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# Fabrication of 2D Metal-Organic Framework Nanosheet@Fiber Composites by Spray Technique

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## EXPERIMENTAL SECTION

### Materials

Cooper acetate ($Cu(CH_3COO)_2$), 1,4-benzenedicarboxylic acid ($H_2BDC$), 1,4-naphtalenedicarboxylic acid (1,4-$H_2NDC$), 2,6-naphtalenedicarboxylic acid (2,6-$H_2NDC$), 2-aminoterephthalic acid (2-atp), 1,3,5-benzenetricarboxylic acid ($H_3BTC$) were purchased from Energy Chemical China. 4-nitrophrnol (4-NP) and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF), ethanol (EtOH) and acetonitrile ($CH_3CN$) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Deionized water was used. Carbon fiber (CF) was purchased from Liso Composite Material Technology. Cotton cloth and nylon cloth were purchased from Xinke. All chemicals used in this study without any further purification.

### Preparation of 2D MOF nanosheets@fiber

Six kinds of 2D MOF nanosheets@fiber were fabricated by spray technique. The metal ion solution was evenly sprayed on the surface of non-woven CFs which had been adsorbed with organic ligands.

Taking copper 1,4-benzenedicarboxylate@CFs (CuBDC@CF) as an example, $Cu(CH_3COO)_2$ were dissolved in a mixture of $CH_3CN$ and DMF (V:V=2:1, 0.018 mol/L), $H_2BDC$ were dissolved in a mixture of $CH_3CN$ and DMF (V:V=1:2, 0.013 mol/L). Firstly, CFs were wetted by $H_2BDC$ solution and adsorbed $H_2BDC$. Then $Cu(CH_3COO)_2$ solution was injected into ultrasonic atomizer and sprayed on CFs with

$H_2BDC$ at the flow rate of 30 μL/min for 400 s. Subsequently the obtained composite material CuBDC@CF was washed with DMF three times (each time for 30 min) and dried at 50℃ for 24 h.

The other five kinds of 2D MOF nanosheets@fiber were successfully synthesized by similar spray technique under mild conditions, denoted as CuBDC@cotton fiber, CuBDC@nylon fiber, Cu(1,4-NDC)@CF, Cu(2,6-NDC)@CF and Cu(2-atp)@CF.

The control experiments in the fabrication of CuBDC@CF without spray technique were carried out by two method. In the method 1, Sample 1 was prepared by mixing the $Cu(CH_3COO)_2$ solution with the $H_2BDC$ solution under the presence of CF. In the method 2, Sample 2 was prepared by immersing the CFs in $Cu(CH_3COO)_2$ solution, as the CFs are firstly absorbed with BDC.

**Preparation of HKUST@CF**

Firstly, CFs were wetted by $H_3BTC$/EtOH solution (0.067 mol/L) and adsorbed $H_3BTC$. Then aqueous solution of $Cu(CH_3COO)_2$ (0.1 mol/L) was injected into ultrasonic atomizer and sprayed on CFs with $H_3BTC$ at the flow rate of 30 μL/min for 400 s. Subsequently the obtained composite material HKUST@CF was washed with water and EtOH three times and dried at 50℃ for 24 h.

**Catalytic Test**

The catalytic performance of NiCo-MOFs in the reduction 4-NP was tested. The $NaBH_4$ aqueous solution (2.5 mL, 0.1 mol/L), 4-NP (20 μL, 5 mmol/L) and Cu-based 2D MOF nanosheets@CF (CuBDC@CF, Cu(1,4-NDC)@CF, Cu(2,6-NDC)@CF and Cu(2-atp)@CF) were mixed. The reaction progress was monitored by UV-Vis spectrometry.

**Continuous catalytic operation**

The Cu-based 2D MOF nanosheets@CF (CuBDC@CF, Cu(1,4-NDC)@CF, Cu(2,6-NDC)@CF and Cu(2-atp)@CF) were used as a heterogenous catalysis for the catalytic reduction of 4-NP in the presence of $NaBH_4$ to produce 4-aminophenol (4-

AP). Reaction mixture of 4-NP aqueous solution (0.05 mmol/L) with excessive amounts of $NaBH_4$ was prepared, then were pumped through Cu-based 2D MOF nanosheets@CF by peristaltic pump at a flow rate of 1.92 mL/s. The effluent was collected and measured by UV-Vis absorption spectrum to monitor the reaction progress.

**Measurements**

The morphologies of 2D MOF nanosheets@fiber were characterized by scanning electron microscopy (SEM, Hitachi SU8010) and corresponding elemental mapping images were recorded by energy-dispersive X-ray (EDX, Oxford Instruments). The X-ray diffraction (XRD, Shimadzu XRD-600) was used with Cu Kα radiation source (λ=1.5406 Å) in 2θ range of 5-50°. The Fourier transform infrared spectroscopy (FT-IR) was collected on Bruker VERTEX 70 equipped with a deuterated triglycine sulphate (TGS) detector (32 scans) for pressed KBr pellets with a resolution of 4 $cm^{-1}$. Thermogravimetric analysis (TGA) was carried out on a NETZSCH TGA 209C in flowing air under a heating rate of 10 °C·$min^{-1}$ ranging from 35 °C·to 800 °C. The catalytic efficiency of CuBDC@CF was measured by optics spectrometer (Maya2000 Pro).

**Calculation of CuBDC loading fraction in CuBDC@CF (wt%)**

$wt\% = (R1 - R2) \times M_{CuBDC}/M_{CuO}$

R1 = 7.9%

R2 = 2.9%

Here, $M_{CuO}$ and $M_{CuBDC}$ represent the molecular mass of CuO and CuBDC, respectively. R1 and R2 are the residues weight percent of CuBDC@CF and CF at 800 °C in flowing air from TGA analysis.

## RESULTS AND DISSCUSION

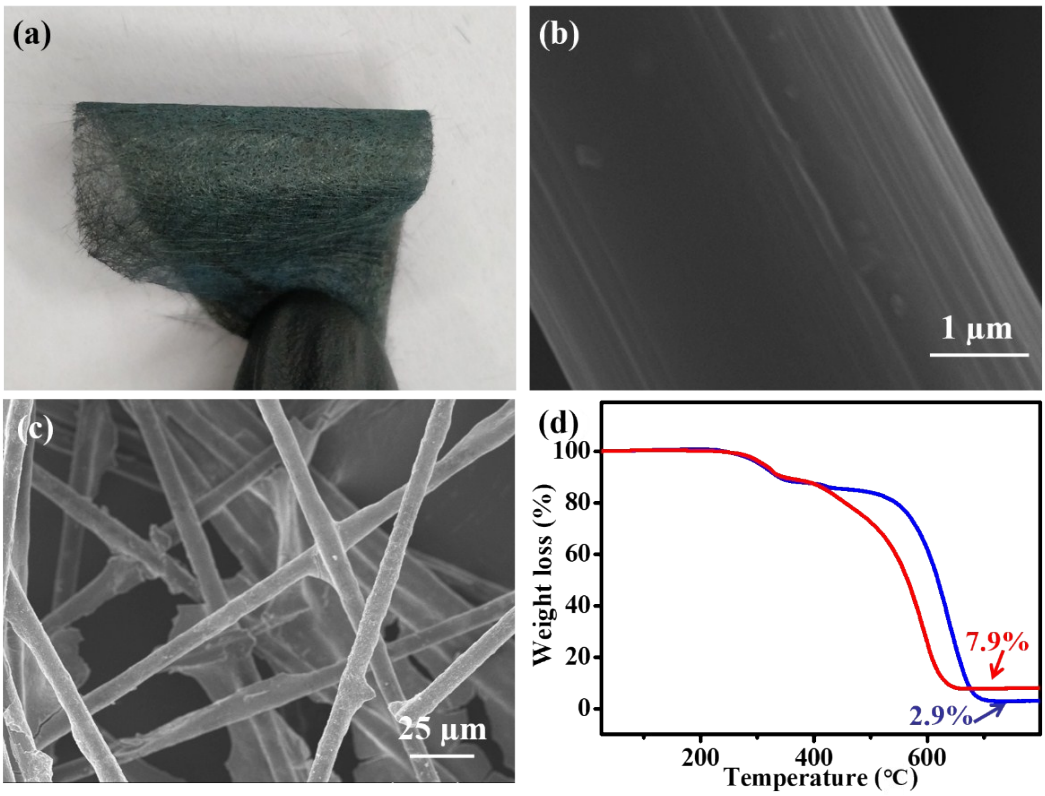


**Figure S1.** (a) The photograph of CuBDC@CF, the SEM images of (b) CFs and (c) CuBDC@CF, (d) the TGA curves of CFs (blue) and CuBDC@CF (red).

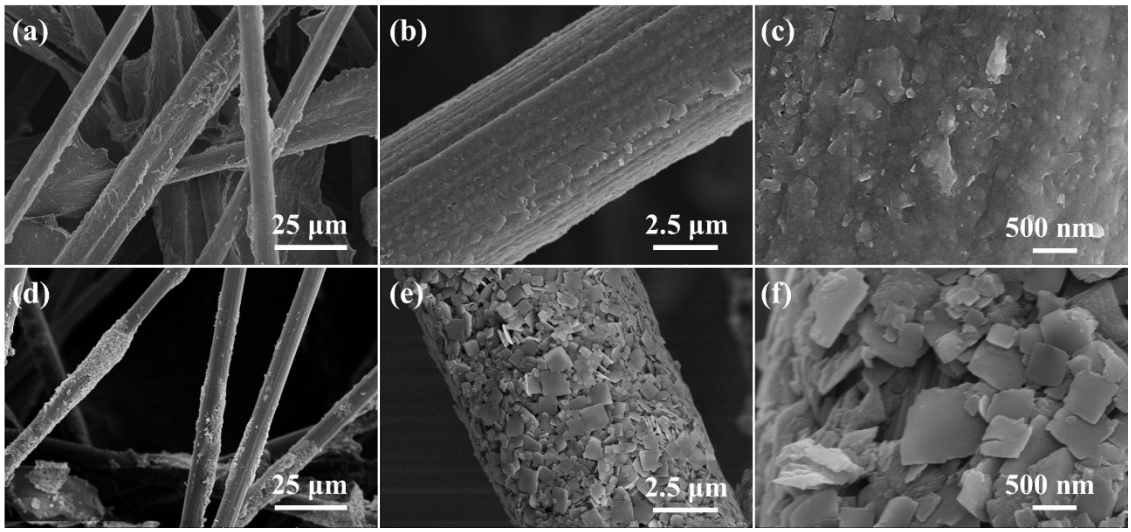


**Figure S2.** The SEM iamges of (a-c) Sample 1 and (d-f) Sample 2 with different magnification, which are fabricated without spray technique.

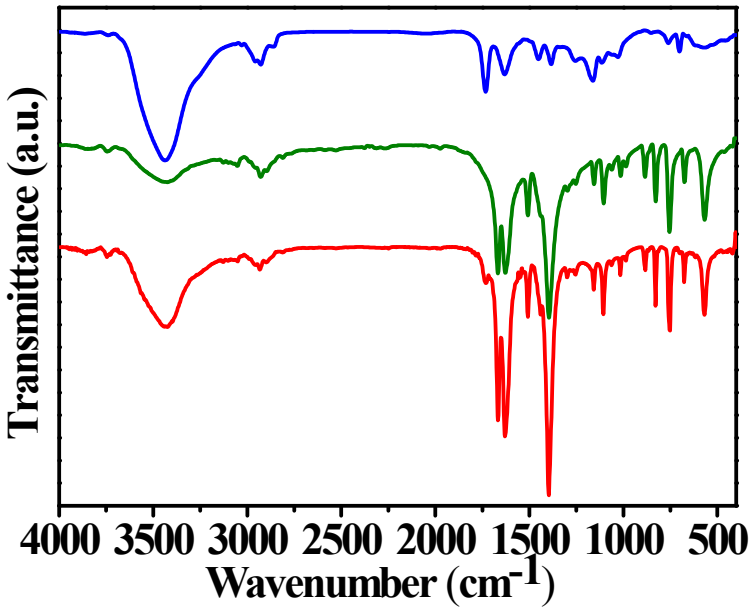


**Figure S3.** FT-IR spectra of CFs (blue), CuBDC@CF (red) and CuBDC (green) with larger wavenumber region.

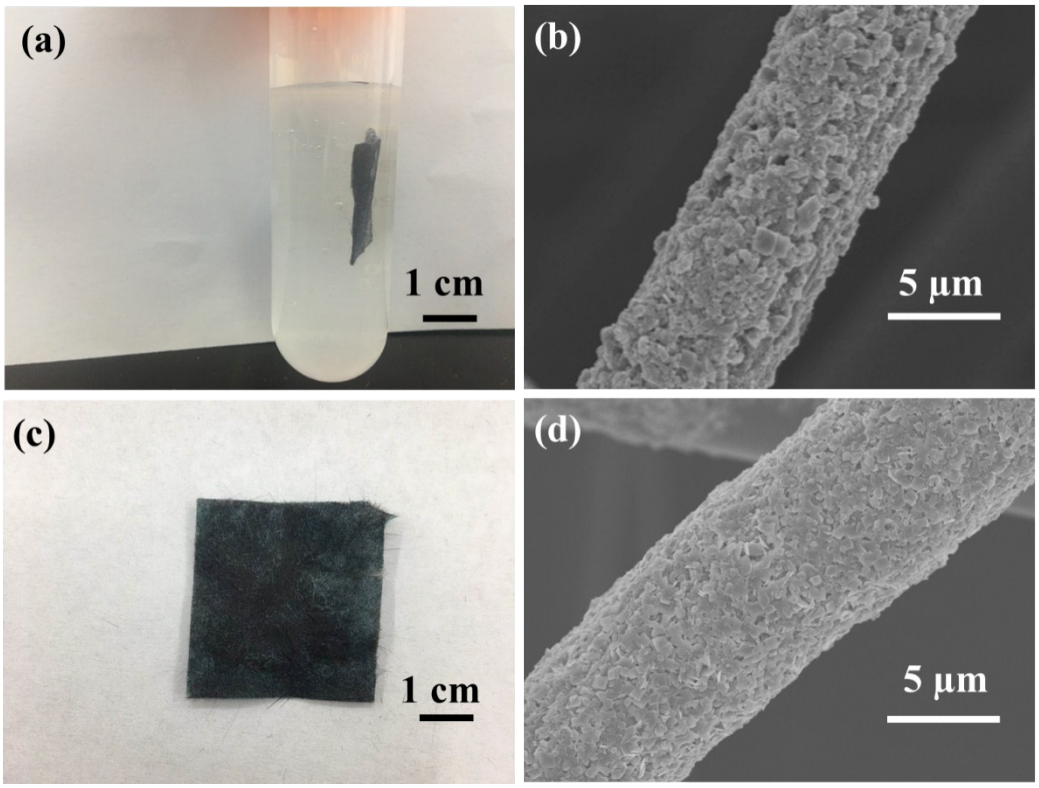


**Figure S4.** The photographs of CuBDC@CF after (a) shaking in DMF and (c) rubbing; the SEM images of CuBDC@CF after (b) shaking in DMF and (d) rubbing.

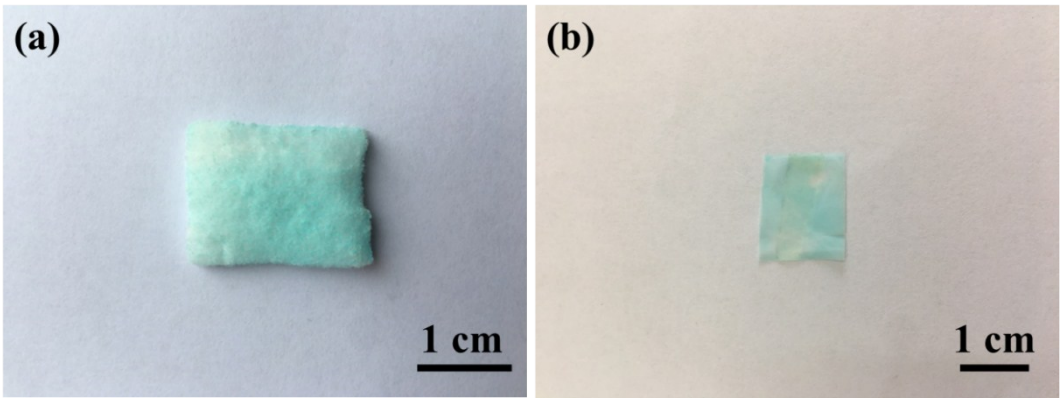


**Figure S5.** The photographs of (a) CuBDC@cotton fiber and (b) CuBDC@nylon fiber.

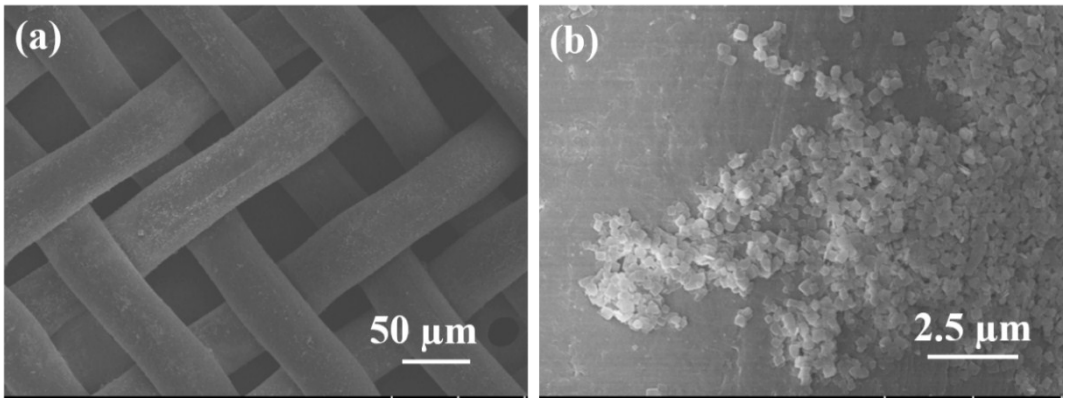


**Figure S6.** The SEM images of CuBDC@nylon fiber.

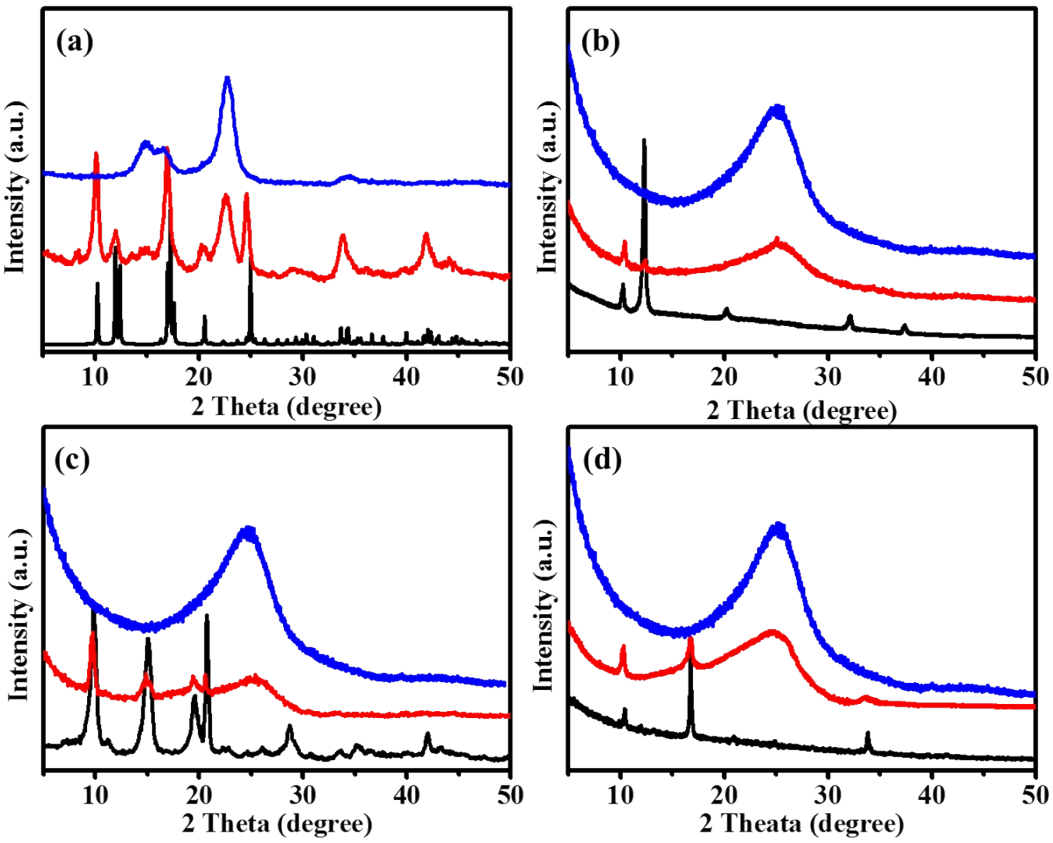


**Figure S7.** The XRD patterns of (a) CuBDC (black), CuBDC@cotton fiber (red) and cotton fibers (blue); (b) Cu(1,4-NDC) (black), Cu(1,4-NDC)@CF (red) and CFs(blue); (c) Cu(2,6-NDC) (black), Cu(2,6-NDC)@CF (red) and CFs(blue); (d) Cu(2-atp) (black), Cu(2-atp)@CF (red) and CFs (blue).

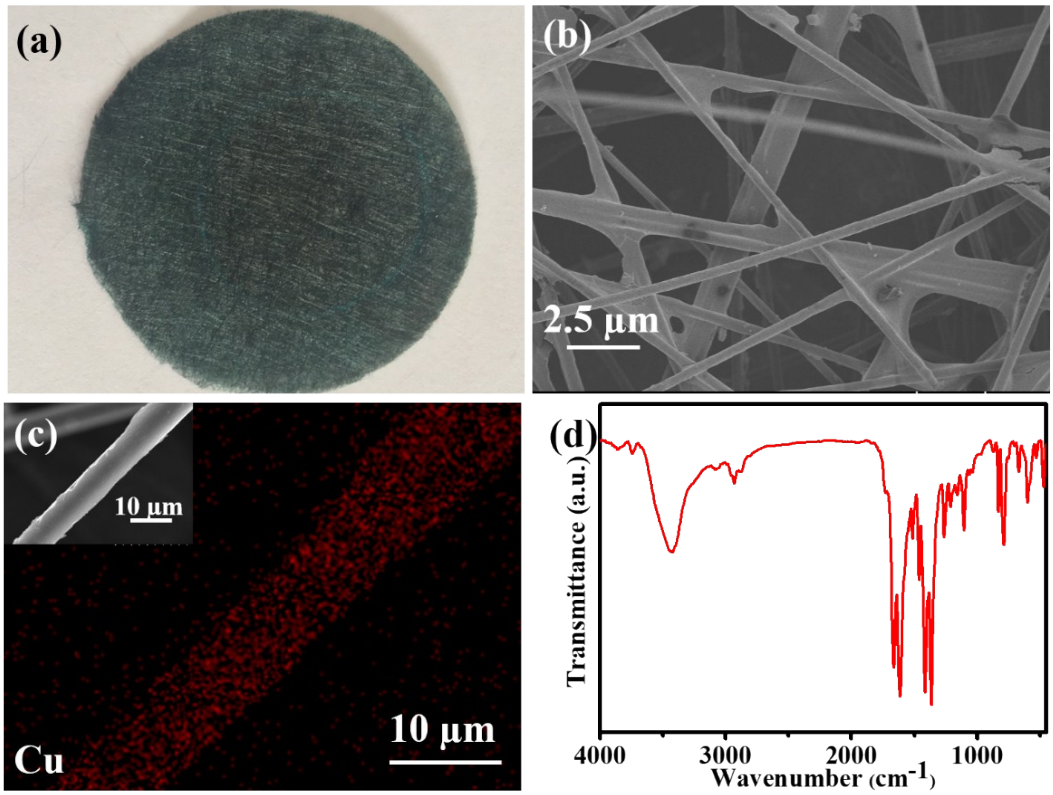


**Figure S8.** The (a) photograph, (b) SEM image, (c) EDS elemental mapping image and corresponding SEM image (insert), (d) FT-IR spectrum of Cu(1,4-NDC)@CF.

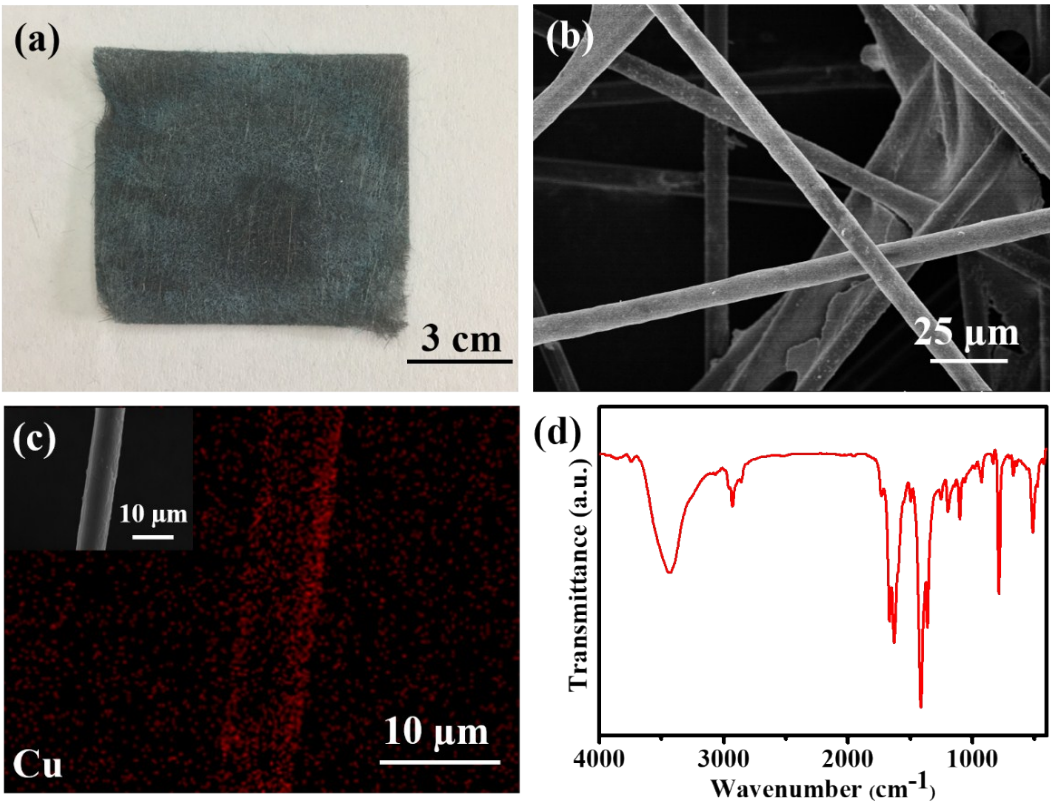


**Figure S9.** The (a) photograph, (b) SEM image, (c) EDS elemental mapping image and corresponding SEM image (insert), (d) FT-IR spectrum of Cu(2,6-NDC)@CF.

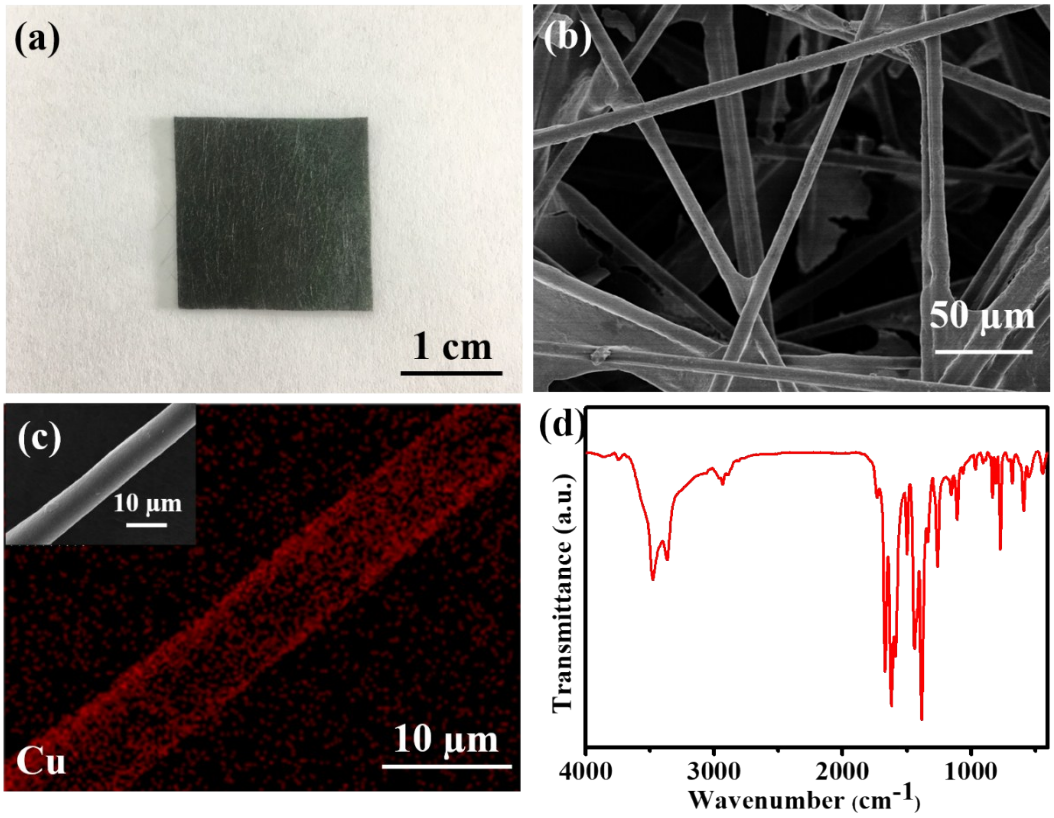


**Figure S10.** The (a) photograph, (b) SEM image, (c) EDS elemental mapping image and corresponding SEM image (insert), (d) FT-IR spectrum of Cu(2-atp)@CF.

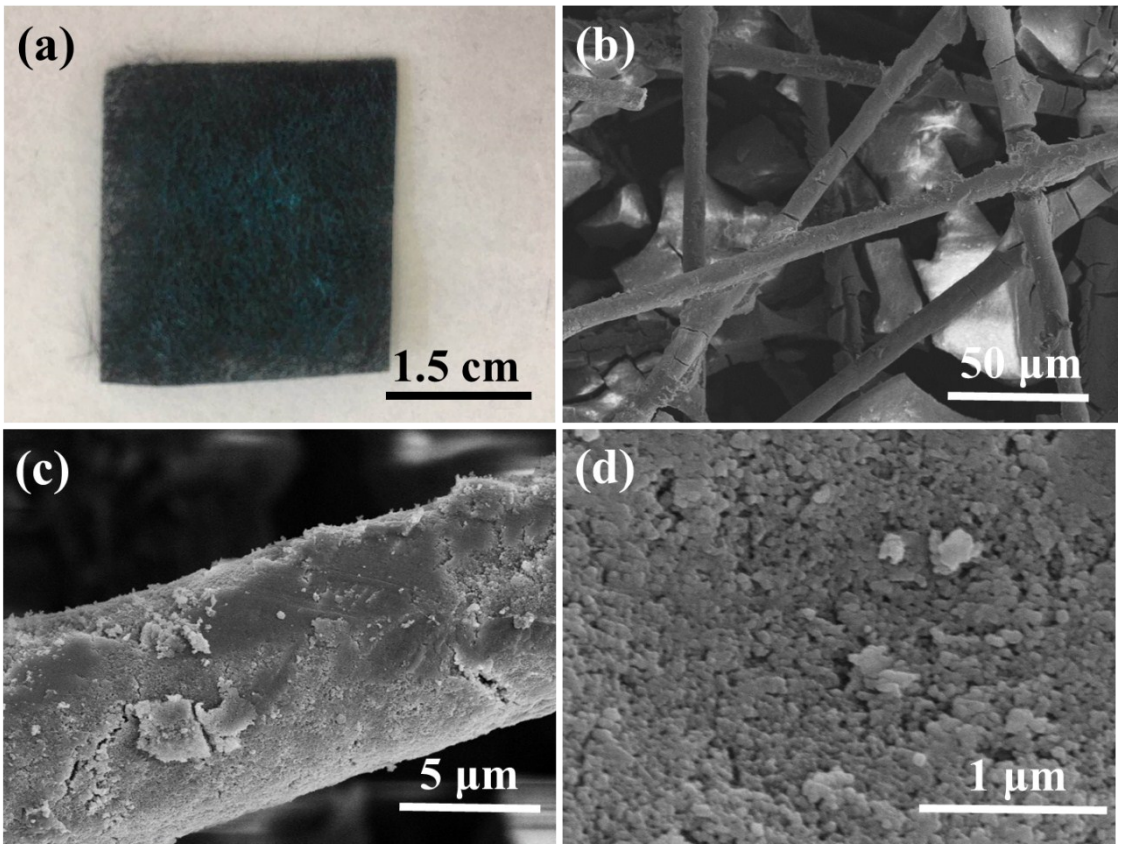


**Figure S11.** The (a) photograph and (b-d) SEM images of HKUST@CF prepared by spraying technique.

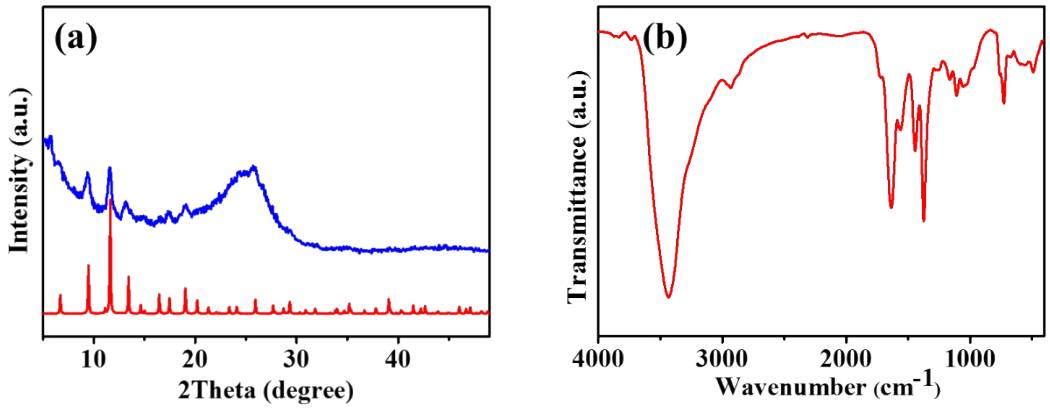


**Figure S12.** The (a) simulated XRD pattern of HKUST (red), XRD pattern of HKUST@CF (blue) and (b) IR spectrum of HKUST@CF.

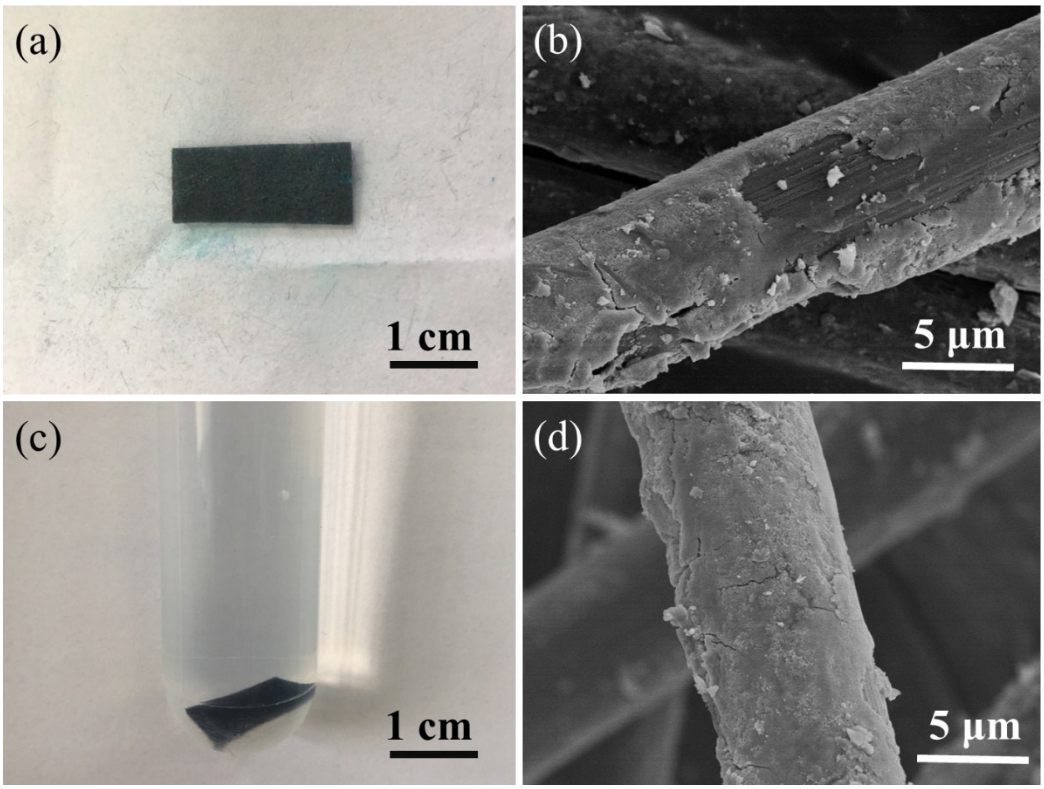


**Figure S13.** The photographs of HKUST@CF after (a) rubbing and (c) shaking in DMF; the SEM images of HKUST@CF after (b) rubbing and (d) shaking in DMF.

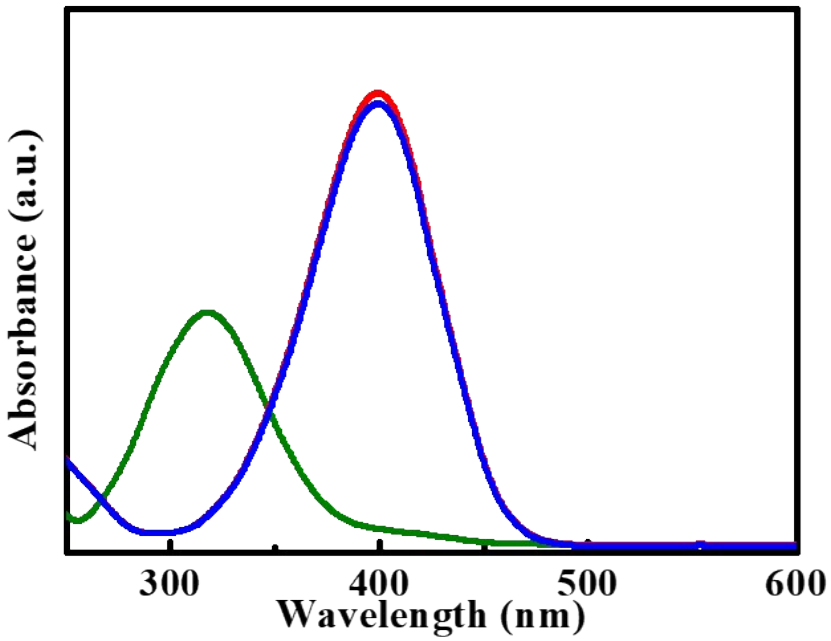


**Figure S14.** The UV-Vis absorption spectra of 4-NP without $NaBH_4$ (green), reaction mixture (red), reaction mixture for 10 h (blue).

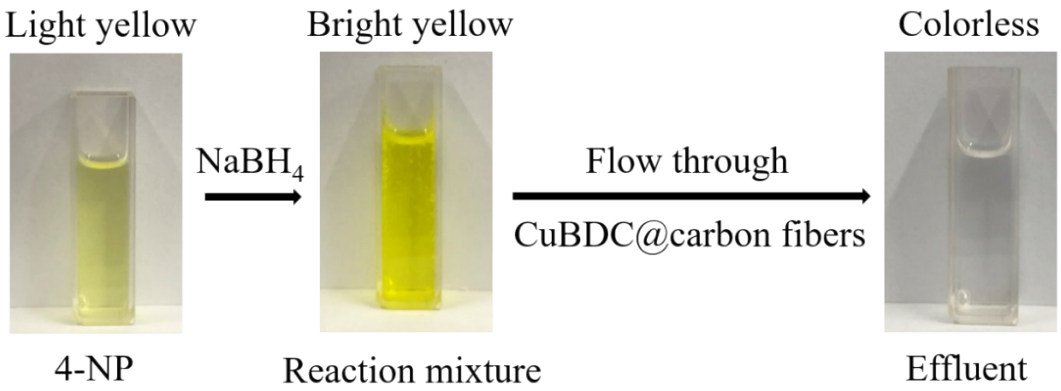


**Figure S15.** The photographs of 4-NP solution, reaction mixture solution and effluent solution (4-AP).

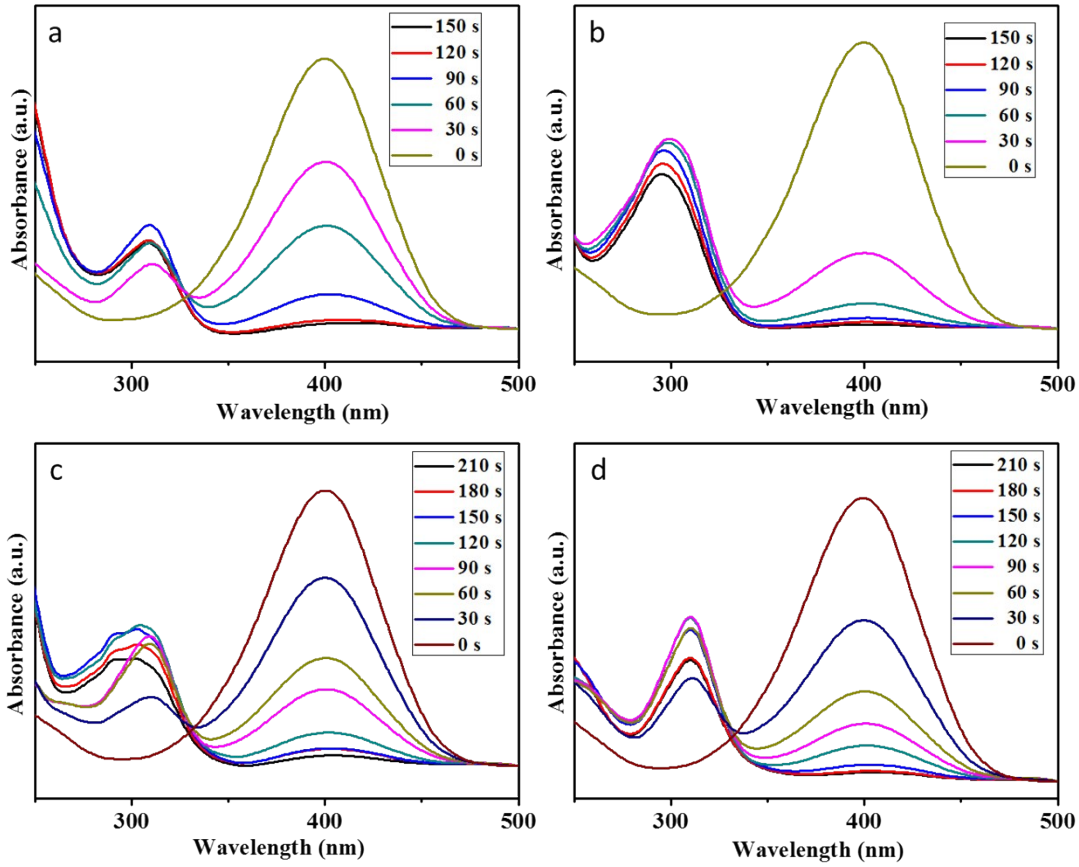


**Figure S16.** UV-Vis absorption spectra of the 4-NP reduction versus reaction time under the catalysis of (a) CuBDC@CF, (b) Cu(1,4-NDC)@CF, (c) Cu(2,6-NDC)@CF and (d) Cu(2-atp)@CF.

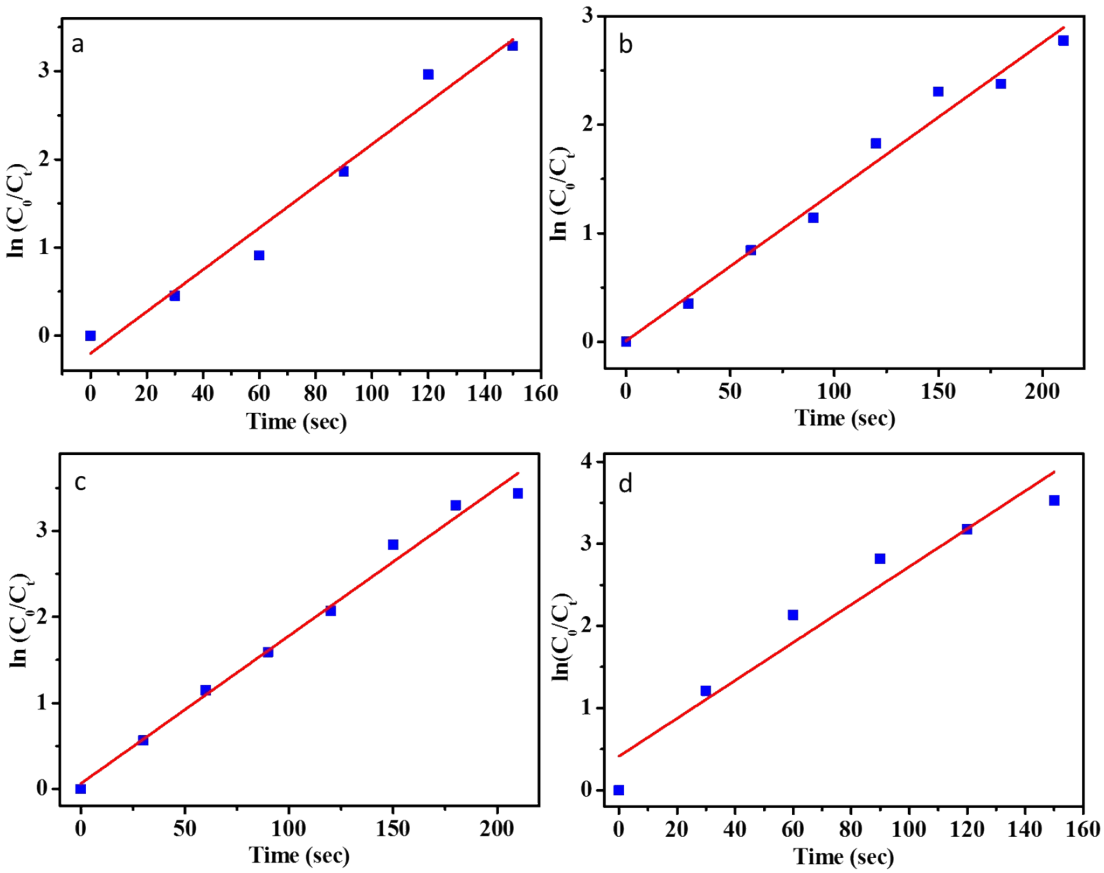


**Figure S17.** Plots of $\ln(c_0/c_t)$ versus reaction time for the 4-NP reduction with (a) CuBDC@CF, (b) Cu(1,4-NDC)@CF, (c) Cu(2,6-NDC)@CF and (d) Cu(2-atp)@CF.

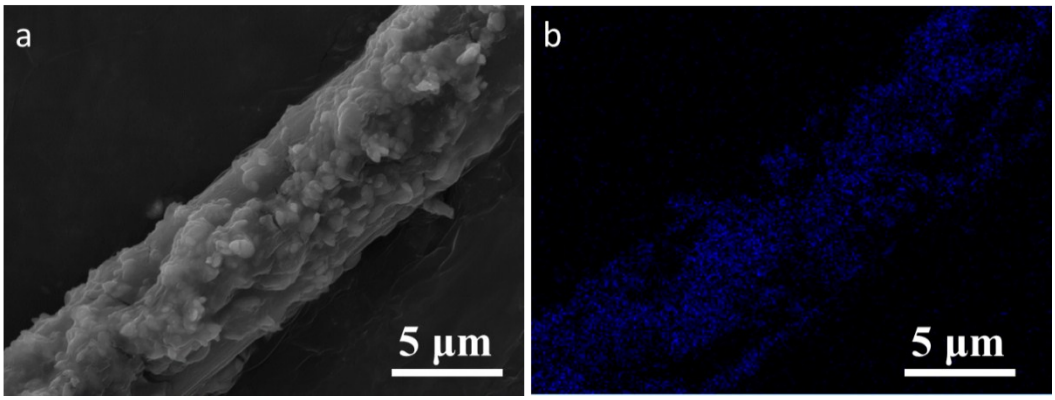


**Figure S18.** The (a) SEM image and (b) corresponding EDX elemental mapping image of CuBDC@CF after catalytic test.

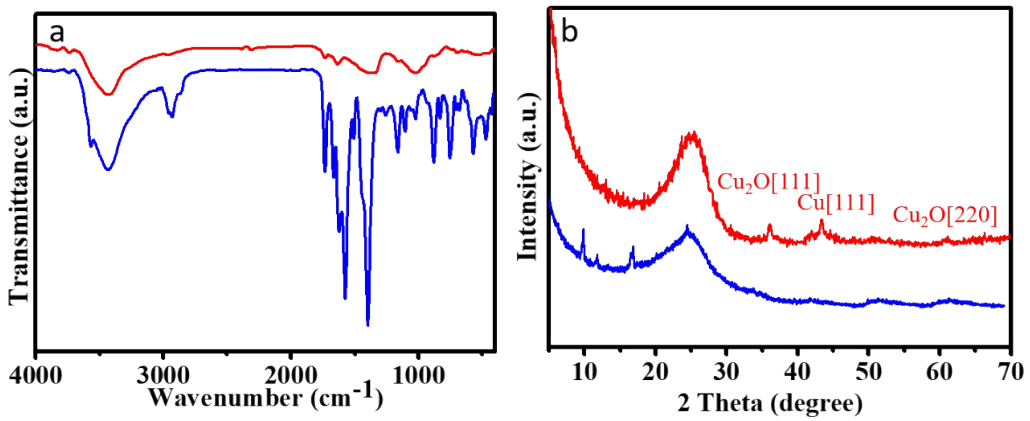


**Figure S19.** The (a)IR spectra and (b) XRD patterns of CuBDC@CF before (blue) and after (red) catalytic test.

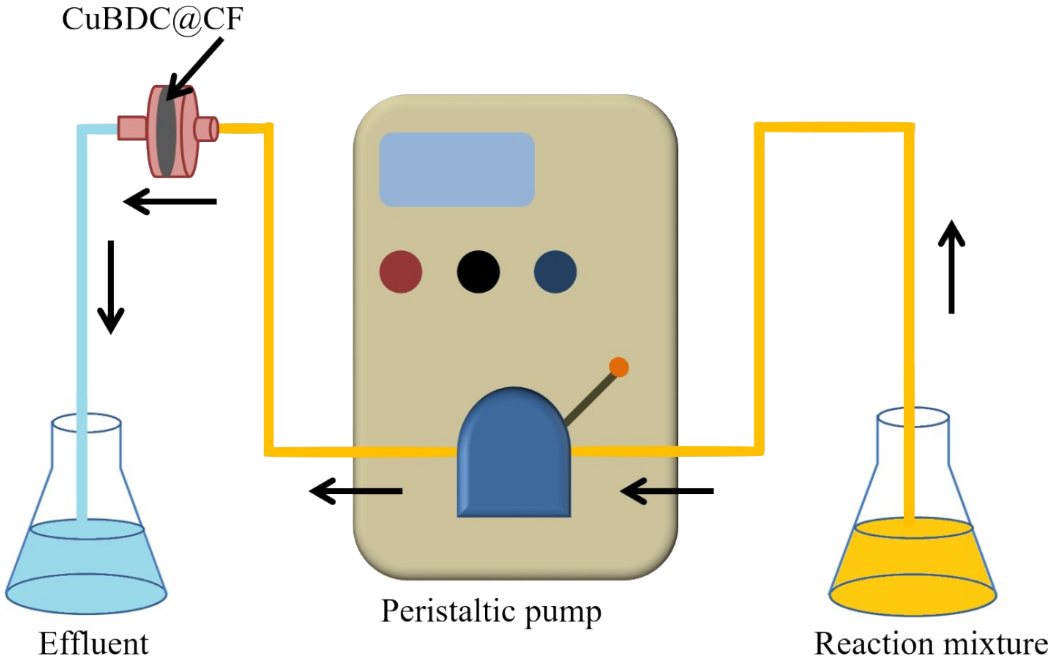


**Figure S20.** The schematic diagram of filtration system.

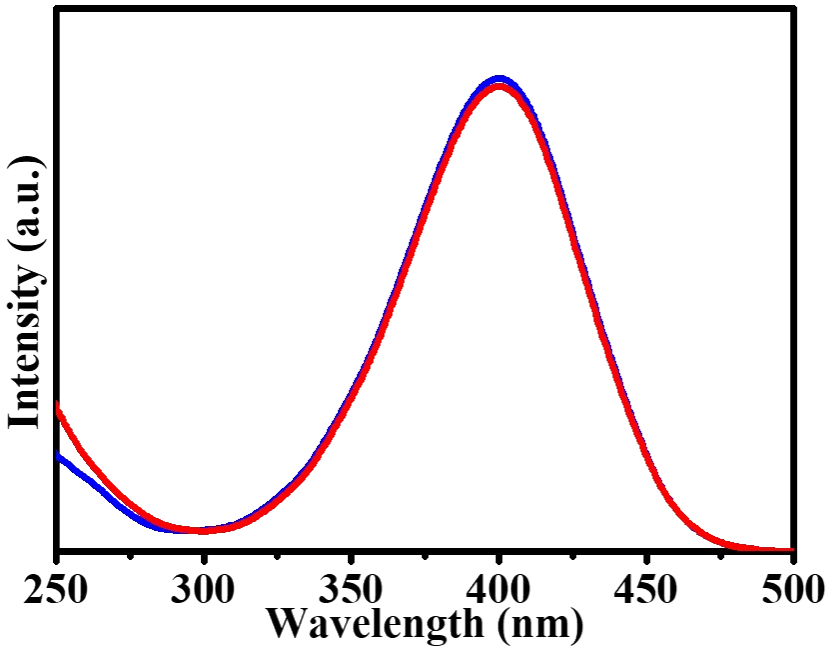


**Figure S21.** UV-Vis absorption spectra of the reaction mixture (blue), effluent collected through CFs (red).

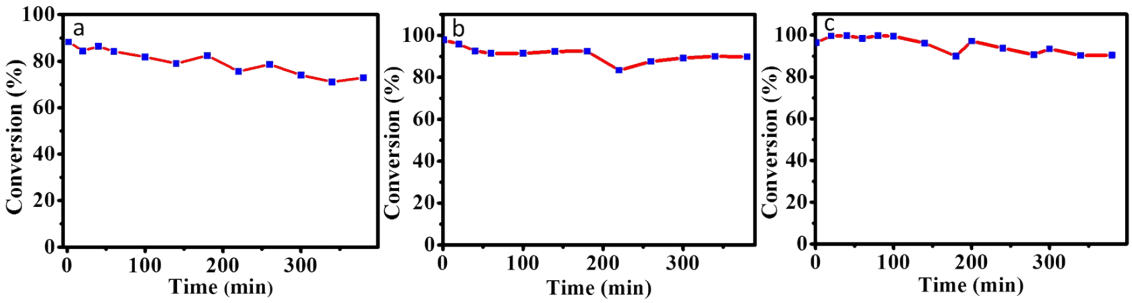


**Figure S22.** The conversion rate of 4-NP reduction by (a) Cu(1,4-NDC)@CF, (b) Cu(2,6-NDC)@CF and (c) Cu(2-atp)@CF.