Supplementary Material

MOF-5 derived ZnO-C nanoparticles combined with α-MnO_2 for efficient degradation of tetracycline under visible light

Fang Zhao [a], Yingdi Wang [a], Yishan Shi [a], Yuming Dong [a], Xiang Liu [a] *

[a] Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China.

*Corresponding Authors, E-mail addresses: liuxiang@jiangnan.edu.cn (Xiang Liu).

1. The TG analysis

The thermogravimetry (TG) curve of MOF-5 was displayed in Fig. S1. As we could see, the pyrolysis of MOF-5 was main starting at 400℃, and the organic components gradually pyrolyzed at 400℃-500℃. According to the thermal stability, the as-prepared MOF-5 was pyrolyzed at 450℃ under the air atmosphere, which could ensure that the organic components of MOF-5 were pyrolyzed at a mild condition, so as to retain part of the C component.

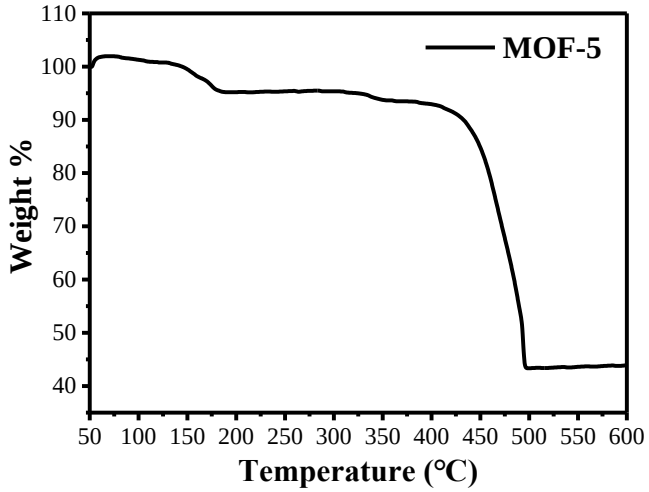

Fig. S1 TG curve of the as-prepared MOF-5.

2. The EDS spectrum of the 15-MZ composite

According to the EDS spectrum (Fig. S2), the C, O, Zn and M elements could be detected, which meant the binary 15-MZ composite was successfully synthesized. Apparently, the pyrolysis of the organic crosslinking structure left a large amount of C species, this was attributed to the incomplete pyrolysis of MOF structure during calcination and a large proportion of ZnO-C in the 15-MZ composite. Part of the remaining C was present in the composite as an electron transfer medium, while a part of the C elements was doped in ZnO crystal structure to form Zn-C bond.

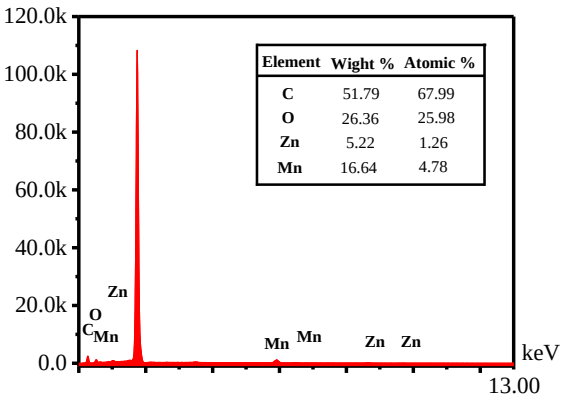

Figure. S2 EDS spectrum of the 15-MZ composite.

3. The survey XPS spectrum of 15-MZ composite

The survey XPS spectrum of 15-MZ illustrated the presence of Zn, Mn, O, and C elements, which was consistence with the results of EDS.

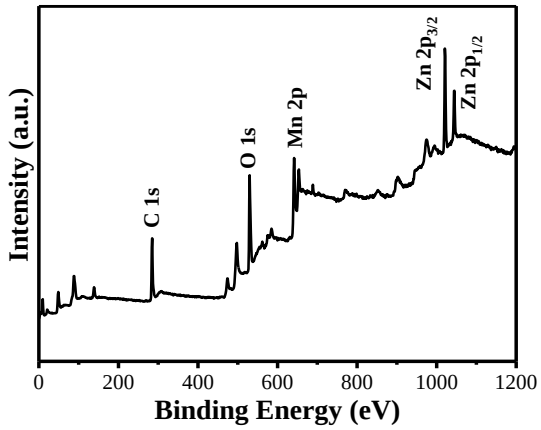

Figure. S3 The survey XPS spectrum of 15-MZ composite.

4. The pore diameter distribution curves of 15-MZ composite

The pore diameter distribution curves were shown in Fig. S4. The pore size of α-MnO_2 (mainly at 10-20 nm) is larger than that of ZnO-C nanoparticles (mainly < 5 nm), which makes the pore size distribution of 15-MZ composite expand significantly.

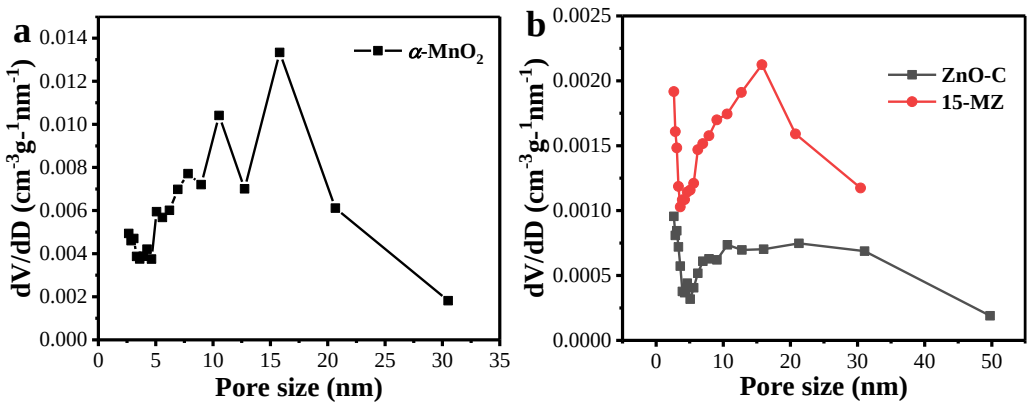

Figure. S4 The pore diameter distribution curves of (a) α-MnO_2; (b) ZnO-C and 15-MZ composite.

5. The absorption experience for TC

The adsorption experiment (Fig. S5) showed that the adsorption-desorption equilibrium of TC on photocatalysts could be achieved within 30 min.

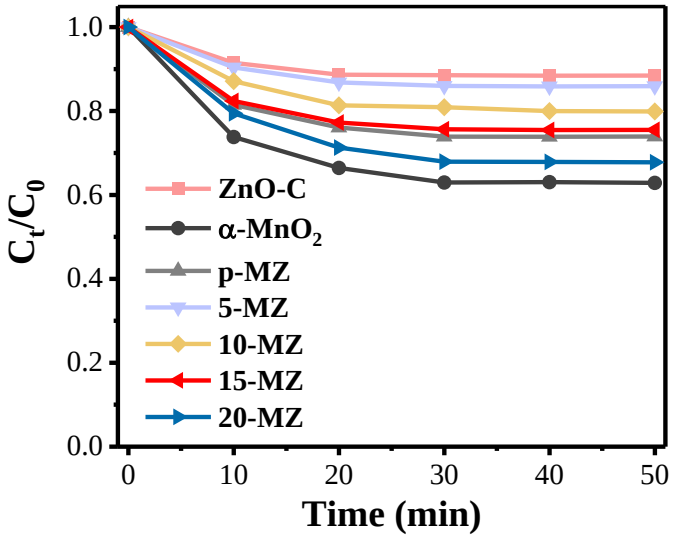

Fig. S5 The absorption performance of the catalysts for TC (0.2 g/L of catalyst dose, 10ppm of TC).

6. Effects of pH and concentration for TC degradation

As shown in the Fig. S5, the degradation efficiency corresponding to pH neutral environment was the optimum, and when the TC concentration is 10ppm, the degradation reaction is most favorable.

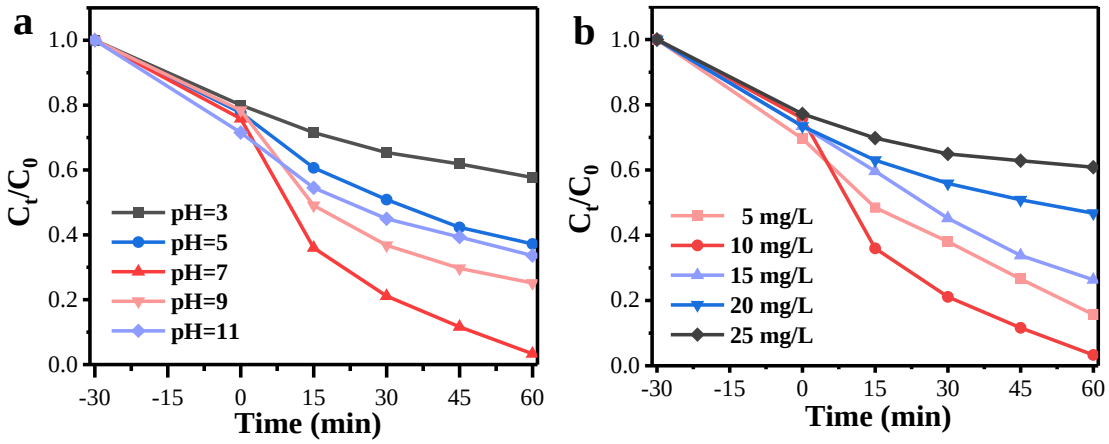

Fig. S6 (a) Effects of pH for TC degradation under visible light (0.2 g/L of catalyst dose, 10ppm of TC) and (b) effects of TC concentration for TC degradation under visible light (0.2 g/L of catalyst dose, pH=7).

7. Semi-quantitative analysis of the generated free radicals

The indirect analysis was carried to further detect the generation of free radicals. From the Fig. S6a, the fluorescence intensity of DMA was significantly reduced with the gradually increase of irradiation time, indicating that $^1O_2$ was generated in the degradation system. The UV-vis adsorption peak intensity (Fig. S6b) of NBT at 259 nm was gradually decreased with the generation of $\bullet O_2^-$. And from the Fig. S6c, the generation of •OH made the fluorescence intensity of 2-HTA at 425 nm increase with the increase of irradiation time.

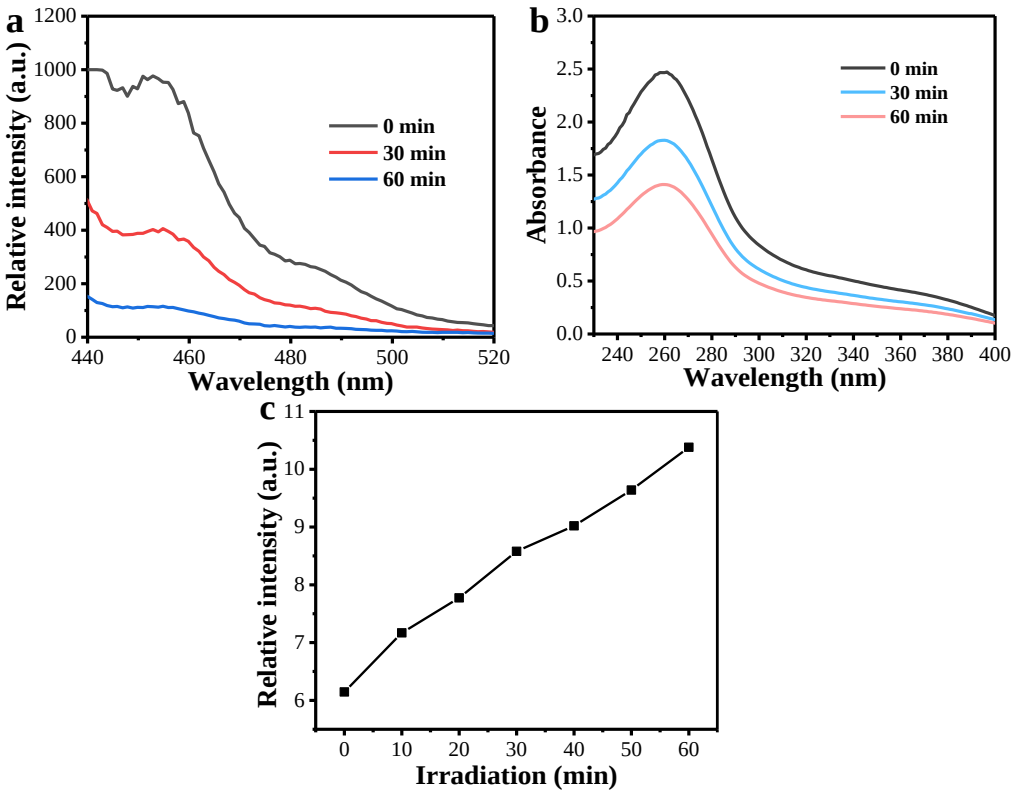

Fig. S7 The fluorescence spectrum of 10-DMA (a), UV-vis spectrum of NBT (b) and fluorescence intensity of 2-HTA at 425 nm (c).