Electronic supplementary information (ESI)

Magnetically Recyclable Bi/Fe-based Hierarchical Nanostructures via Self-assembly for Environmental Decontamination

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Synthesis of nanostructured $Bi_2Fe_4O_9$ clusters (the precursor P-BFO):

P-BFO with cuboid-like shape were prepared via combining low-temperature co-precipitation with hydrothermal treatment. Typically, $Bi(NO_3)_3 \cdot 5H_2O$ (1.21 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (2.02 g) were completely dissolved in 2 mL of 2 M HNO_3 and citric acid (3.2 g) was dissolved in 5 mL of water, respectively. A transparent solution could be obtained after mixing them together in a Teflon vessel. Then, 33 mL of 12 M NaOH was instantly added into the solution with vigorous stirring. After stirring for 1 h, the Teflon vessel containing the deep-brown slurry was transferred to an oil bath and heated at 95°C with constant stirring. After 12 h, the reaction was cooled down naturally to room temperature. The precipitate was collected and washed using water until pH ~10, followed by re-suspended into 6 mL of methanol/water (1:1 v/v) co-solvent by ultrasonication for 10 min. Thereafter, the suspended precipitate was surface-modified by addition of citric acid solution (0.6 g dissolved into 3.5 mL of the co-solvent) to promote its dispersion (noted as "A"). Then, 3.82 g of urea was dissolved in 7 mL of the co-solvent at 65°C in water bath, which was then added slowly into the A with continuous stirring at room temperature. After 120 min, the dispersion was transferred into a 50-mL Teflon-lined stainless steel autoclave and heated at 200°C for 20 min in an electric oven. After the autoclave reaction chamber was cooled down naturally to room temperature, the product was collected and washed thoroughly with water followed by absolute ethanol. This prepared material is stored in ethanol for further use.

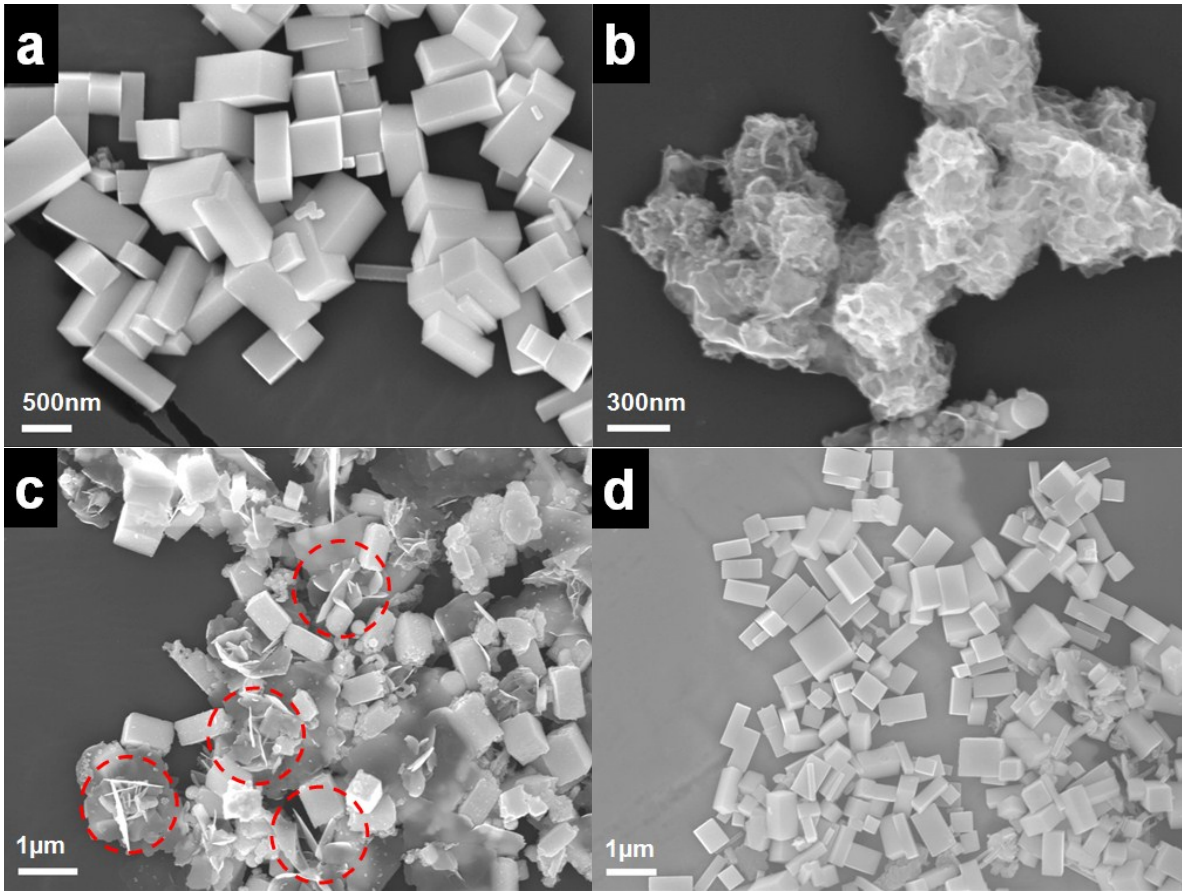

Fig. S1. FESEM images of as-prepared (a) BFO-A, (b) BFO-M, (c) BFO-E and (d) BFO-G.

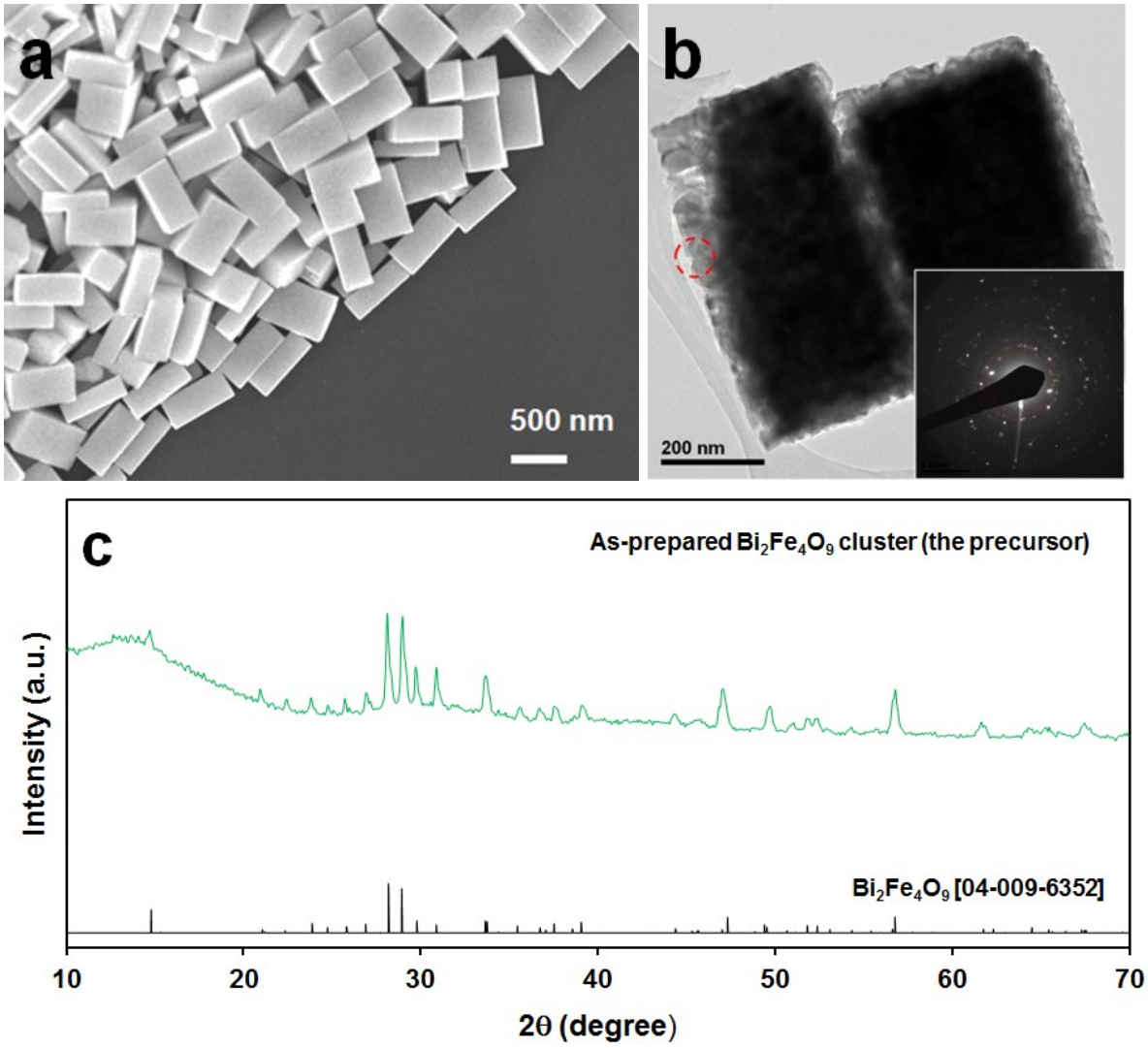

Fig. S2. (a) FESEM, (b) TEM and (c) XRD pattern of P-BFO.

Fig. S3 shows XRD patterns of the as-prepared BFO-M and the different standard samples. The mainly observed characteristic peaks for BFO-M are numbered as 1 to 12. As shown in the figure, the marked peak 1 could be ascribed to $Bi_2Fe_4O_9$ or Fe_2O_3. The marked peak 2 and 11 could be ascribed to $Bi_2Fe_4O_9$ or $Bi_{25}FeO_{40}$. The marked peak 3 and 10 could be ascribed to $Bi_2Fe_4O_9$, Fe_2O_3 or Fe_3O_4. The marked peak 4, 6 and 12 could be ascribed to $Bi_2Fe_4O_9$. The marked peak 5 could be ascribed to $BiFeO_3$ or Fe_2O_3. The marked peak 7 could be ascribed to $BiFeO_3$ or Bi_2O_3. The marked peak 8 could be ascribed to Fe_2O_3. The marked peak 9 could be ascribed to $Bi_2Fe_4O_9$, $BiFeO_3$ or Fe_3O_4. Hence, it possibly indicates that the fabricated BFO-M is a Bi/Fe-based mixed material.

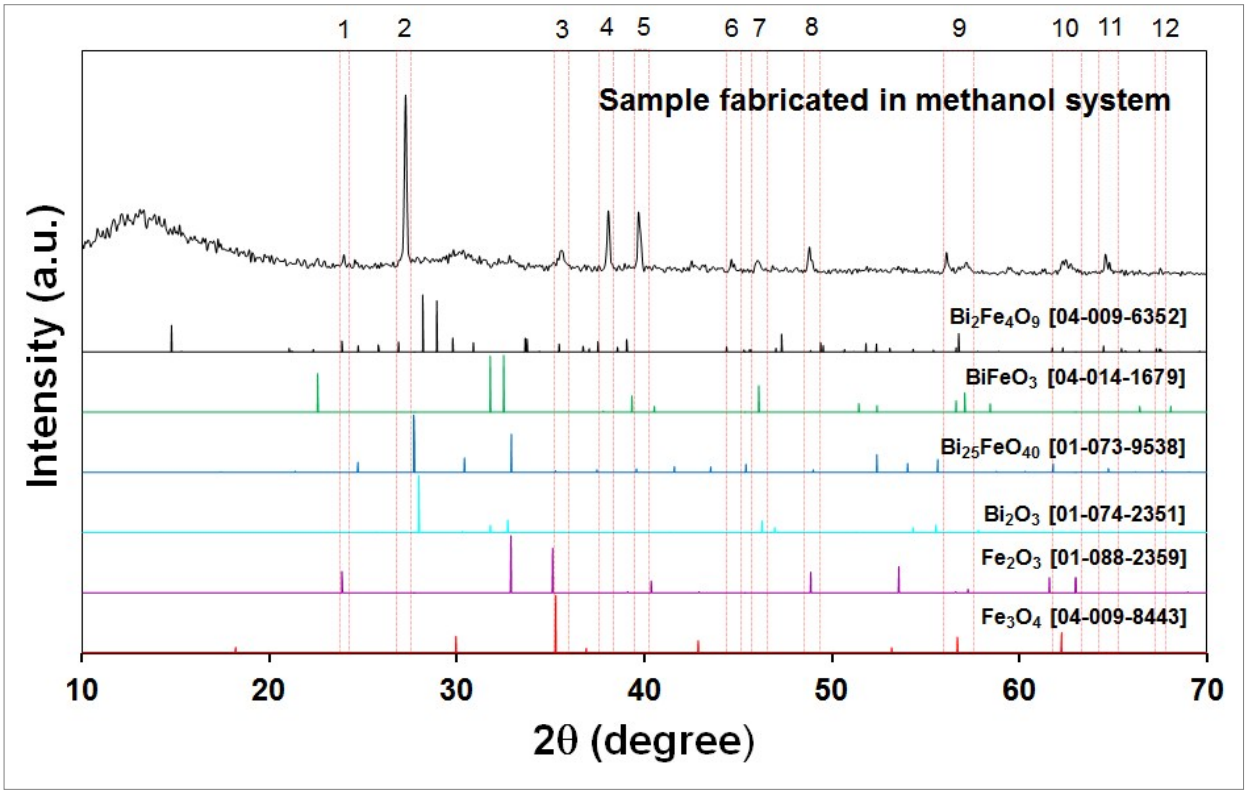

Fig. S3. Phase purity analysis of as-prepared BFO-M. The standard XRD patterns corresponding to mullite bismuth ferrite ($Bi_2Fe_4O_9$), perovskite bismuth ferrite ($BiFeO_3$), sillenite bismuth ferrite ($Bi_{25}FeO_{40}$), bismuth oxide (Bi_2O_3), hematite iron oxide (Fe_2O_3) and magnetite iron oxide (Fe_3O_4).

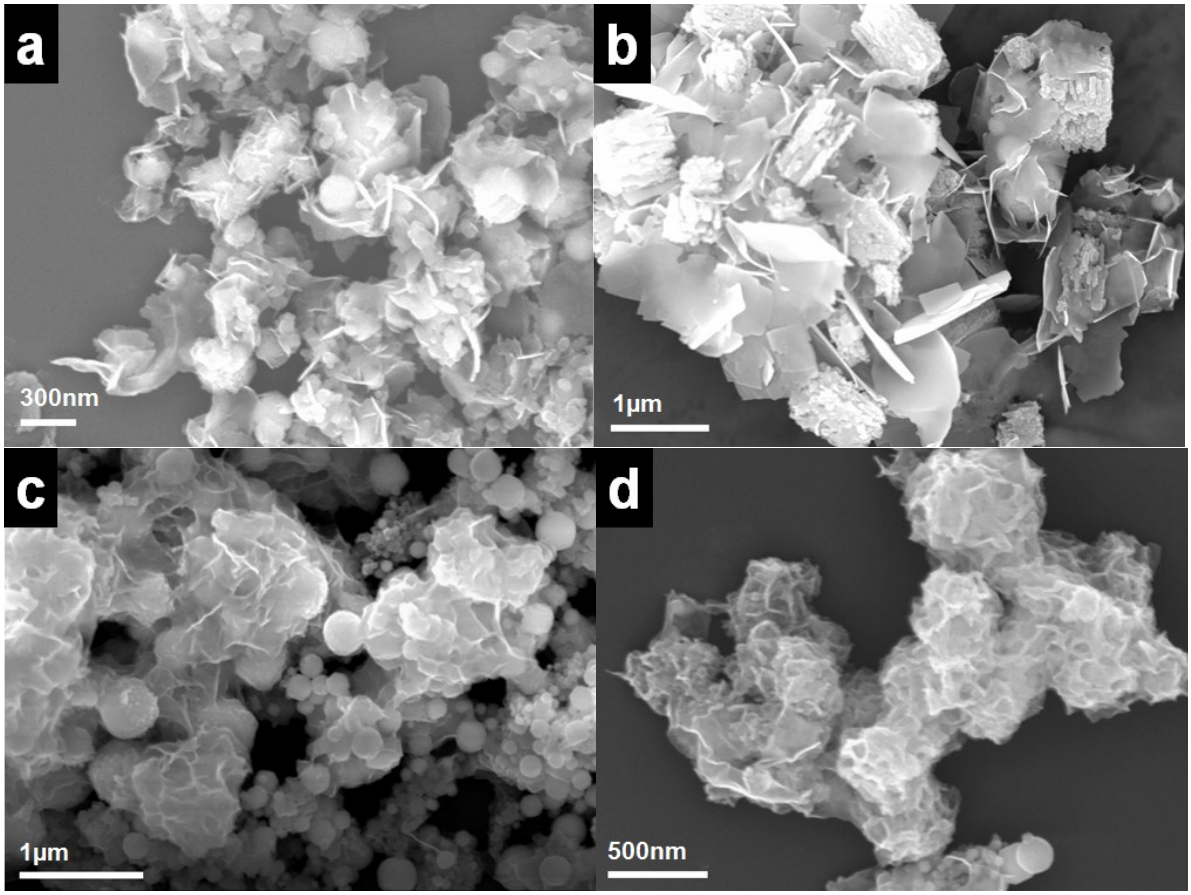

Fig. S4. FESEM images of products obtained via solvothermal treatment in (a) 2 mL, (b) 5 mL, (c) 7.5 mL, (d) 10 mL methanol. (Note: the P-BFO loading is 50 mg; the reaction temperature is 200°C; the reaction time is 3 d.)

As shown in Fig. S5, under keeping other conditions (i.e., 10 mL volume reaction and 3 d reaction time), the precursor P-BFO (Fig. S2a) could still be its morphology after undergoing solvothermal treatment in methanol system at temperatures of up to 150°C (Fig. S5a, b), whereas the morphology for the final product could be changed to coral-like shape at temperature of 200°C (Fig. S5c). If further increased reaction temperature, the final product could be sphere-like shape (Fig. S5d).

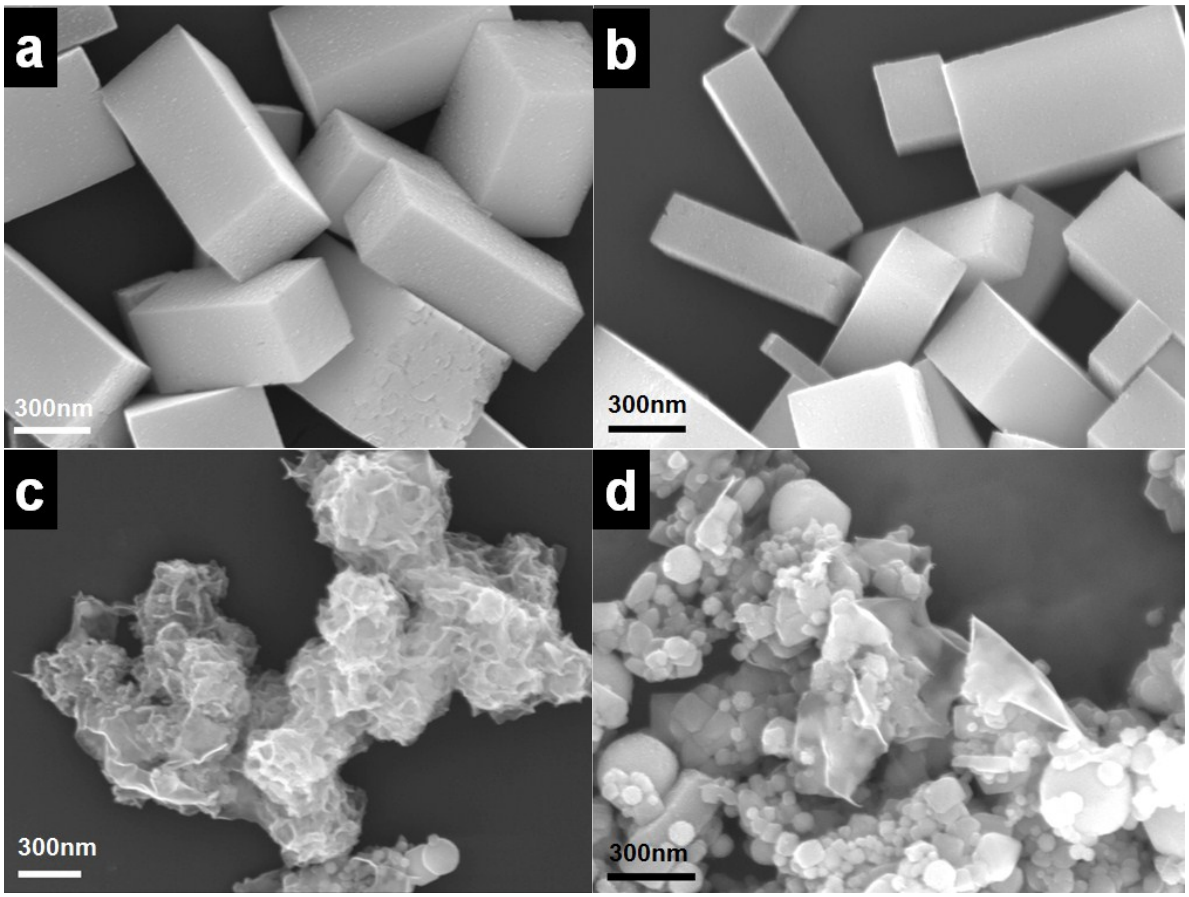

Fig. S5. FESEM images of products obtained via methanol solvothermal treatment at reaction temperature of (a) 90°C, (b) 150°C, (c) 200°C, (d) 220°C. (Note: the P-BFO loading is 50 mg; the volume of methanol is 10 mL; the reaction time is 3 d.)

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As shown in Fig. S6, under keeping other conditions (i.e., 10 mL volume reaction and 200°C reaction temperature), the final product is composed of incompletely dissolved precursors (Fig. S6a) with new generation of coral-like shape (Fig. S6a, inset) when the reaction time is 1 d. With the extension of reaction time to 3 d, a product with coral-like hierarchical morphology could be fabricated (Fig. S6b). If further prolonged reaction time to 6 d, the resultant product contains sphere-like particles with no noticeable hierarchical structure.

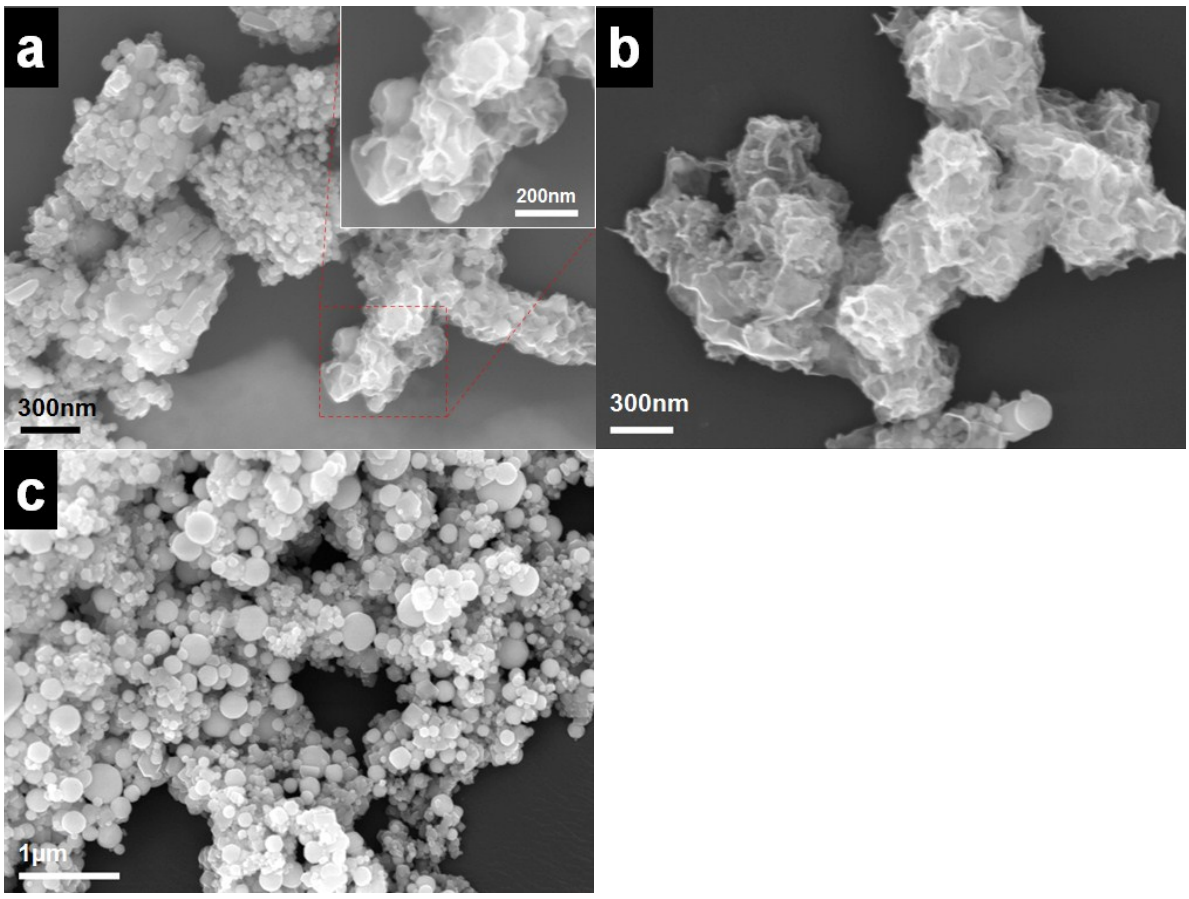


Fig. S6. FESEM images of products obtained via methanol solvothermal treatment at reaction time of (a) 1 d, (b) 3 d, (c) 6 d. (Note: the P-BFO loading is 50 mg; the volume of methanol is 10 mL; the reaction temperature is 200°C.)

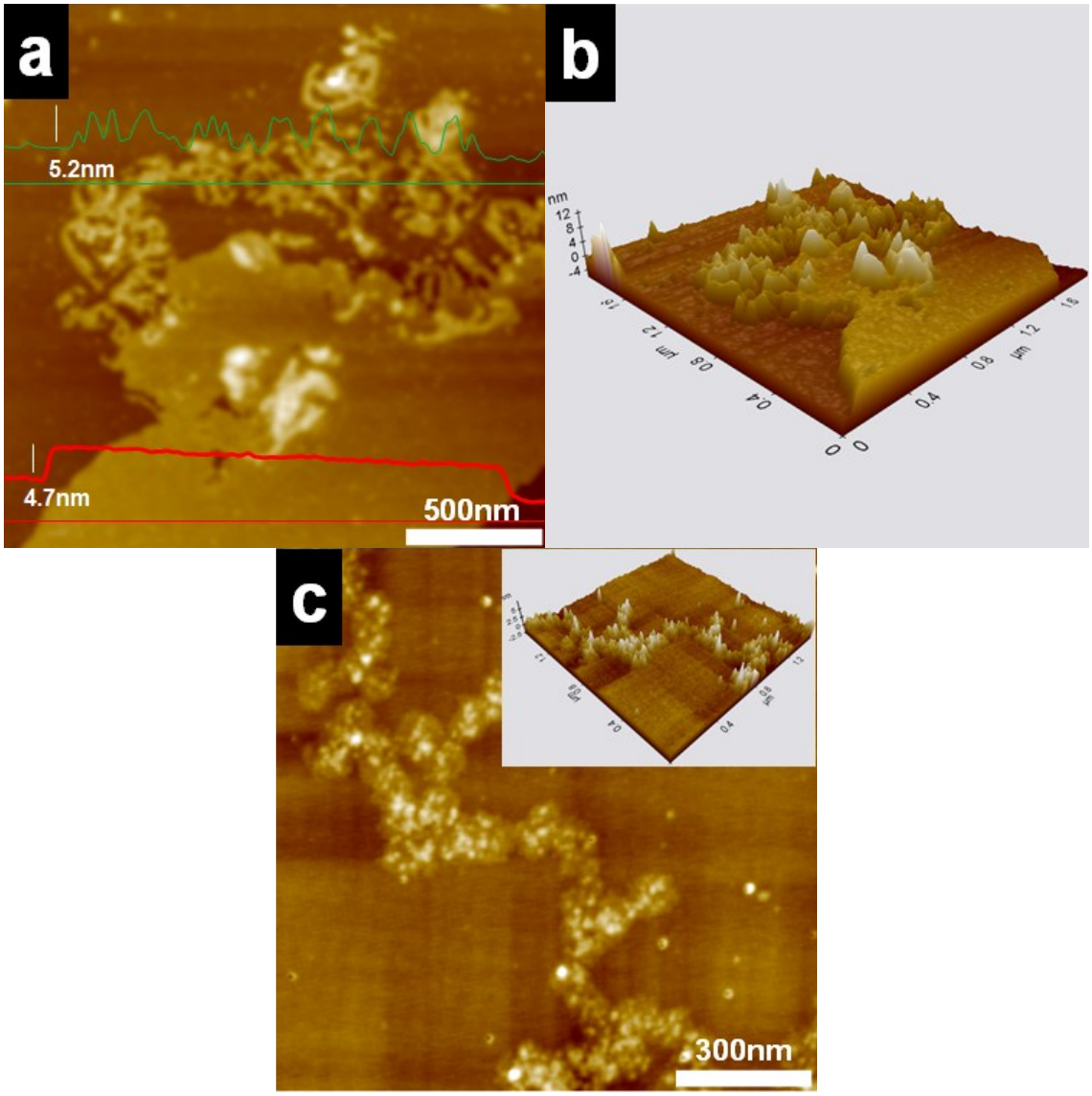


Fig. S7. AFM images of as-prepared BFO-M. (a) 2D AFM image with two line scans, (b) 3D AFM image, (c) 2D AFM image of local magnification and the corresponding 3D AFM image.

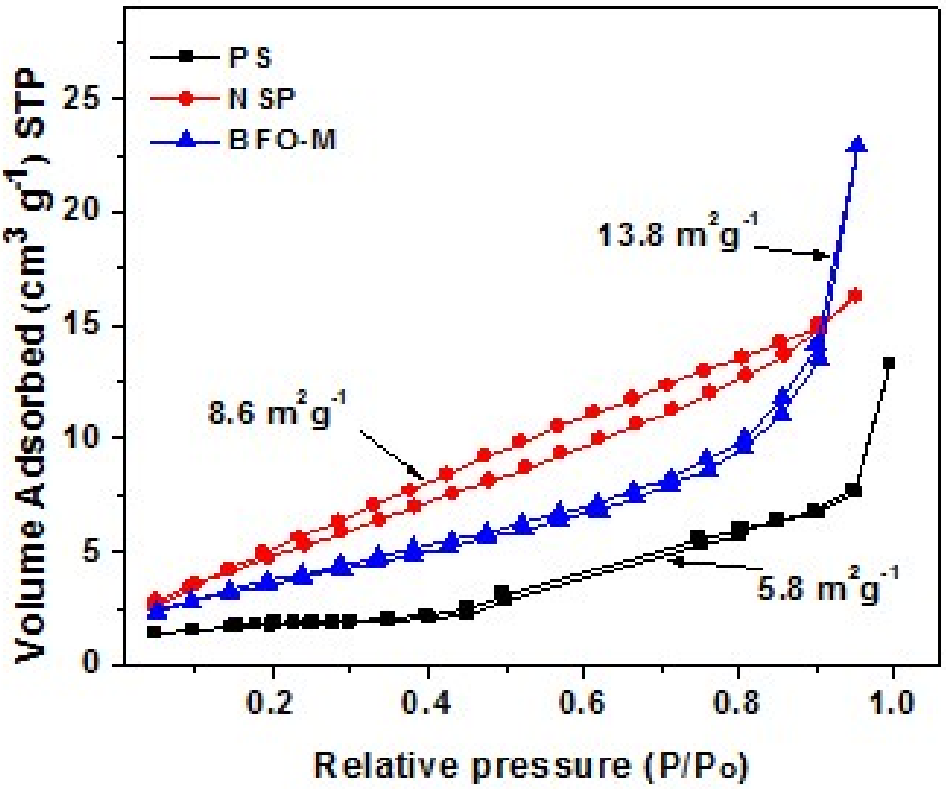


Fig. S8. Nitrogen adsorption/desorption isotherms of as-prepared BFO-M, NSP and PS. (Note: PS is a pad-like single crystalline $Bi_2Fe_4O_9$; NSP is a plate-like nanostructured $Bi_2Fe_4O_9$ cluster; BFO-M is a coral-like product synthesized from $Bi_2Fe_4O_9$ precursor.)

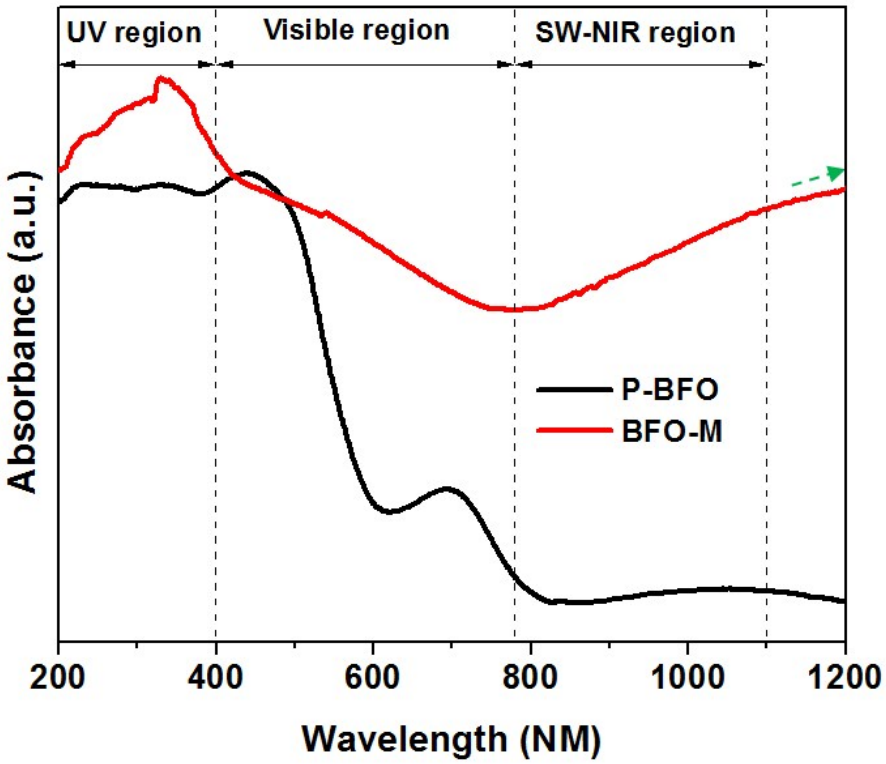


Fig. S9. UV-vis and short-wavelength near-infrared absorption spectrum of as-prepared BFO-M and P-BFO.

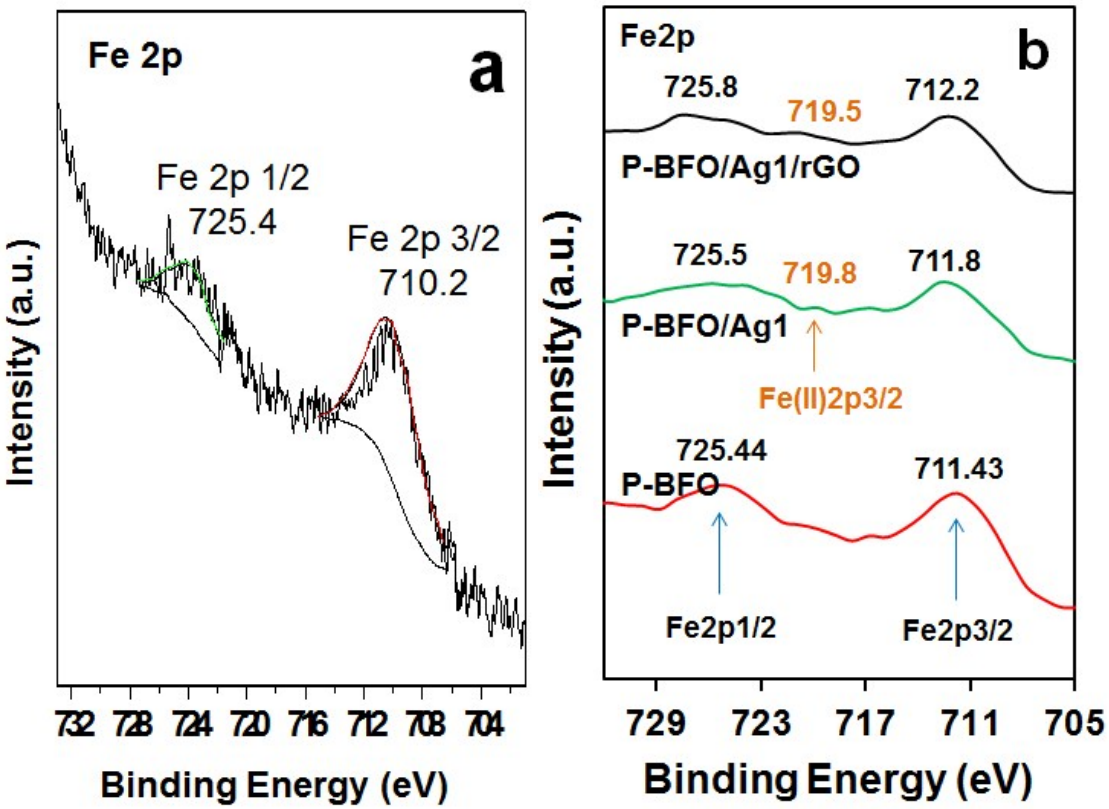


Fig. S10. (a) High-resolution XPS spectrum of Fe 2p for BFO-M. (b) High-resolution XPS spectrum of Fe 2p for P-BFO shown as red curve (quoted from our published report previously [1]).

Herein, the re-used BFO-M on the removal of IPU was recovered by magnetic separation and rinsed with DI water thoroughly, while the adsorption of IPU on BFO-M in the dark (~3.5%) was neglected. Moreover, the re-used BFO-M on the removal of Pb(II) was recovered by magnetic separation and washed with dilute acid solution (HNO_3 at pH ~4.5) and DI water thoroughly.

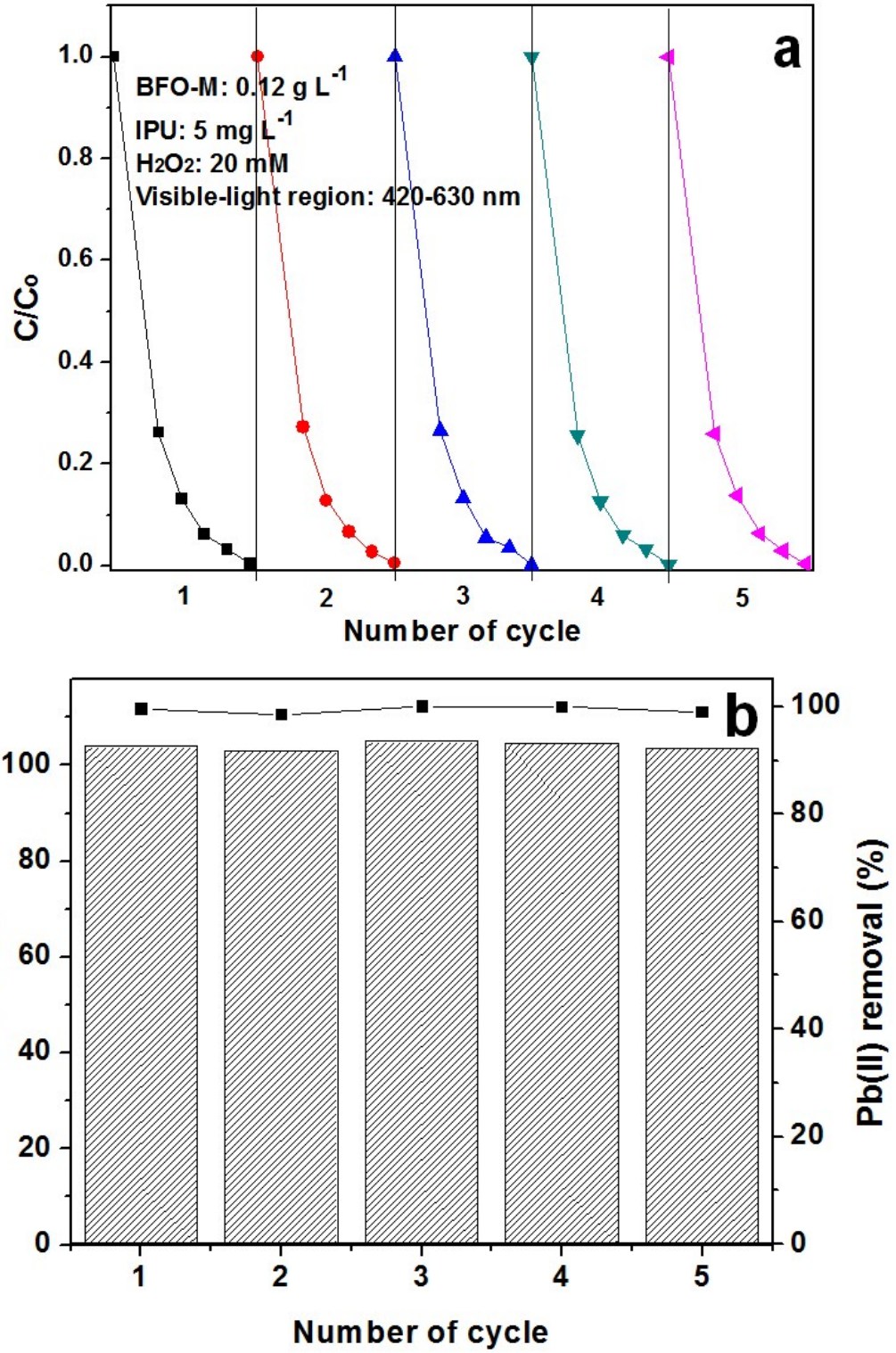


Fig. S11. Efficiency of reused BFO-M on removal of IPU using visible light photo-Fenton oxidation (a), and Pb(II) at the condition of 50 mg L^{-1} initial metal concentration, 0.5 g L^{-1} BFO-M (b).

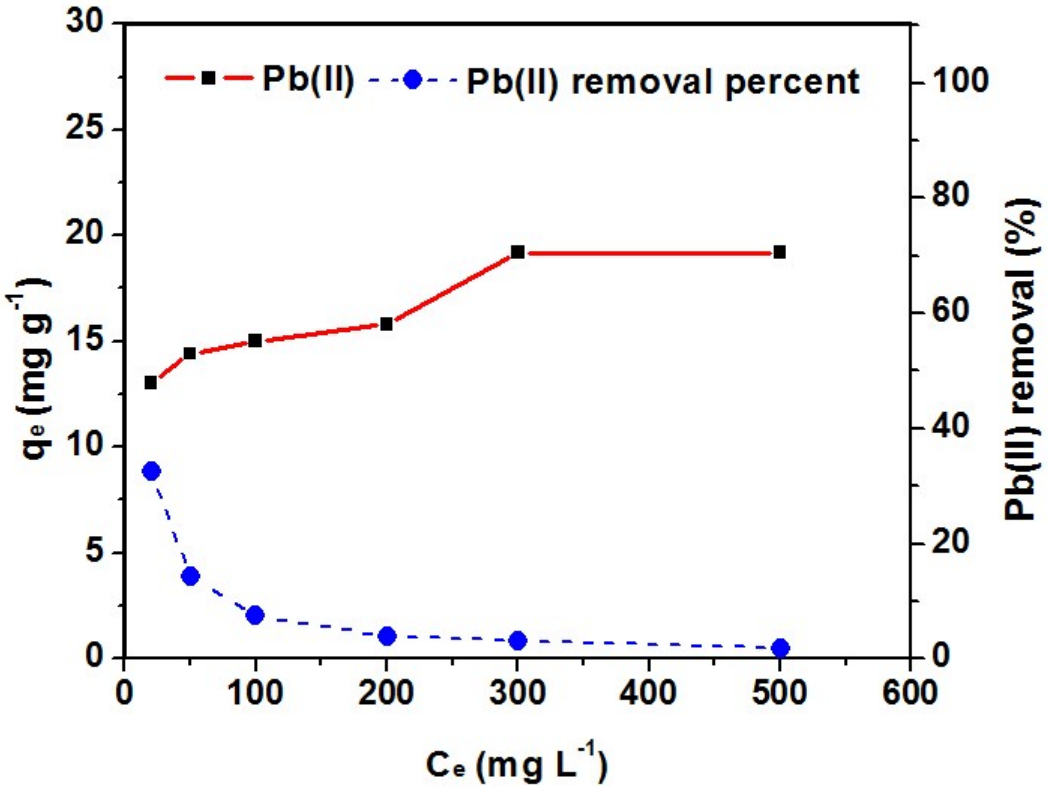


Fig. S12. Adsorption of P-BFO on Pb(II) at different concentrations of Pb(II) (20, 50, 100, 200, 300 and 500 mg L^{-1}) and the corresponding percentage removal of Pb(II).

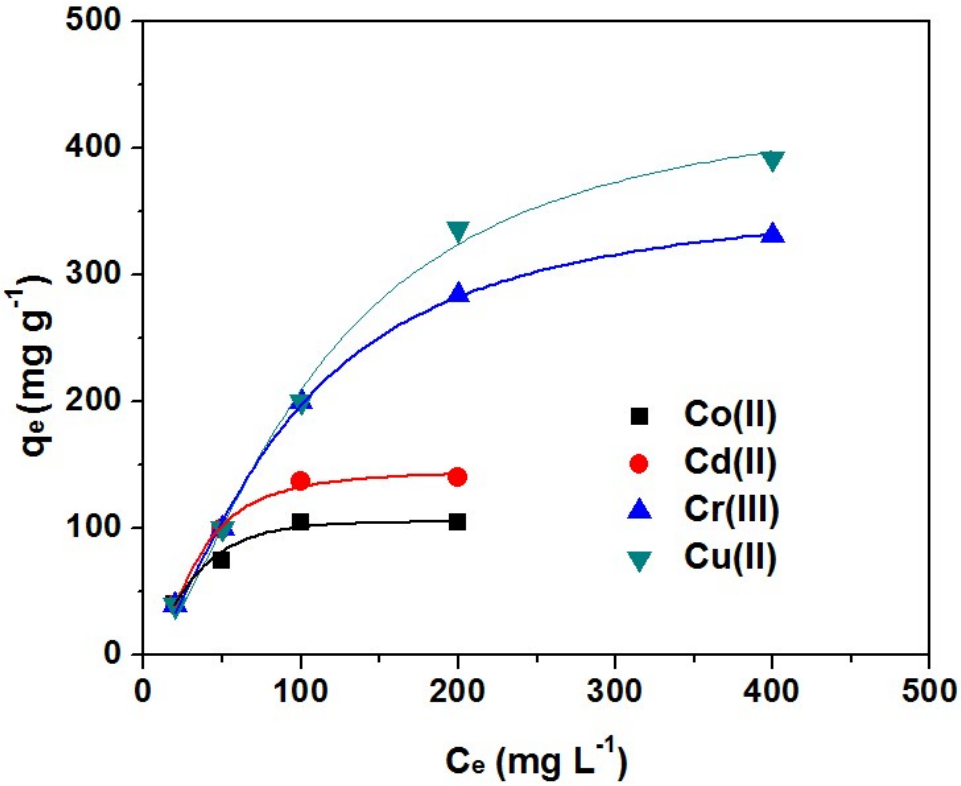
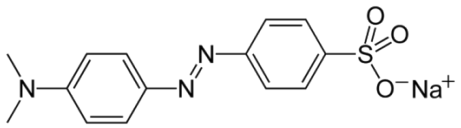
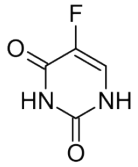
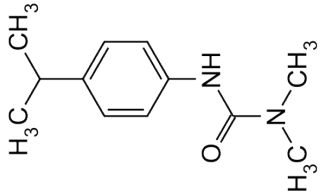


Fig. S13. Langmuir isotherm of metal ions (e.g., Cu(II), Cr(III), Cd(II), Co(II)) for BFO-M adsorption and the corresponding maximal adsorption capacities are 448, 366, 146 and 107 mg g^{-1} respectively.

Tabel S1 Physiochemical properties of investigated pollutants.

Pollutant	Type	Chemical structure	Chemical formula	Molar mass (g mol^{-1})	Solubility in water (mg L^{-1})	LD_{50} (mg kg^{-1}, rat, oral)
Methyl orange (MO)	Dye		$C_{14}H_{14}N_3NaO_3S$	327.33	5000	60
5-Fluorouracil (5-FU)	Pharmaceutical		$C_4H_3FN_2O_2$	130.08	12000	230
Isoproturon (IPU)	Pesticide		$C_{12}H_{18}N_2O$	206.29	72	1830