

## Supporting Information for

### The Construction of Palladium-Hydrogen Accelerated Catalytic Fenton System

#### Enhanced by UiO-66(Zr)

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## Detailed Characterization information of the synthesized UiO-66(Zr)

The FT-IR spectrum of terephthalic acid, which was different from that of the synthesized UiO-66(Zr), was displayed in Fig.S1. The C=C stretch (at 1678  $\text{cm}^{-1}$ ), the C=O stretching vibration (at 1573  $\text{cm}^{-1}$ ), O-H in-plane bending vibrations (at 1440–1260  $\text{cm}^{-1}$ ), C-C aromatic stretch (at 1423  $\text{cm}^{-1}$ ), C-H in plane ring bending vibrations (at 1300-1000  $\text{cm}^{-1}$ ), C-O stretch (at 1282  $\text{cm}^{-1}$ ) and C-H out of plane bending vibration (at 935 and 779  $\text{cm}^{-1}$ ) were observed. This was consistent with the previous reports.<sup>1-3</sup> Compared with the FT-IR spectrum of synthesized UiO-66(Zr), these typical peaks were not obvious. The peaks of 663  $\text{cm}^{-1}$  and 746  $\text{cm}^{-1}$  corresponded to the vibration of carbon-hydrogen bond and oxygen-hydrogen bond, respectively. The peaks of 1018  $\text{cm}^{-1}$ , 1106  $\text{cm}^{-1}$  and 1157  $\text{cm}^{-1}$  corresponded to the stretching vibration of zirconium-oxygen bond, respectively. The peaks of 1506  $\text{cm}^{-1}$  and 1658  $\text{cm}^{-1}$  corresponded to the vibration of carbon-carbon double bond in benzene ring and the carboxyl group, respectively. The peaks of 1398  $\text{cm}^{-1}$  and 1585  $\text{cm}^{-1}$  corresponded to the symmetric/asymmetric stretching vibrations of carboxyl group. It indicated that the terephthalic acid PTA undoubtedly participated in the reaction of preparing UiO-66(Zr). It constituted the skeleton structure of UiO-66(Zr).

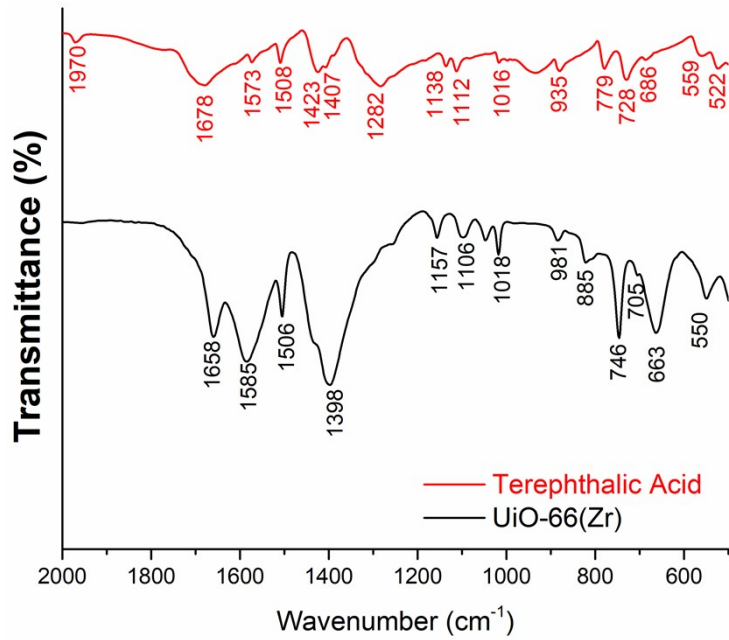


Fig.S1 The FT-IR spectrums of synthesized UiO-66(Zr) and terephthalic acid

The XRD pattern of the synthesized UiO-66(Zr) was displayed in Fig.S2. The characteristic diffraction peaks at 7.29°, 8.42°, 11.92°, 13.99°, 14.61°, 23.98°, 25.46°, 30.40°, 36.31° and 43.98° could be observed. It matched well with the theoretical one of UiO-66(Zr) produced by using Diamond software with versatile Crystallographic Information Framework file. <sup>4</sup>

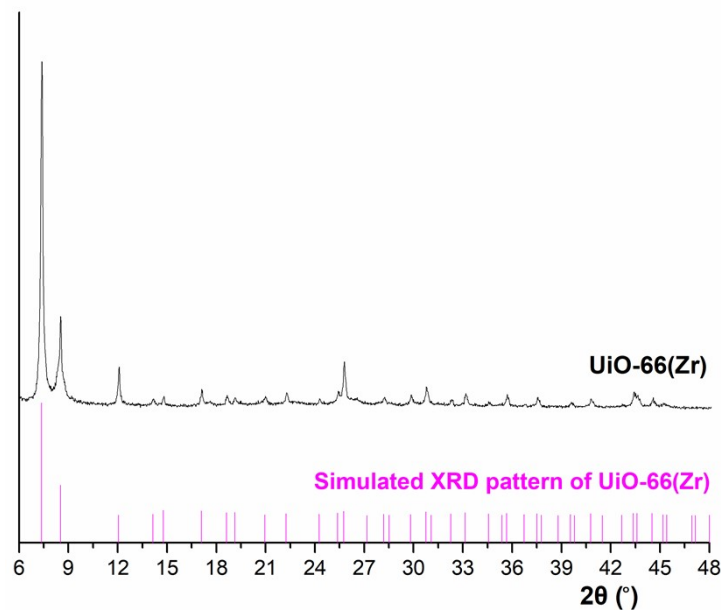


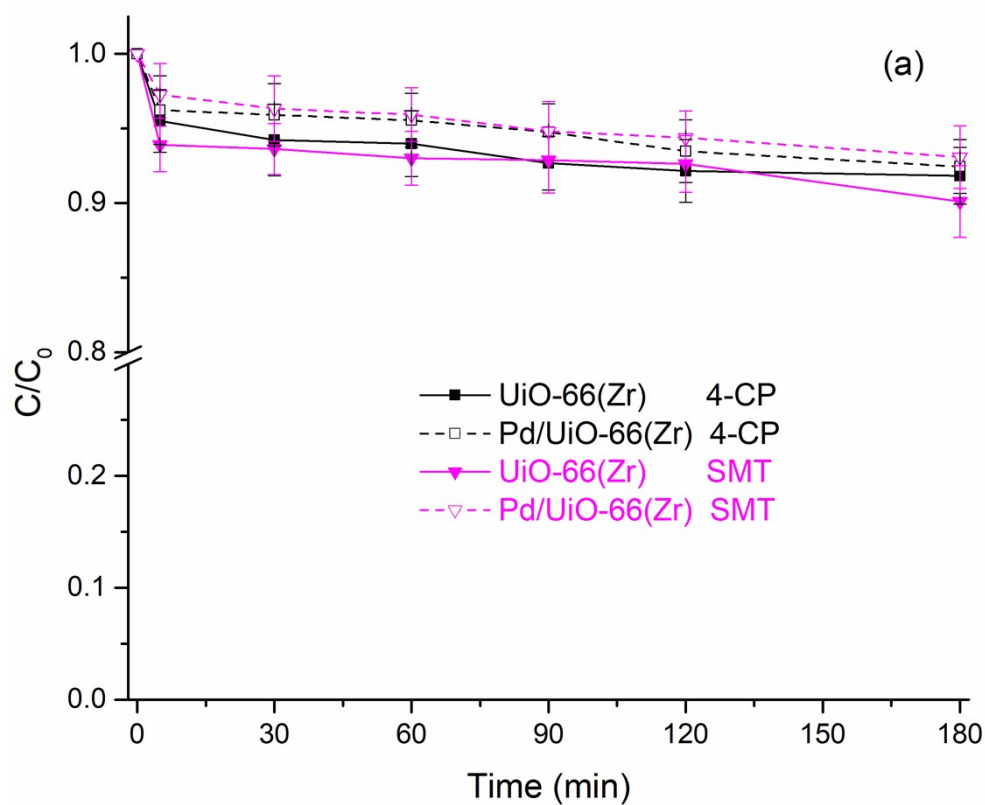
Fig.S2 The simulated ref. XRD pattern of UiO-66(Zr) and XRD pattern of synthesized UiO-66(Zr)

### Control Tests

The adsorption of UiO-66(Zr) for the removal of SMT and 4-CP was displayed in Fig.S3(a). Only 8.17 % of 4-CP and 9.90 % of SMT could be adsorbed by UiO-66(Zr), respectively. After the UiO-66(Zr) was substituted by Pd/UiO-66(Zr), the removal of 4-CP and SMT was lower to 7.54 % and 6.92 %, respectively. According to the characterization of these two materials, after the nano Pd<sup>0</sup> particle was loaded on the outer surface of UiO-66(Zr), the surface area was reduced. That may be attributed to the occupation of cavities or blocking of the outer surfaces of UiO-66(Zr) by the Pd<sup>0</sup> particle. Therefore, the adsorption of Pd/UiO-66(Zr) was weaker than that of UiO-66(Zr).

In the current Fenton reaction project in actual operation, the molar ratio of ferrous to hydrogen peroxide is usually 1:2 to 1:20. In this work, the molar ratio of ferrous iron to hydrogen peroxide was 1:800. The molar ratio 1:4 of ferrous to hydrogen peroxide were chosen to conduct a controlled experiment. As seen in Fig.S3(b), increasing the dosage of ferrous can promote the production of ·OH. And the degradation efficiency of pollutants could be further promoted. Under the condition of 1:4 molar ratio of ferrous to H<sub>2</sub>O<sub>2</sub>, the SMT could be thoroughly removed in 90 min and the 4-CP could be thoroughly removed in 60 min, while in the MHACF-UiO-66(Zr) system, about 95 % SMT could be removed, and the 4-CP could be thoroughly removed in 120 min. Although under the condition of 1:4 molar ratio, both of the removal efficiency of organics in Fenton reaction system were higher than that of MHACF system, the addition of ferrous in former was 200 times that of the latter. In order to maintain the production of ·OH, the ferrous salt must be

continuously added into the Fenton system. The TFe in MHACF-UiO-66(Zr) system was about 25  $\mu\text{M}$ . It is in accordance with the emission limits for TFe in most countries.<sup>5</sup> According to the law of conservation of mass and dissolution balance, when the solution pH is adjusted to 6-9 to meet the effluent discharge standard, except a small amount of iron element dissolved in the solution could discharge from the system with the effluent, most of the iron element will form iron sludge precipitation. Therefore, the iron sludge derived from the MHACF-UiO-66(Zr) system was much less than that in Fenton system.



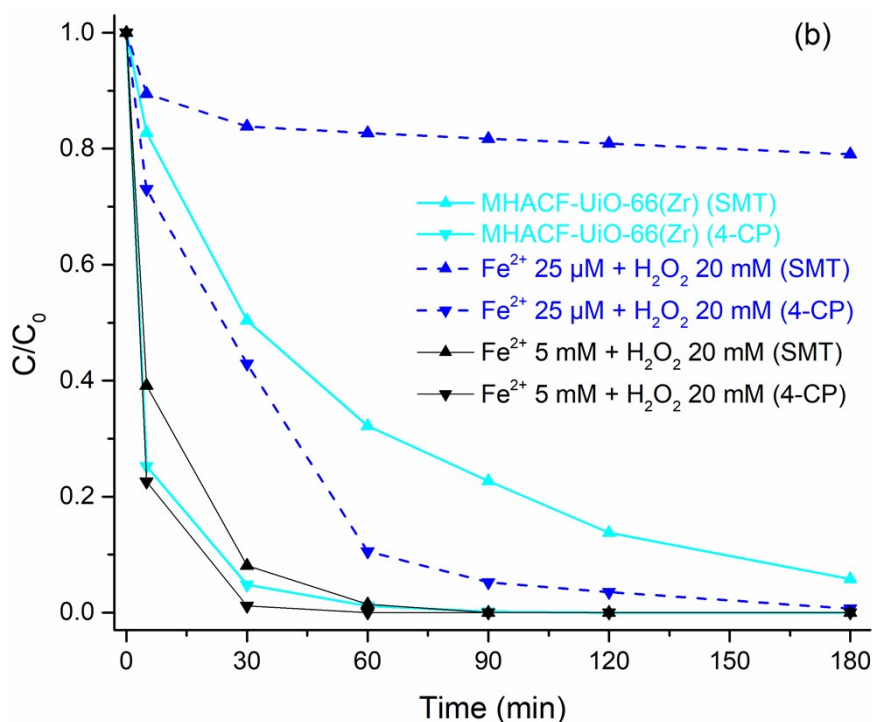


Fig.S3 (a) The Control tests of adsorption; (b) The Control tests of Fenton reaction. The initial parameter was UiO-66(Zr)  $2 \text{ g}\cdot\text{L}^{-1}$  Pd/UiO-66(Zr)  $2 \text{ g}\cdot\text{L}^{-1}$ , Pd content 0.536 % ( $W_{Pd}:W_{Pd/UiO-66(Zr)}$ ), pH 3, SMT  $15 \text{ mg}\cdot\text{L}^{-1}$  and 4-CP  $10 \text{ mg}\cdot\text{L}^{-1}$ .

## References

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