

Supporting Information

In Situ-Induced Synthesis of Magnetic Cu-CuFe₂O₄@HKUST-1 Heterostructures with Enhanced Catalytic Performance for Selective Aerobic Benzylic C-H Oxidation

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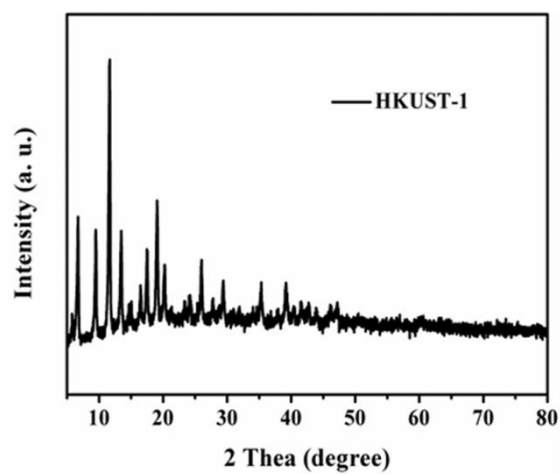


Figure S1. Powder XRD patterns of the as prepared HKUST-1.

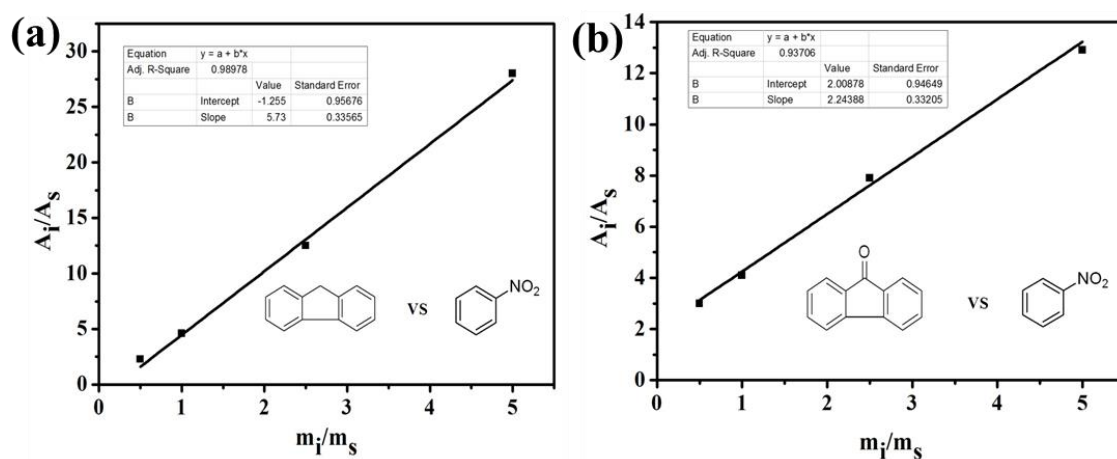


Figure S2. (a) Fluorene and (b) 9-Fluorenone vs. nitrobenzene internal standard for GC/MS analysis

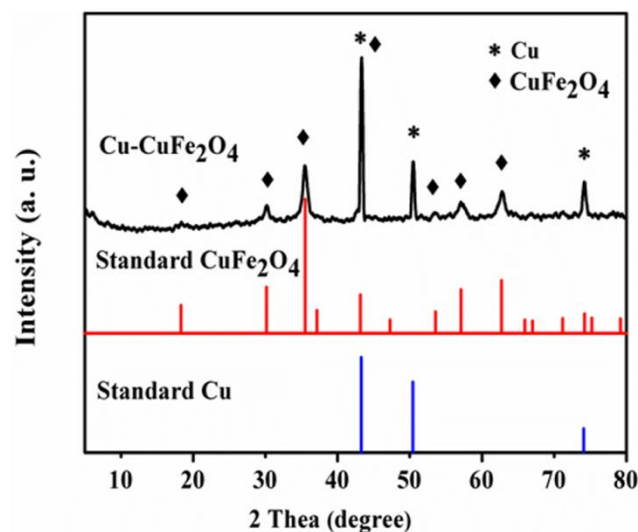


Figure S3. XRD patterns of the as-prepared Cu-CuFe₂O₄ nanoparticles, standard CuFe₂O₄ and standard CuFe₂O₄.

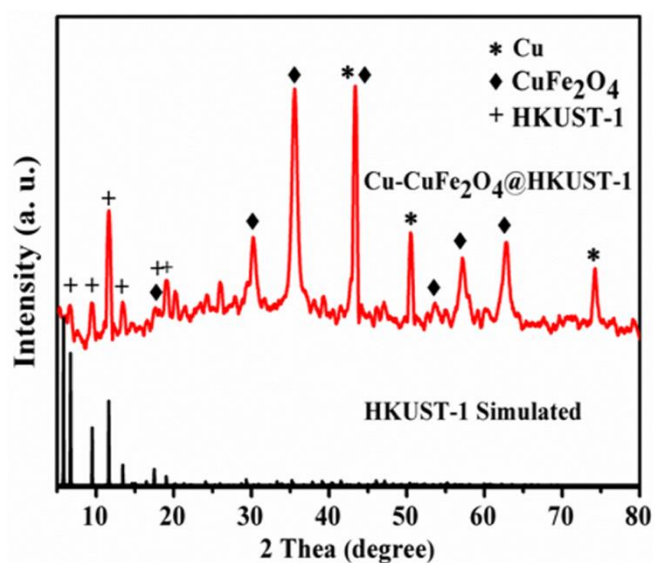


Figure S4. XRD patterns of the experimentally acquired Cu-CuFe₂O₄@HKUST-1 nanoparticles and simulated HKUST-1.

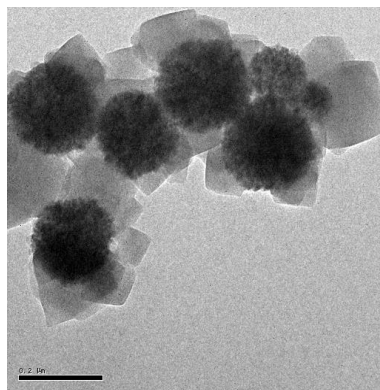


Figure S5. TEM images of Cu-CuFe₂O₄@HKUST-1 heterostructures obtained after reaction time of 24 h

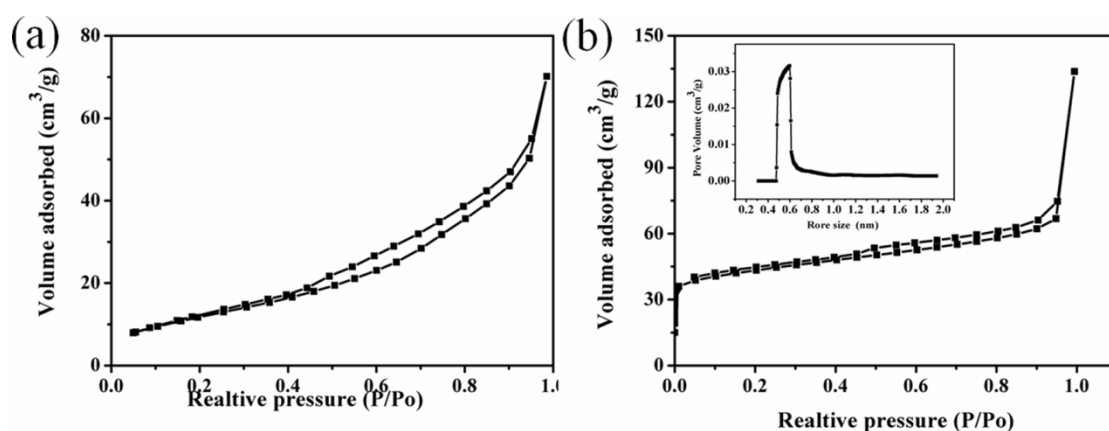


Figure S6. Nitrogen sorption isotherms of (a) as-prepared Cu-CuFe₂O₄ and (b) Cu-CuFe₂O₄@HKUST-1 nanoparticles.

The porous structure and surface area of Cu-CuFe₂O₄ and Cu-CuFe₂O₄@HKUST-1 nanocomposites were investigated by N₂ sorption isotherm measurement (Figure S6). From the adsorption isotherms, the Brunauer-Emmett-Teller (BET) surface areas of Cu-CuFe₂O₄ core and Cu-CuFe₂O₄@HKUST-1 are 41 m²g⁻¹ and 158 m²g⁻¹, respectively. Compared to the type IV plots for mesopores of Cu-CuFe₂O₄, the isotherm curves of Cu-CuFe₂O₄@HKUST-1 nanoparticles appear type I plots, which is related to microporous materials. The pore size of the as-synthesized Cu-CuFe₂O₄@HKUST-1 nanocomposites distributes narrowly around 0.55 nm. The higher surface area and the micropore structure of Cu-CuFe₂O₄@HKUST-1

nanocomposite are mainly assigned to the MOF shell.

The FT-IR spectras of the Cu-CuFe₂O₄ and Cu-CuFe₂O₄@HKUST-1 to further Characterize the formation of Cu-CuFe₂O₄@HKUST-1 nanocomposites were performed according to the review's suggestion. As shown in Figure S7, all of the characteristic peaks of HKUST-1 are showed in the FT-IR spectrum of Cu-CuFe₂O₄@HKUST-1 nanocomposites. The characteristic vibration of C-C-C in the benzene ring were observed at 630, 728 and 764 cm⁻¹. The peaks at 1059, 1103 and 1165 cm⁻¹ are caused by C-O-C bending of the ethylenedioxy moiety; the peaks at 1362, 1456 and 1556 cm⁻¹ are associated with the C-H stretching vibration of the benzene ring. Concomitant with the encapsulation of Cu-CuFe₂O₄ MNCs by the HKUST-1 shell, structural vibrations of the aromatic C-C-C bond and C-O-C bond are obviously shifted, indicating that HKUST-1 has been formed on the surface of the Cu-CuFe₂O₄ core through coordination interactions.

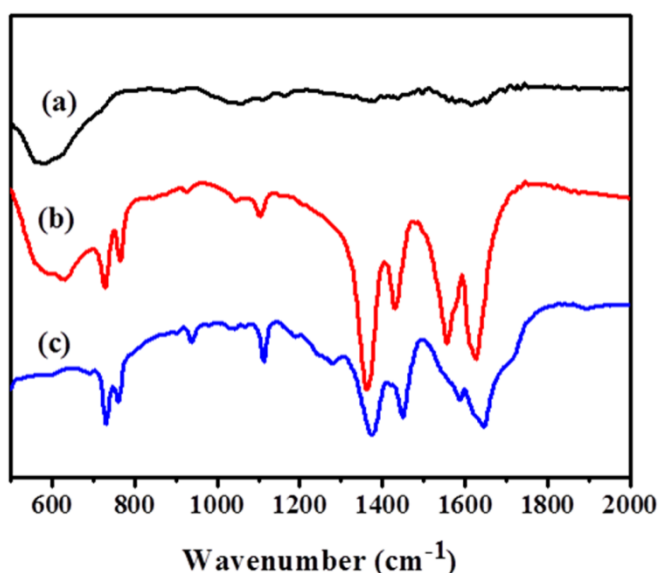


Figure S7. IR spectra of (a) Cu-CuFe₂O₄ (black), (b) Cu-CuFe₂O₄@HKUST-1 (red) and (c) HKUST-1 (blue) nanocomposites.

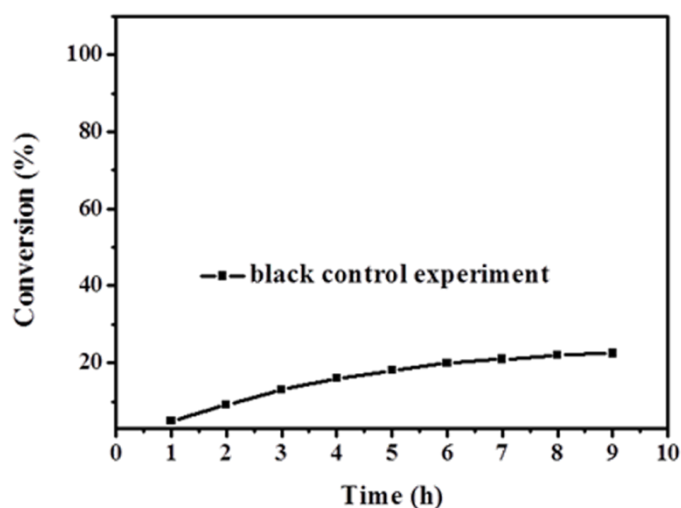


Figure S8. Change of conversion over the reaction time for model reaction in absence of catalyst

Table S1 Benzylic oxidation in presence of different solvents.^a

Entry	Solvent	Conv. (%) ^b	Selec. (%) ^b
1	acetonitrile	>99	>99
2	ethanol	-	-
3	acetone	80	>99
4	ethyl acetate	36	>99

^a Reaction conditions: fluorene (1.0 mmol), 15 mg of Cu-CuFe₂O₄@HKUST-1 catalyst, N-Hydroxyphthalimide (10 mol%), solvent (5.0 mL), at 60 °C under 1 atm. of atmosphere stirring for 9 h.

^b Conversion and selectivity were determined by GC/MS using nitrobenzene as internal standard.

To identify the optimal solvent for the benzylic oxidation, solvent screening was

proceeded. Reaction results are summarized in Table S1. In our studies, only acetonitrile, acetone, ethyl acetate gave significant conversions with high selectivity, during which the acetonitrile giving the best conversion of >99% (Table S1, entry 1 and 3-4). However, no benzylic oxidation reaction was observed in ethanol solvent owing to the coordination of ethanol with copper (II) (Table S1, entry 2). Thus, acetonitrile was employed as optimized solvent for further reactions.

The fresh and recovered Cu-CuFe₂O₄@HKUST-1 catalyst has been characterized by FTIR and SEM (Figure S9). The FTIR (Figure S9a) results of fresh and recovered catalyst show that the composition of the catalyst has no obvious change after reaction. While the SEM images (Figure S9b-c) shows that the structure of the catalyst is slightly conglobate.

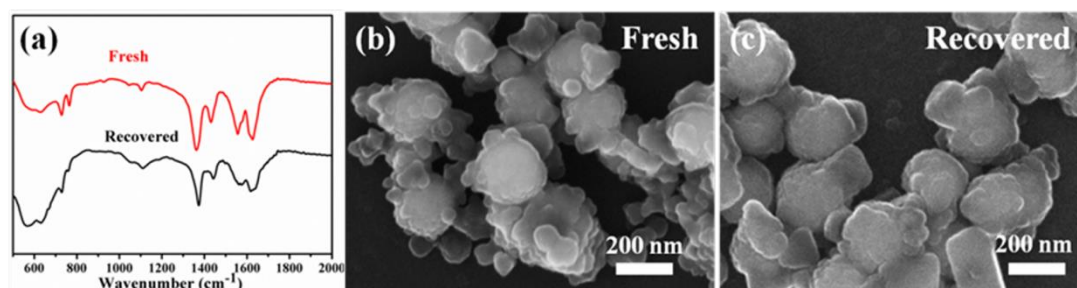


Figure S9. FTIR curves (a) and SEM images of fresh (b) and recovered (c) Cu-CuFe₂O₄@HKUST-1 catalyst.