photodegradation activity of RhB at neutral conditions. The Fe element in the photocatalyst plays the role of an active site to facilitate the production of •OH. However, the possible existence of ferromagnetism may cause the photocatalyst to disperse unevenly in the solution via a magnetic agitator, which is unfavorable for the photocatalytic reaction.

Recently, an iron-free semiconducting material was utilized in the photo-Fenton reaction. A ZnS/SnO2 nanosheet acts in
the degradation reaction of roxithromycin and clarithromycin antibiotics under ultraviolet light. A supramolecular Cu-containing polymeric structure was synthesized for the degradation of naphthol blue black in water via the photo-Fenton process. A series of Cu$_x$P$_2$O$_5$+$x$ (x = 2, 3, 4) semiconducting materials were obtained via a traditional solid-state method, which were utilized in the photo-Fenton reaction for the first time under visible−infrared light irradiation.

Herein, an iron-free material, Sr$_{0.76}$Ce$_{0.16}$WO$_4$, was used as a photocatalyst for the photo-Fenton degradation of simulated wastewater. Four kinds of metal elements, CuO, Ag, Au, and Pt, were loaded on the as-prepared photocatalyst via the photodeposition method. A pseudo first-order kinetic constant was employed to quantitatively assess the photocatalytic performance of RhB.

2. RESULTS AND DISCUSSION

Figure 1a shows that the Sr$_{0.76}$Ce$_{0.16}$WO$_4$ sample was successfully synthesized without any impurities compared to the simulated XRD pattern of SrWO$_4$. The sample has high crystallinity, revealed by the sharp characteristic peak (112) and its high intensity. In addition, other diffraction peaks are consistent with the standard XRD pattern.
Sr$_{0.76}$Ce$_{0.16}$WO$_4$, which are compared with those of the undoped SrWO$_4$ sample. Pandey et al. studied the FT-IR spectra of the Er$^{3+}$-Yb$^{3+}$-codoped SrWO$_4$ sample, which are similar to ours. Ju et al. reported that the characteristic peak of Eu$^{3+}$-doped SrWO$_4$ was at around 820 nm, which originates from the stretching mode of O-W-O in the [WO$_4$] tetrahedron. In our experiment, the characteristic peak of SrWO$_4$ is at 834.2 nm, which highlights the yellow rectangle shows the change after doping with Ce, which can help to indicate that Ce was successfully doped into the SrWO$_4$ sample. The higher the content of Ce, the more obvious this small peak is, and the characteristic peak with a wavenumber of 834.2 nm also appears to be a significant broadening phenomenon (see Figure S1a). In the crystal structure of SrWO$_4$, Sr$^{2+}$ is 8-fold coordinated and W$^{6+}$ is 4-fold coordinated. However, after Ce doping, the coordinate environment of Sr$^{2+}$ and W$^{6+}$ remains unchanged, but there are more 8-fold-coordinated Ce-O and Ce-O-W units in the crystal structure. Therefore, the FT-IR spectra of SrWO$_4$, which originally had a single peak at 834 nm$^{-1}$, split into multiple peaks due to the introduction of Ce, which can be seen in the spectrum as the peak broadening. It should be pointed out that due to the low amount of CuO which is difficult to observe by XRD and FT-IR measurements.

Figure 2a displays that the Sr$_{0.76}$Ce$_{0.16}$WO$_4$ sample is composed of different scales of particles (0.2–8.5 μm). Figure 2b shows the smooth cross section of the sample, indicating good crystallization, consistent with XRD data. The nanoparticles around the surface of the cross section probably are Cu species. The energy-dispersive spectroscopy (EDS) data demonstrate that the average atomic ratio of Sr/Ce/W/O is 0.78:0.14:1:4.8 (see Figure 3a). Nevertheless, the Cu species were tested more than the loaded dosage, which may be because the low concentration of element is hard to detect accurately. Figure 3b–f shows that Cu, Sr, Ce, W, and O are uniformly dispersed on the surface layer of the 3%-CuO/Sr$_{0.76}$Ce$_{0.16}$WO$_4$ photocatalyst.

Figure 4 shows the XPS spectra of 3%-CuO/Sr$_{0.76}$Ce$_{0.16}$WO$_4$ in comparison with the unloaded Sr$_{0.76}$Ce$_{0.16}$WO$_4$ sample. Based on the previous SEM mapping results, the measurement
spectra reconfirmed the presence of Cu, Ce, Sr, O, and W in the 3%-CuO/Sr0.76Ce0.16WO4 photocatalyst (see Figure 4a). The specific type of Cu species cannot be identified by the SEM analysis. However, the chemical valence of the Cu element is +2, which was determined by the characteristic peaks of Cu 2p1/2 and 2p3/2 at 955.0 and 935.0 eV, respectively (see Figure 4b).17,22,23 Hence, the Cu species is CuO. Figure 4c–e shows no change in the high-resolution Sr 3d, Ce 3d, and W 4f between the 3%-CuO/Sr0.76Ce0.16WO4 and Sr0.76Ce0.16WO4 samples. The valency of Sr was determined via the characteristic peaks of Sr 3d3/2 and 3d5/2 at 135.0 and 133.2 eV, respectively (see Figure 4c). The valency of Ce was determined via the characteristic peaks of Ce 3d3/2 and 3d5/2 at 903.8 and 880.8 eV, respectively (see Figure 4d).24 The valency of W was determined via the characteristic peaks of W 3d5/2 and 3d7/2 at 37.7 and 35.4 eV, respectively (see Figure 4e).25 The chemical valences of Sr2+, Ce3+, and W6+ were identified. The 1s band spectra of oxygen are ∼529.7 and ∼533.4 eV, generally considered surface lattice oxygen and chemisorbed oxygen, respectively.21,25–30 The O 1s bands of Figure 4f are distributed at ∼530.6 eV, a mixture of surface lattice oxygen and chemisorbed oxygen. The chemisorbed oxygen was dramatically increased by the influence of the CuO compound, which is different from the Au-loaded Sr0.76Ce0.16WO4 sample (see Figure S2 and Table S1).

In this paper, the pH value of a 20 ppm RhB solution was adjusted by HCl and NaOH aqueous solutions. The results show that the absorbance of the RhB solution remains stable in a pH range from 1.2 to 10.6 (see Table S2). To avoid using extra acids and bases, a series of photo-Fenton experiments over modified Sr0.76Ce0.16WO4 samples were performed in a neutral aqueous solution under sunlight irradiation. The Sr0.76Ce0.16WO4 photocatalyst is the optimal one in comparison with the other Ce-doped SrWO4 samples (see Figure S3). H2O2, which is the chief source of hydroxyl radicals, is a key factor in the photo-Fenton process.31,32 Figure 5a presents the photocatalytic activities of Sr0.76Ce0.16WO4 and SrWO4 samples in the presence of different dosages of H2O2. The dosage of H2O2 exhibits a relatively optimal amount. Therefore, in the subsequent experiments in this paper, the amount of hydrogen peroxide was determined to be 1.5 mL. In our previous work, an inexpensive Cu species was utilized as a cocatalyst, which enhanced the photocatalytic activity.12,17 Figure 5b shows that the optimal photocatalyst is 3%-CuO/Sr0.76Ce0.16WO4. Furthermore, commensurable dosages of noble metal cocatalysts (Ag, Au, and Pt) were loaded on the Sr0.76Ce0.16WO4 sample as a reference (see Figure 5c). Their kinetic constants are 0.0099, 0.0089, and 0.0051 min⁻¹ (see Table S3). In addition, there is no change in the FT-IR spectra of these samples after photocatalysis (see Figure S1b). The cyclic experiments were performed to detect the photostability of photocatalytic activity over the 3%-CuO/Sr0.76Ce0.16WO4 photocatalyst, as shown in Figure 5d.33 The photocatalytic performance of the 3%-CuO/Sr0.76Ce0.16WO4 photocatalyst after 3 h is 93.2%. Even in the third cycle, the photocatalytic activity maintains a high value of 91.6%. Besides, no change is observed in the crystal structure of the 3%-CuO/Sr0.76Ce0.16WO4 photocatalyst after the cyclic experiment (see Figure S4).

Since the toxicity of copper has a great influence on organisms and human health, the concentration of copper ions in the solution before and after a single illumination experiment was also measured. The experimental results show that the concentration of copper ions in the solution decreases a little after illumination (see Figure S5 and Table S3), probably within the error range, as a result of continued photoreduction of copper ions in the solution. The source of copper ions in the solution before illumination is because the supported cocatalyst has not been completely reduced in the set time. In conclusion, the results indicate that copper ions do not leach during photocatalysis.
CuO nanoparticles is 1.37 eV. Hence, the electron affinity (χ) of Sr0.76Ce0.16WO4 sample, a possible mechanism is shown in Figure 6a, which is obtained independently in them. Then, these photogenerated electrons react with H2O2 to form *OH. The photogenerated holes react with H2O to form *OH as well. Photo-Fenton experiments can still be carried out efficiently without iron.

4. EXPERIMENTAL SECTION

4.1. Synthesis of the Photocatalyst. The Sr0.76Ce0.16WO4 sample was obtained via a solid-state method at a high temperature. In a run, to obtain 1.3000 g of the sample, 0.3926 g of SrCO3, 0.8111 g of WO3, and 0.0963 g of CeO2 were mixed evenly by hand. The mixture was first preheated at 700 °C for 10 h and finally heated at 1000 °C for 15 h in a high-temperature box furnace. After the preheating and heating processes, the obtained powders were ground adequately for half an hour. Sr1−xCeWO4 (0 ≤ x ≤ 0.20) solid solutions were synthesized by the same method.

4.2. Loading Cocatalyst. The cocatalysts, CuO, Ag, Au, and Pt, were loaded on the Sr0.76Ce0.16WO4 sample for improving its photocatalytic activity. For instance, 3%-CuO/Sr0.76Ce0.16WO4 means loading 3.0 wt % Cu element on the Sr0.76Ce0.16WO4 sample via the photodeposition method. One hundred milligrams of the Sr0.76Ce0.16WO4 powder sample and 9.42 mL of a 0.3182 mg/mL Cu(CH3COO)2 solution were mixed in 10 mL of a 10 vol % methanol solution. The mixture was mixed evenly via ultrasound treatment for 10 min. After that, the suspension solution was irradiated using a 300 W Hg lamp for 1 h. Finally, the obtained powder was dried in a drying oven at 65 °C and named 3%-CuO/Sr0.76Ce0.16WO4.

4.3. Characterization. Powder X-ray diffraction (XRD) data were measured via a PANalytical X’pert diffractometer with Cu Kα radiation. Fourier transform infrared spectroscopy (FT-IR, PerkinElmer Spectrum 100) was adopted to determine the structure information of the photocatalyst.

Finally, the photocatalytic mechanism was discussed to understand the photo-Fenton process without the presence of the Fe element. The potentials of the conduction band (CB) and the valence band (VB) are significant for analyzing the photocatalytic mechanism. There is a classical method that is called Mulliken electronegativity (χ). The applied equations are as follows

\[ E_{VB} = \chi - E_f + 0.5E_g \]

\[ E_{CB} = E_{VB} - E_g \]

where \( E_{VB}, E_{CB}, \) and \( E_f \) are the VB potential, CB potential, and band gap of the photocatalyst, respectively; the magnitude of \( E_g \) is 4.50 eV. The χ values of Sr0.76Ce0.16WO4 and CuO are 5.67 and 5.81 eV, respectively. The band gap of Sr0.76Ce0.16WO4 is 3.13 eV (see Figure S6). The band gap of CuO; meanwhile, the photogenerated holes move from the VB of Sr0.76Ce0.16WO4 to the CB of CuO. Although the increase of photogenerated carriers on CuO increases the probability of recombination, it provides the opportunity to improve the photocatalytic activity.

Because \( E_{CB} (\text{CuO}) > E (\text{O}_2^*/\text{O}_2^-) \), \( \text{O}_2^- \) cannot be produced in the CB of CuO, which is also consistent with the quenching experiment of free radicals; that is, superoxide anions have the least influence on the photocatalytic process. On the CB of CuO, the photogenerated electrons react with \( \text{H}_2\text{O}_2 \) to produce \( \text{O}_2^* \). The photogenic holes clustered in the other half of the valence band can only oxidize water to form hydroxyl radicals due to the relationship of electric potential or directly oxidize pollutants. From the results of free radical quenching experiments, photogenerated holes tend to oxidize water to form hydroxyl radicals. This is also the reason for the sharp decrease in activity after the addition of IPA to the solution.

3. CONCLUSIONS

An iron-free material, 3%-CuO/Sr0.76Ce0.16WO4, based on the photo-Fenton process, degrades simulated wastewater with RhB. The kinetic constant of the photocatalyst is 0.0127 min⁻¹, which is 2.8-fold that of an intrinsic Sr0.76Ce0.16WO4 photocatalyst. The photocatalytic performance of the photocatalyst maintains stability in three cyclic experiments. The experiment of radical quenching reveals that *OH plays a major role in the photo-Fenton process. The photogenerated electrons react with H2O2 to form *OH. The photogenerated holes react with H2O to form *OH as well. Photo-Fenton experiments can still be carried out efficiently without iron.
Photodegradation RhB activity was assessed as follows:

\[ \text{photodegradation RhB efficiency} = \frac{(A_0 - A_t)}{A_0} \times 100\% \]

where \( A_0 \) means the absorption of the first sample before simulated sunlight irradiation, and \( A_t \) means the absorption of the last sample after simulated sunlight irradiation.

Kinetic constant \( k \) can be calculated by the following equation:

\[ \ln\left(\frac{A_0}{A_t}\right) = kt \]

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04107.

Summary of the photo-oxidation RhB activity of the as-prepared photocatalyst: O 1s orbital composition of St0.76Ce0.16WO4 and 3%-CuO/St0.76Ce0.16WO4 samples are based on the analysis of XPS data; summary of the absorbance of a 20 ppm RhB solution at different pH values; absorbance and concentration of copper ions before and after the photocatalytic reaction were measured by copper reagent spectrophotometry; XRD image of the 3%-CuO/St0.76Ce0.16WO4 sample after the cyclic experiment; DRS image of the St0.76Ce0.16WO4 sample; and (a) FT-IR spectra of St1-xCe_xWO4 solid solutions and (b) FT-IR spectra of St0.76Ce0.16WO4, which loaded different cocatalysts after photocatalysis.

## ACKNOWLEDGMENTS

This work was financially supported by Chongqing Municipal Education Commission (KJQN202101405 and CQXQ20026), and Talent Introduction Project of Yangtze Normal University (2017KYQD22). The authors would like to thank Ting Du from Shiyanjia Lab (www.shiyanjia.com) for SEM analysis.

## REFERENCES

1. Lam, S. S.; Nguyen, V.; Dinh, M. T. N.; Khiueu, D. Q.; La, D. D.; Nguyen, H. T.; Vo, D. V. N.; Xia, C.; Varma, R. S.; Shokouhimehr, M.; et al. Mainstream avenues to boost graphitic carbon nitride efficiency: Toward enhanced solar-driven photocatalytic hydrogen production and environmental remediation. J. Mater. Chem. A 2020, 8, 10571–10603.
2. (Lang, X.; Ma, W.; Chen, C.; Ji, H.; Zhao, J. Selective aerobic oxidation mediated by TiO2 photocatalysis. Acc. Chem. Res. 2014, 47, 355–363.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04107.

Summary of the photo-oxidation RhB activity of the as-prepared photocatalyst: O 1s orbital composition of St0.76Ce0.16WO4 and 3%-CuO/St0.76Ce0.16WO4 samples are based on the analysis of XPS data; summary of the absorbance of a 20 ppm RhB solution at different pH values; absorbance and concentration of copper ions before and after the photocatalytic reaction were measured by copper reagent spectrophotometry; XRD image of the 3%-CuO/St0.76Ce0.16WO4 sample after the cyclic experiment; DRS image of the St0.76Ce0.16WO4 sample; and (a) FT-IR spectra of St1-xCe_xWO4 solid solutions and (b) FT-IR spectra of St0.76Ce0.16WO4, which loaded different cocatalysts after photocatalysis.

## ACKNOWLEDGMENTS

This work was financially supported by Chongqing Municipal Education Commission (KJQN202101405 and CQXQ20026), and Talent Introduction Project of Yangtze Normal University (2017KYQD22). The authors would like to thank Ting Du from Shiyanjia Lab (www.shiyanjia.com) for SEM analysis.

## REFERENCES

1. Lam, S. S.; Nguyen, V.; Dinh, M. T. N.; Khiueu, D. Q.; La, D. D.; Nguyen, H. T.; Vo, D. V. N.; Xia, C.; Varma, R. S.; Shokouhimehr, M.; et al. Mainstream avenues to boost graphitic carbon nitride efficiency: Toward enhanced solar-driven photocatalytic hydrogen production and environmental remediation. J. Mater. Chem. A 2020, 8, 10571–10603.
2. (Lang, X.; Ma, W.; Chen, C.; Ji, H.; Zhao, J. Selective aerobic oxidation mediated by TiO2 photocatalysis. Acc. Chem. Res. 2014, 47, 355–363.
(3) Garcia-Segura, S.; Bellotindos, L. M.; Huang, Y.; Brillas, E.; Lu, M. Fluidize d-b e d Fenton process as alternative wastewater treatment technology-A review. J. Taiwan Inst. Chem. Eng. 2016, 67, 211–225.

(4) Bello, M. M.; Raman, A. A. A.; Asghar, A. A review on approaches for addressing the limitations of Fentonoxidation for recalcitrant wastewater treatment. Process Saf. Environ. 2019, 126, 119–140.

(5) Faheem, M.; Jiang, X.; Wang, L.; Shen, J. Synthesis of CuO–CuFe2O4 microparticles from Fenton sludge and its application in the Fenton process: the key role of CuO in the catalytic degradation of phenol. RSC Adv. 2018, 8, 5740–5748.

(6) Lu, H.; Chen, H.; Kao, C.; Chao, I.; Chen, H. Computational study of the Fenton reaction at 1 different pH ranges. Phys. Chem. Chem. Phys. 2018, 20, 22890–22901.

(7) Jeong, J.; Yoon, J. pH effect on OH radical production in photo/ferrioxalate system. Water Res. 2005, 39, 2893–2900.

(8) Zhu, Y.; Zhu, R.; Xi, Y.; Zhu, J.; Zhu, G.; He, H. Strategies for enhancing the heterogeneous Fenton catalytic reactivity: A review. Appl. Catal., B 2019, 255, 117739–117754.

(9) Zhang, M.; Dong, H.; Zhao, L.; Wang, D.; Meng, D. A review on Fe-containing catalysts for organic wastewater treatment based on optimization perspective. Sci. Total Environ. 2019, 670, 110–121.

(10) Peng, Q.; Peng, G.; Wu, L.; Chen, Y.; Han, B.; Su, Q.; Liu, S.; Li, X. Photo-reduction enables catalysts regeneration in Fenton reaction on Fe2O3 decorated TiO2 nanotube-based photocatalyst. Dalton Trans. 2020, 49, 6730–6737.

(11) Demir, N.; Gündüz, G.; Dükkan, M. Degradation of a textile dye, Rhodamine 6G (R6G), by heterogeneous sonophotofenton process in the presence of Fe-containing TiO2 catalysts. Environ. Sci. Pollut. Res. 2015, 22, 3193–3201.

(12) Yang, J.; Sun, X.; Zeng, C.; Wang, X.; Hu, Y.; Zeng, T.; Shi, J. Highly improved photocatalytic degradation of rhodamine B over Bi4Ga4Fe3O12 solid solutions under visible light irradiation. RSC Adv. 2019, 9, 26894–26901.

(13) Hosseini, M.; Kakhka, M. R. R.; Fakhriz, A.; Tahami, S.; Lariche, M. J. Degradation of macrocide antibiotics via sono or photo coupled with Fenton methods in the presence of ZnS quantum dots decorated SnO2 nanosheets. J. Photochem. Photobiol., B 2018, 185, 24–31.

(14) Mestivier, M.; Li, J. R.; Camy, A.; Frangville, C.; Mingotaud, C.; Benoit-Marquié, F.; Marty, J. Copper based hybrid polyion complexes enhanced the photo-oxidation performance of Bi2Ga2.8Al1.2O9 photocatalysts: Insights to the visiblelight photocatalytic activity and structure and property. RSC Adv. 2015, 5, 23556–23562.

(15) Yang, J.; Fu, M.; Liu, H.; Yin, G.; Tan, M.; Sun, X.; Huang, H. An inexpensive CuO nanoparticles as cocatalyst significantly enhanced the photo-oxidation performance of Bi5Ga4Al3O12 photocatalyst under visible-light. Mater. Lett. 2021, 283, 128796–128799.

(16) Zhang, L.; Shan, B.; Yang, H.; Wu, D.; Zhu, R.; Nie, J.; Cao, R. A new heterogeneous photocatalyst based on Wells–Dawson polyoxometalate and nickel coordination compounds: synthesis, structure and property. RSC Adv. 2015, 5, 23554–23562.

(17) Pandey, A.; Rai, V. K.; Kumar, V.; Kumar, V.; Swart, H. C. Upconversion based temperature sensing ability of Er3+–Yb3+ codoped SrWO4: An optical heating phosphor. Sens. Actuators, B 2015, 209, 352–358.

(18) Lu, Z.; Wei, R.; Gao, X.; Liu, W.; Pang, C. Red phosphor SrWO4Eu3+ for potential application in white LED. Opt. Mater. 2011, 33, 909–913.

(19) Xie, X.; Hassan, Q. U.; Rao, F.; Gao, J.; Zhu, G.; et al. In situ construction of oxygen-vacancy-rich Bi6O6(WO4)2 microspheres with enhanced visible light photocatalytic for NO removal. Chin. Chem. Lett. 2021, 32, 2038–2042.

(20) Le Minh Tri, N.; Trung, D. Q.; Thuan, D. V.; Cam, N. T. D.; Tahtamouni, T. A.; Pham, T.; Duc, D. S.; Tung, M. H. T.; Ha, H. V.; Thu, N. H. A.; Trang, H. T. The advanced photocatalytic performance of V doped CuWO4 for water splitting to produce hydrogen. Int. J. Hydrogen Energy 2020, 45, 18186–18194.

(21) Liu, L.; Ji, Z.; Zou, W.; Gu, X.; Deng, Y.; Gao, F.; Tang, C.; Dong, L. In situ loading transition metal oxide clusters on TiO2 nanosheets as co-catalysts for exceptional high photocactivity. ACS Catal. 2013, 3, 2052–2061.

(22) Nie, J.; Zhu, G.; Zhang, W.; Gao, J.; Zhang, P.; Xie, X.; Huang, Y.; Hjamberdiev, M. Oxygen vacancy defects-boosted deep oxidation of NO by β-Fe2O3/Co3O4 p-n heterojunction photocatalyst in situ synthesized from Bi/Co(CO3)(OH) precursor. Chem. Eng. J. 2018, 424, No. 130327.
(38) Asadzadeh-Khaneghah, S.; Habibi-Yangjeh, A.; Abedi, M. Decoration of carbon dots and AgCl over g-C₃N₄ nanosheets: Novel photocatalysts with substantially improved activity under visible light. *Sep. Purif. Technol.* **2018**, *199*, 64–77.

(39) Wan, Z.; Zhang, G.; W, X.; Yin, S. Novel visible-light-driven Z-scheme Bi₁₂GeO₂₀/g-C₃N₄ photocatalyst: Oxygen-induced pathway of organic pollutants degradation and proton assisted electron transfer mechanism of Cr(VI) reduction. *Appl. Catal., B*, **2017**, *207*, 17–26.

(40) Yang, J.; Fu, M.; Tan, M.; Tian, Y.; Sun, X.; Huang, H. Photocatalytic reduction of Cr(VI) on a 3.0% Au/Sr₀.₇₀Ce₀.₃₀WO₄ photocatalyst. *ACS Omega* **2020**, *5*, 26755–26762.