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Supplementary Information

Hydrophobic Titanium Doped Zirconium-based Metal Organic Framework for Photocatalytic Hydrogen Peroxide Production in Two-phase System

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Characterization results

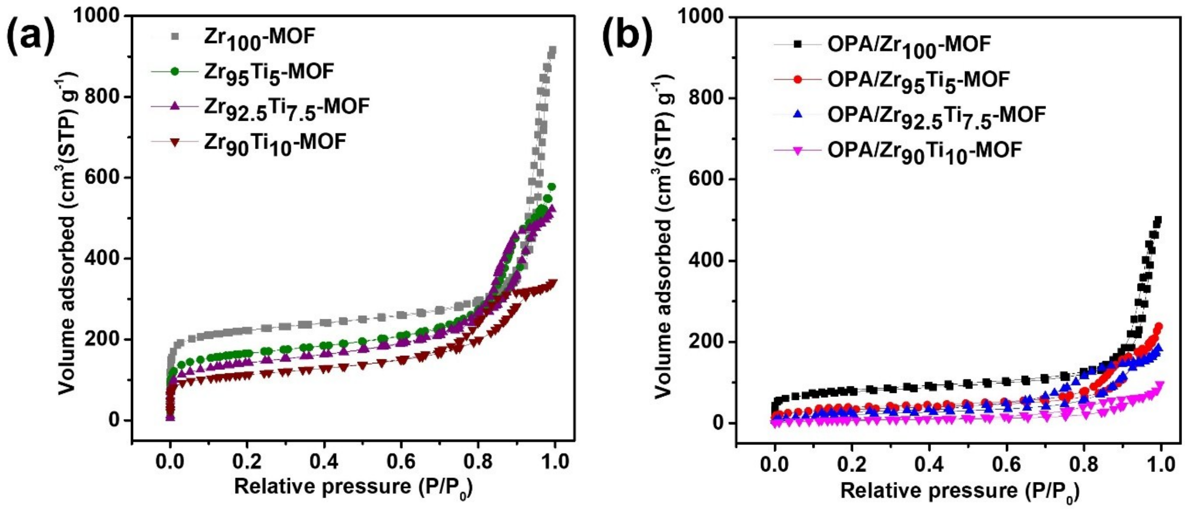

Fig. S1 N_2 adsorption/desorption isotherms at 77 K of (a) $Zr_{100-x}Ti_x$-MOF and (b) OPA/$Zr_{100-x}Ti_x$-MOF.

Table S1. Structural parameters of different samples.

Sample	S_{BET}($m^2 \cdot g^{-1}$)^a	d_p (nm)^b	V_p ($cm^3 \cdot g^{-1}$)^c
Zr_{100}-MOF	648	0.65	0.32
$Zr_{95}Ti_5$-MOF	495	0.65	0.24
$Zr_{92.5}Ti_{7.5}$-MOF	439	0.60	0.20
$Zr_{90}Ti_{10}$-MOF	346	0.70	0.16
OPA/Zr_{100}-MOF	237	0.65	0.11
OPA/$Zr_{95}Ti_5$-MOF	108	1.00	0.05
OPA/$Zr_{92.5}Ti_{7.5}$-MOF	75	1.05	0.03
OPA/$Zr_{90}Ti_{10}$-MOF	25	1.15	0.01

^{a}Surface area (S_{BET}) calculated by the BET method. ^{b}Average pore diameter (d_p) calculated using Saito Foley (SF) method. ^{c}Micropore volume (V_p) calculated using SF method (diameter < 2 nm).

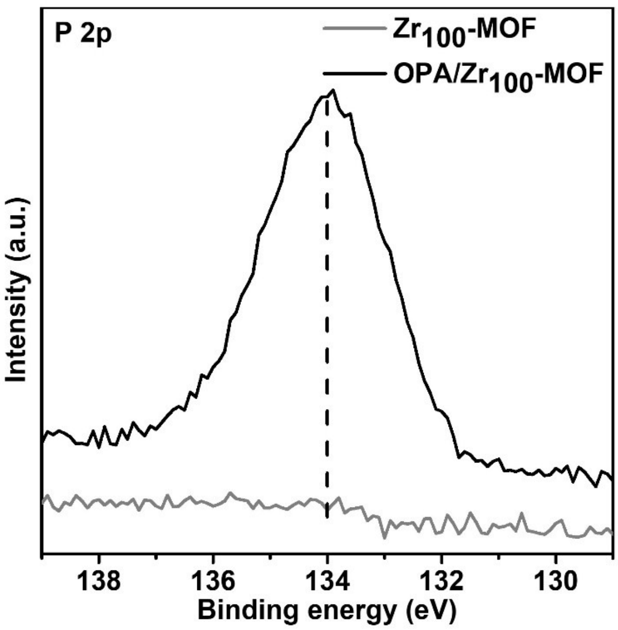

Fig. S2. XPS spectra of the synthesized samples: P 2p of Zr-MOF and OPA/Zr_{100}-MOF.

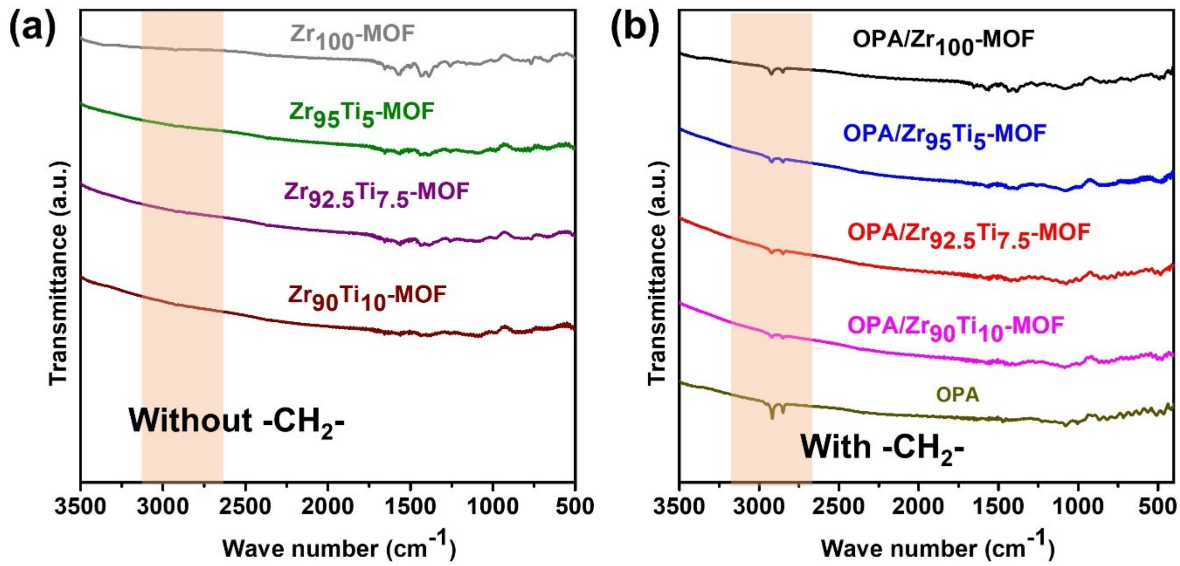

Fig. S3. FT-IR spectra of (a) $Zr_{100-x}Ti_x$-MOF and (b) OPA/$Zr_{100-x}Ti_x$-MOF.

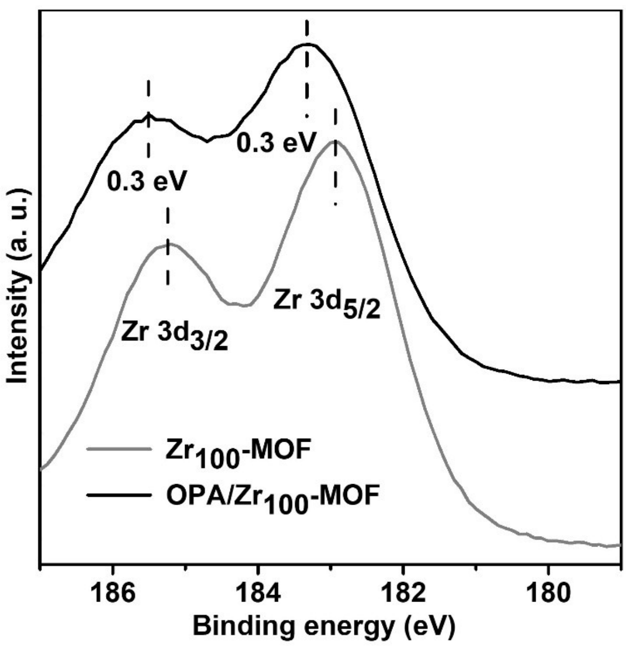

Fig. S4. The XPS spectra of the synthesized samples: Zr 3d of Zr_{100}-MOF and OPA/Zr_{100}-MOF.

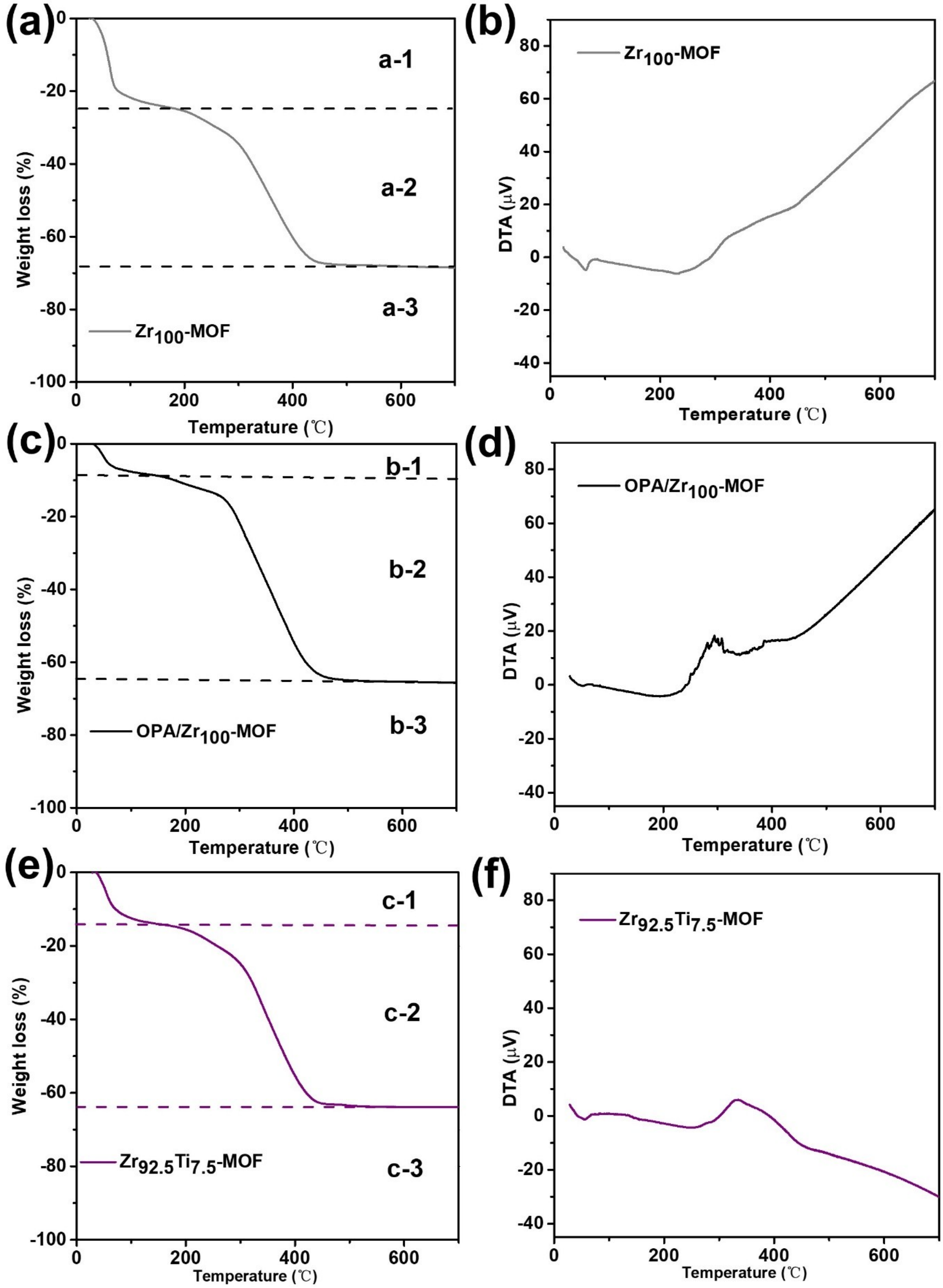

Fig. S5. (a, c, e, g) TG and (b, d, f, h) DTA profiles of Zr_{100}-MOF, OPA/Zr_{100}-MOF, $Zr_{92.5}Ti_{7.5}$-MOF and OPA/$Zr_{92.5}Ti_{7.5}$-MOF.

Calculation of the population of the alkylated clusters in OPA/Zr_{100}-MOF and OPA/$Zr_{92.5}Ti_{7.5}$-MOF:

TG-DTA measurements were performed to determine the amount of atoms alkylated by OPA in the clusters of OPA/Zr_{100}-MOF and OPA/$Zr_{92.5}Ti_{7.5}$-MOF (Fig. S5).

For Zr_{100}-MOF (NH_2-UiO-66(Zr)), the unit cell is $Zr_6O_4(OH)_4$-L_6, where L is 2-aminoterephthalic acid linker. After combustion, this unit cell is expected to yield $6ZrO_2$. The theoretical ratio of weight of 6L (1075 g mol^{-1}) to $6ZrO_2$ (739.32 g mol^{-1}) is equal to 1.45. In the TG-DTA pfofiles of Zr_{100}-MOF (Fig. S5a and b), the endothermal weight loss in region noted a-1 is attributed to desorption of H_2O. The exothermal weight loss in a-2 is attributed to the weight loss due the to combustion of the organic linkers during the decomposition of Zr_{100}-MOF into ZrO_2 (a-3), respectively. The experimental weight loss due to the combustion of the organic linkers (43.8 % in a-2) to $6ZrO_2$ (31.7 % in a-3) was calculated to be 1.38, which is similar with the expected value calculated above (1.45).

For OPA/Zr_{100}-MOF, the unit cell can be expressed as $OPA_nZr_6O_4(OH)_4$-L_6, where n is the average number of OPA that modify the clusters per unit cell. When combusted, assuming the monodentate species, 1 mol of this unit cell loses (179.1*6+334.5*n) g due to the combustion of the organic linkers and OPA (6 mol of L and n mol of OPA), and leaves 739.32 g due to residual $6ZrO_2$. The weight loss due to the combustion of the organic linkers in OPA of OPA/Zr_{100}-MOF is 56.4 % (b-2 region in Fig. S5c). The weight of the residual $6ZrO_2$ of

OPA/Zr_{100}-MOF is 34.2 % (b-3 region). Therefore, the ligand (linkers and OPA) content is 62.3% [56.4 %/(56.4 %+34.2 %)] in pure OPA/Zr_{100}-MOF. By comparing the ratios of these values with the theoretical values, n can be calculated as 0.436 for 1 mol of OPA/Zr_{100}-MOF according to the following equation:

$$(6L + nOPA + 6ZrO_2)* 62.3 \% = 6L + nOPA$$

Thus, alkylated Zr atoms in the $Zr_6O_4(OH)_4$-L_6 clusters of OPA/Zr_{100}-MOF is 7.3 % (0.436/6*100 %).

For $Zr_{92.5}Ti_{7.5}$-MOF, the unit cell is $(Zr_{0.925}Ti_{0.075})_6O_4(OH)_4$-$L_6$. After combustion, this unit cell is expected to yield $5.55ZrO_2$+$0.45TiO_2$. The theoretical ratio of weight of 6L (1075 g mol^{-1}) to ($5.55ZrO_2$+$0.45TiO_2$) (719.826 g mol^{-1}) is equal to 1.49. In the result of TG-DTA profiles for $Zr_{92.5}Ti_{7.5}$-MOF (Fig. S5e and f), The exothermal weight loss in c-2 and residual c-3 were attributed to the weight loss due to the combustion of the organic linkers and weight of residual ZrO_2 and TiO_2, respectively. The experimental ratio of weight loss due to the combustion of the organic linkers (49.8 %) to ($5.55ZrO_2$+$0.45TiO_2$) (35.9 %) was calculated to be 1.39, which is close to the expected value calculated above (1.49).

For $OPA/Zr_{92.5}Ti_{7.5}$-MOF, the unit cell can be expressed as $OPA_n(Zr_{0.925}Ti_{0.075})_6O_4(OH)_4$-$L_6$. The weight losse due to combustion of organic linkers and OPA of $OPA/Zr_{92.5}Ti_{7.5}$-MOF is 60 % (d-2 region in Fig. S5g). Residual ZrO_2 and TiO_2 is 35% (d-3). Then, the ligand (linkers and OPA) content is about 63.2 % [60 %/(60 %+35 %)]. Thus, n can be calculated as 0.483 for 1 mol of OPA/$Zr_{92.5}Ti_{7.5}$-MOF according to the following equation:

$$(6L + nOPA + 5.55ZrO_2 + 0.45TiO_2)* 63.2 \% = 6L + nOPA$$

Only the Zr atoms was alkylated by the OPA, thus, alkylated Zr atoms in the $(Zr_{0.925}Ti_{0.075})_6O_4(OH)_4$-$L_6$ clusters of OPA/$Zr_{92.5}Ti_{7.5}$-MOF is 8.7 % (0.483/5.55*100 %).

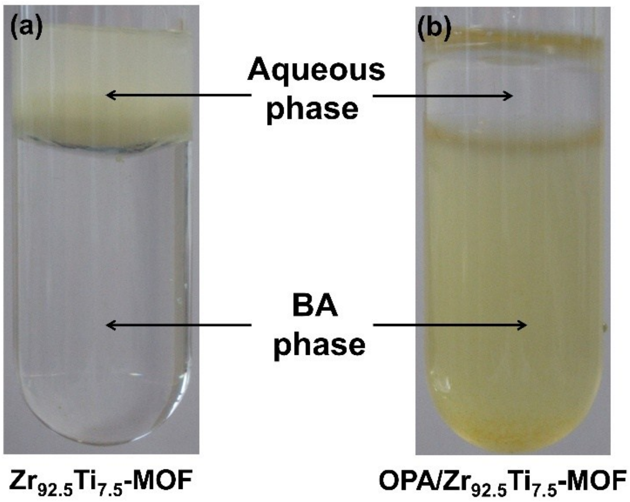

Fig. S6. The digital picture of two-phase system composed of BA/water containing (a) hydrophilic $Zr_{92.5}Ti_{7.5}$-MOF in aqueous phase and (b) hydrophobic OPA/$Zr_{92.5}Ti_{7.5}$-MOF in BA phase.

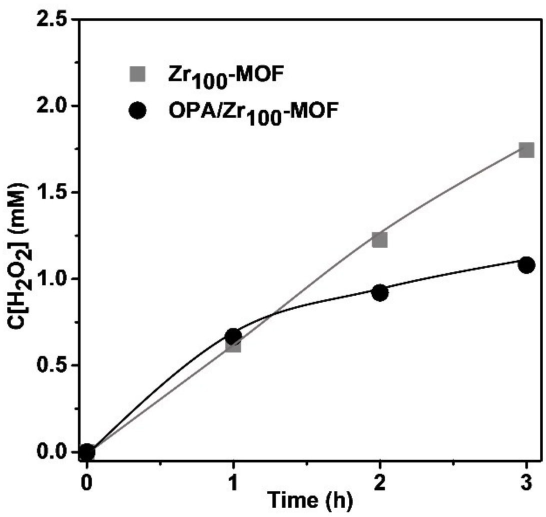

Fig. S7. H_2O_2 production utilizing Zr_{100}-MOF and OPA/ Zr_{100}-MOF in single-phase system composed of an acetonitrile solution (5.0 mL) of BA (1.0 mL).

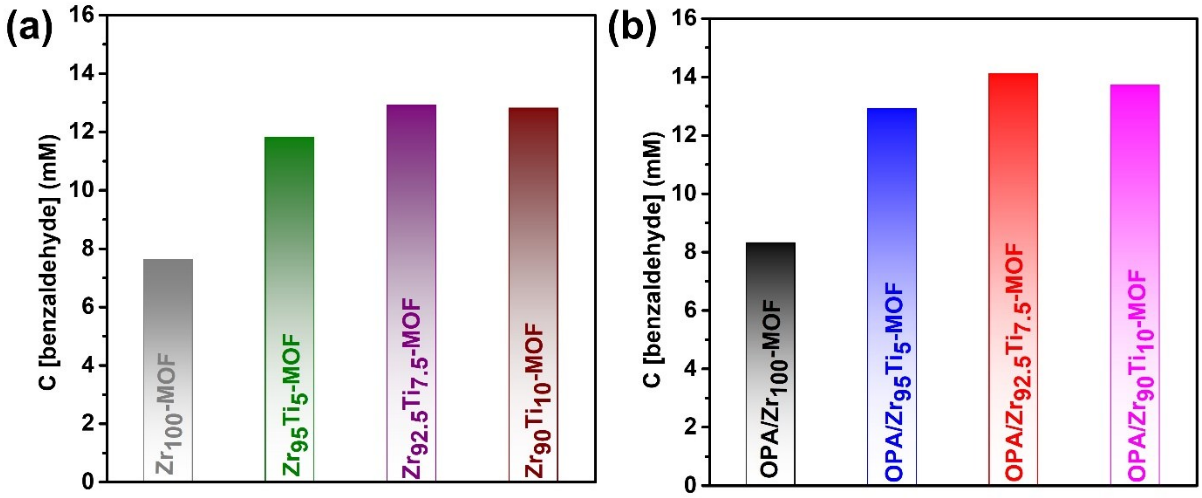

Fig. S8. Benzaldehyde concentration of (a) hydrophilic $Zr_{100-x}Ti_x$-MOF and (b) hydrophobic OPA/$Zr_{100-x}Ti_x$-MOF in two-phase system composed of benzyl alcohol (5.0 mL) and water (2.0 mL) catalyzed by 5.0 mg of photocatalysts under photoirradiation ($\lambda > 420$ nm) after 3h reaction.

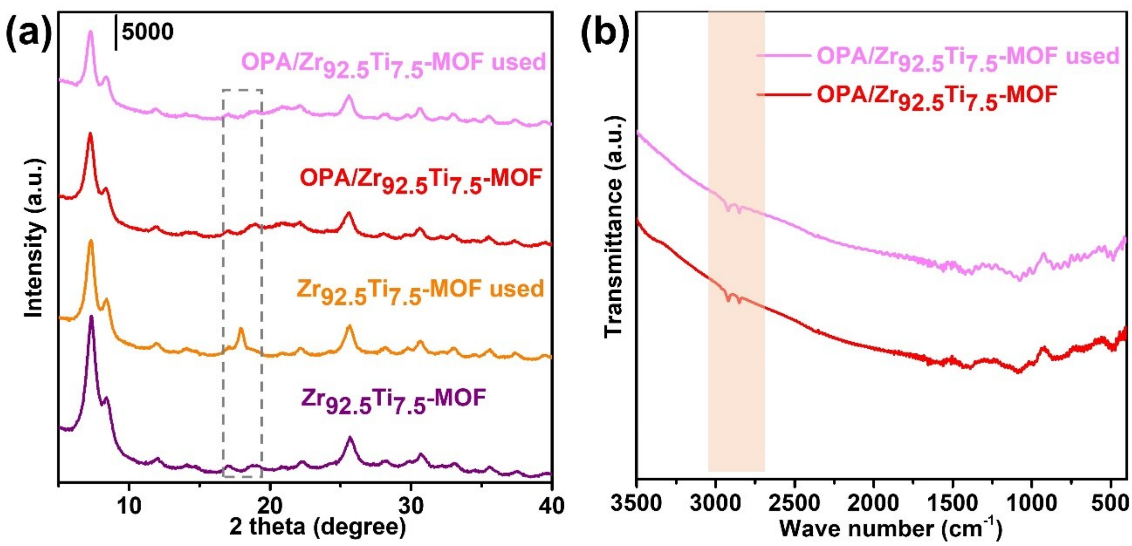

Fig. S9. (a) The XRD patterns and (b) FTIR spectra of $Zr_{92.5}Ti_{7.5}$-MOF and OPA/$Zr_{92.5}Ti_{7.5}$-MOF after recycling tests, compared with the samples before reaction.