Supporting Information for

Cobalt and zinc nanoparticles from pyrolysis of their MOF precursors exhibiting potent organophosphorus hydrolase-mimicking activities

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Experimental notes

2-methylimidazole was obtained from *Macklin* (Shanghai) and Imidazolate-2-carboxaldehyde from *Yuanye Bio-Technology* (Shanghai). $Co(NO_3)_2•6H_2O$ was purchased from *InnoChem* (Beijing) and $Zn(CH_3COO)_2•2H_2O$ from *Energy Chemical* (Shanghai). PM was purchased from *Titan Scientific* (Shanghai). Paraoxon was purchased from *Cato* (Guangzhou). EPN was purchased from *Putian Tongchuang* (Beijing). All solvents and reagents were used as purchased without further purification.

ZIF-67 and the resulting Co@NOC were synthesized based on the modified procedures.[1, 2] 2.3 g of 2-methylimidazole and 1.0 g of $Co(NO_3)_2•6H_2O$ were dissolved in 35 mL of anhydrous methanol, respectively. The two solutions were mixed and stirred at room temperature (22±1°C) for 20 h. The purple product was centrifuged and washed several times with anhydrous methanol. It was then dried at 60°C in a vacuum oven to obtain a purple powder product ZIF-67. The ZIF-67 material was then spread flat in a porcelain boat and put it into a tube furnace. It was then heated to 800°C under N_2 (99.999%) atmosphere for 2 h and cooled down to room temperature. Thus, the black product, OPH-mimicking nanozyme, cobalt nanoparticles incorporated in N and O co-doped carbon matrix (Co@NOC) was obtained.

ZIF-90 were synthesized using the similar procedure reported in the literature.[3] 6 mL of DMF containing 135 mg of $Zn(CH_3COO)_2•2H_2O$ was added into 6 mL of DMF containing 116 mg of imidazolate-2-carboxaldehyde under vigorous stirring. After stirring for 5 min, 30 mL of DMF was added into the suspension. The solid product was centrifuged, washed with DMF and ethanol several times. It was then dried at 60°C

under vacuum condition to obtain a light brown powder product ZIF-90. The yield for the synthesis of ZIF-90 was about 26%. The ZIF-90 material was then spread flat in a porcelain boat and put it into a tube furnace. It was then heated to 800°C under N_2 atmosphere for 2 h and cooled down to room temperature. Thus, the black product, another OPH-mimicking nanozyme, zinc nanoparticles incorporated in N and O co-doped carbon matrix (Zn@NOC) was obtained.

As a general procedure, in a cuvette containing 1.2 mL of pH 9.0, 0.15 M sodium carbonate buffer, 100 μL of 2 mM paraoxon or EPN or PM and 60 μL of 10.0 mg/mL Co@NOC or Zn@NOC were added and mixed under stirring. The final concentration of Co@NOC, Zn@NOC, ZIF-67 or ZIF-90 was 0.44 mg/mL in the cuvette, while the concentration of the OPC substrate paraoxon or EPN or PM was 147 μM. The mixture was incubated at 25°C or 40°C for 12 min to 6 hours in a shaking incubator, and then centrifuged to collect the supernatant. The incubation was also done with paraoxon or EPN or PM in the working buffer without any added Co@NOC, Zn@NOC, ZIF-67 or ZIF-90 for control experiments of spontaneous hydrolysis. The absorbance of the supernatants was measured at 400 nm for detecting or monitoring the product p-nitrophenol. One unit of the activity of OPH-mimicking nanozyme is defined as the amount of the nanozyme that can hydrolyze 1 nmol of paraoxon or EPN or PM per minute at 40°C and pH 9.0. At least three parallel samples were prepared for each activity measurement for Co@NOC, Zn@NOC or the control.

The X-ray diffraction (XRD) was carried out using a miniflex 600 X-ray diffractometer (Japan Rigaku) at a tube voltage of 40 kV with the Cu Kα radiation. TEM images were obtained at a working voltage of 200 kV by a Tecnai F20 transmission electron microscope (USA FEI). The X-ray photoelectron spectroscopy (XPS) was acquired at a working voltage of 12 kV, with a full spectrum scan energy of 150 eV and a narrow spectrum scan energy of 50 eV by a Scientific K-Alpha X-ray photoelectron spectrometer (USA Thermo). All UV-visible spectra were obtained by Agilent UV-8453 spectrophotometer.

Additional results

1. Analysis of XPS and XRD of Co@NOC

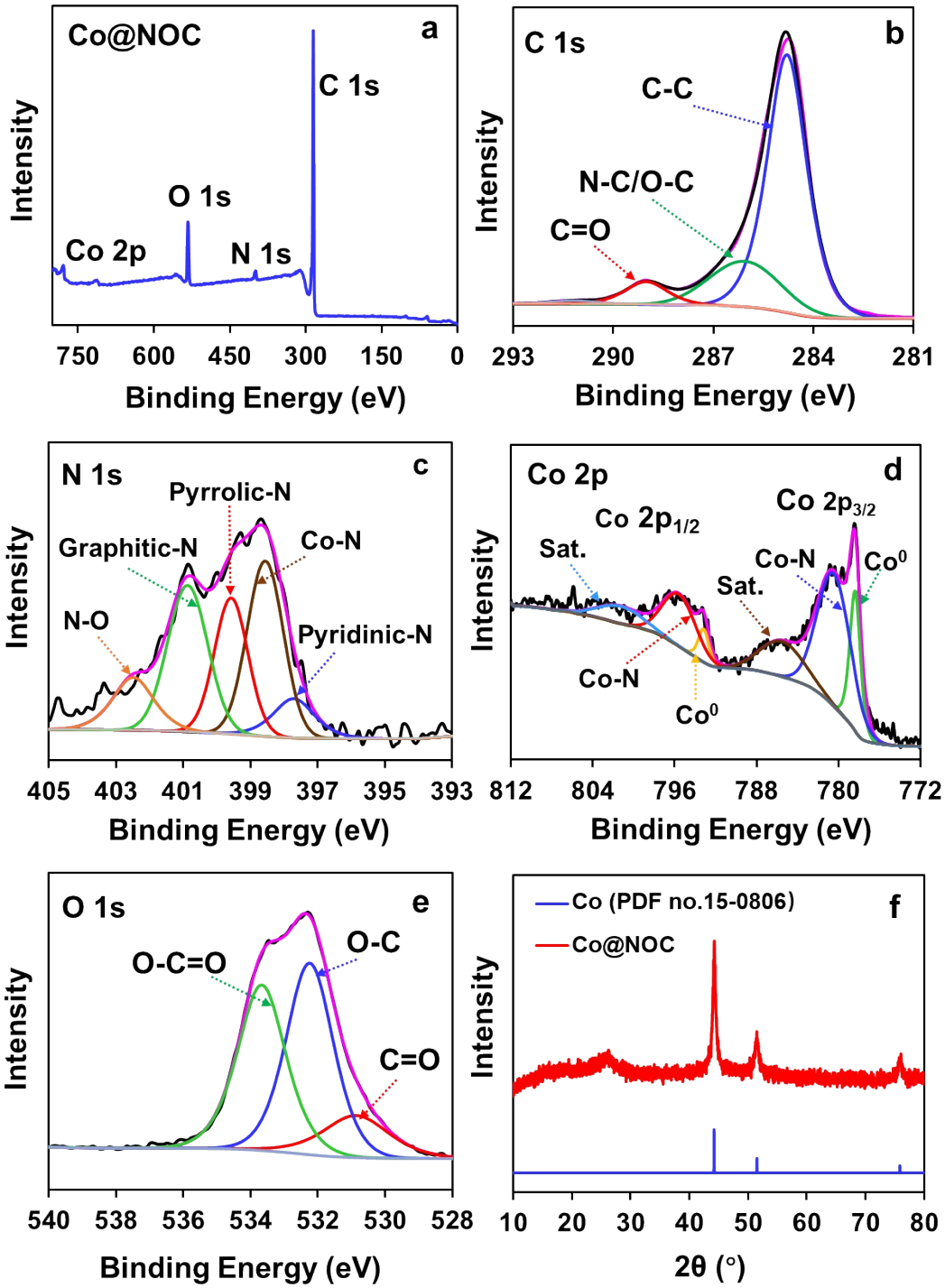
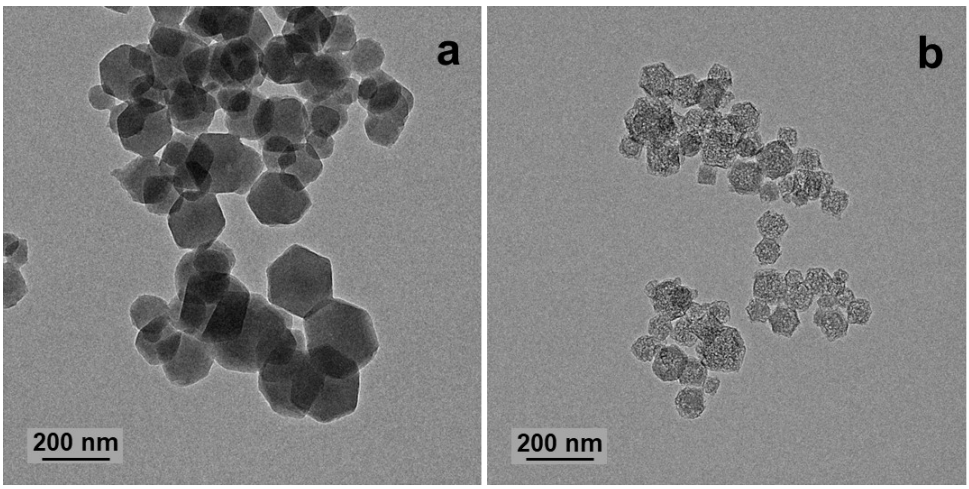


Figure S1.（**a**）XPS spectrum of Co@NOC; (**b**) XPS spectrum of C 1s; (**c**) XPS spectrum of N 1s; (**d**) XPS spectrum of Co 2p; (**e**) XPS spectrum of O 1s; (**f**) XRD diffraction pattern of Co@NOC.

The binding states of C, N, O and Co on the Co@NOC nanozyme were analyzed by XPS (**Figure S1a**). The C 1s spectrum shows the peaks corresponding to C-C, C-O/C- N, and C=O, with binding energies of 284.8 eV, 286.1 eV, and 289.0 eV, respectively (**Figure S1b**).[4] The N 1s spectrum displays the peaks corresponding to pyridinic-N, Co-N, pyrrolic-N, graphite-N and N-O, with binding energies of 397.7 eV, 398.6 eV, 399.6 eV, 400.9 eV and 402.5 eV, respectively (**Figure S1c**).[5, 6] The Co 2p spectrum includes the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks, with binding energies at 778.4 eV and 793.2 eV, respectively (**Figure S1d**). The peaks at 780.5 eV and 795.6 eV are attributed to Co-N resulted from Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively (**Figure S1d**). In addition, there exhibits two satellite peaks at 785.68 eV and 797.68 eV resulted from Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively (**Figure S1d**).[6-8] The O 1s spectrum shows the peaks corresponding to C=O, C-O, O-C=O, with binding energies of 530.9 eV, 532.3 eV, and 533.7 eV (**Figure S1e**).[9] The XRD diffraction pattern shows the diffraction peaks at 44.26°, 52.58°, and 77.76°, corresponding to the (1,1,1), (2,0,0), and (2,2,0) crystal planes of the Co standard card (PDF 15-0806) (**Figure S1f**),[7] indicating that cobalt nanoparticles were formed on the carbon matrix after pyrolysis of ZIF-67. The diffraction peak observed at 25.56° corresponds to the signal of graphitic carbon material (0,0,2).[10]

2. TEM images of ZIF-90 and Zn@NOC



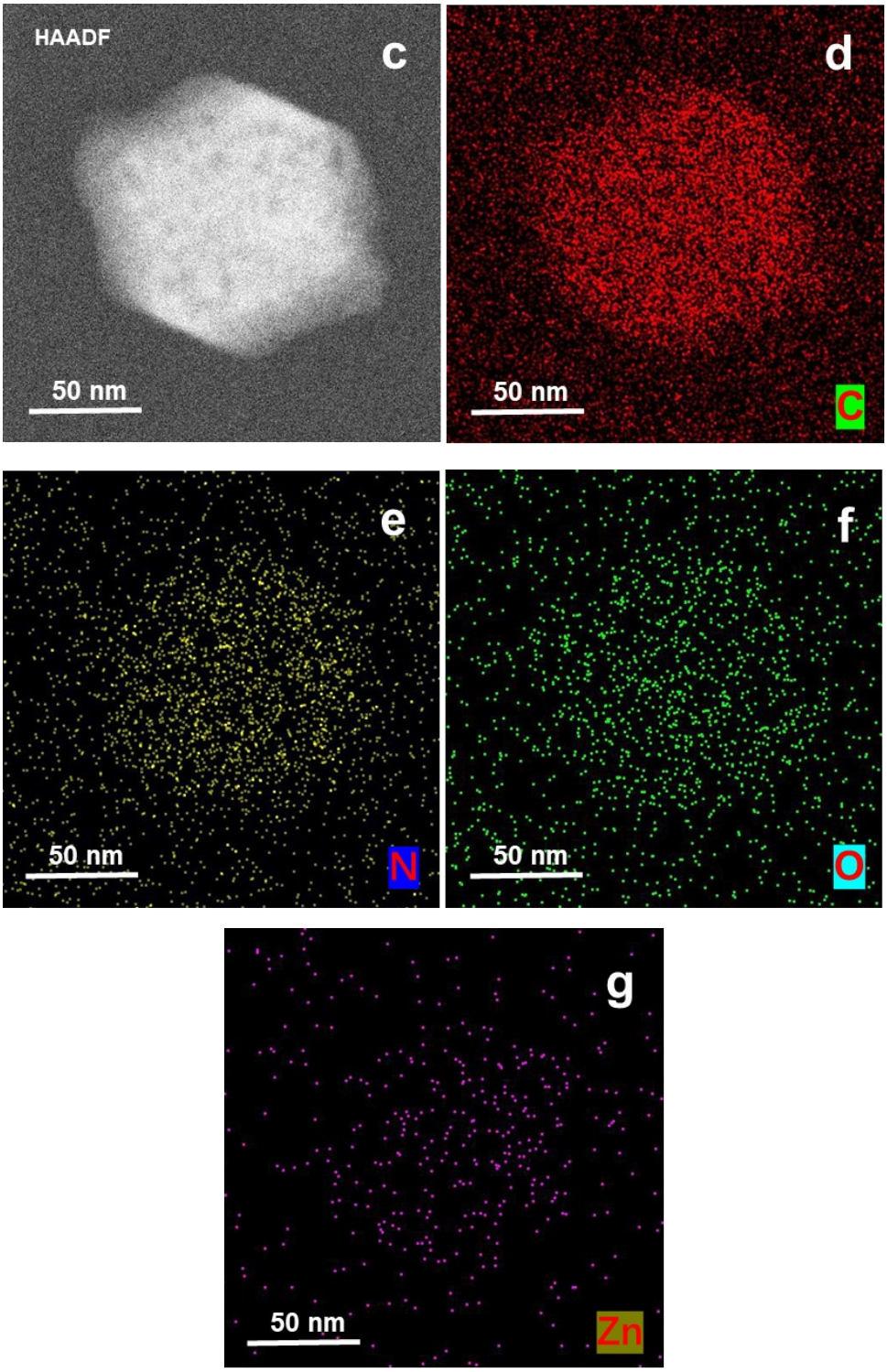


Figure S2. (**a**) TEM image of ZIF-90; (**b**) TEM image of Zn@NOC resulted from calcination of ZIF-90 under N_2 atmosphere at 800°C; (**c**) HAADF-TEM image of the Zn@NOC particle; (**d-g**) EDS elemental dot mappings of C, N, O and Zn, respectively for Zn@NOC.

3. Effects of pH on hydrolysis of paraoxon and EPN when incubated with Co@NOC in the working buffer

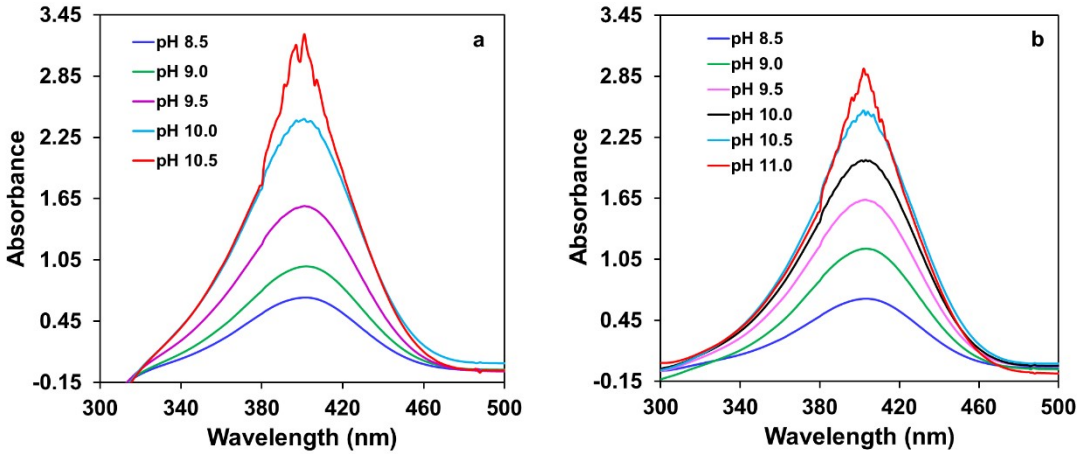


Figure S3. UV-vis spectra of the supernatants after incubation of paraoxon (**a**) and EPN (**b**) with Co@NOC at 40°C for 12 min in 0.15 M sodium carbonate at different pH values. The hydrolyzed product p-nitrophenol of paraoxon and EPN was monitored at 400 nm. [Co@NOC]: 0.44 mg/mL; [Paraoxon] = [EPN]: 147 μM.

4. UV-vis spectra of the supernatants after incubation of paraoxon and EPN with ZIF-67 and Co@NOC at 25°C

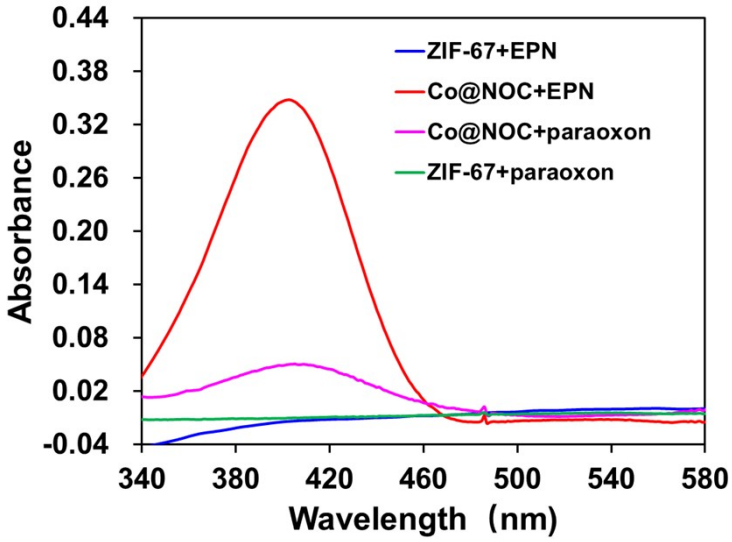


Figure S4. UV-vis spectra of the supernatants after incubation of paraoxon and EPN with ZIF-67 and Co@NOC at 25°C for 6 min. Buffer： pH, 9.0, 0.15 M sodium carbonate; [Co@NOC]: 0.44 mg/mL; [Paraoxon] = [EPN]: 147 μM.

5. Initial kinetic reaction progresses of Co@NOC and Zn@NOC with paraoxon, EPN and PM at 40°C

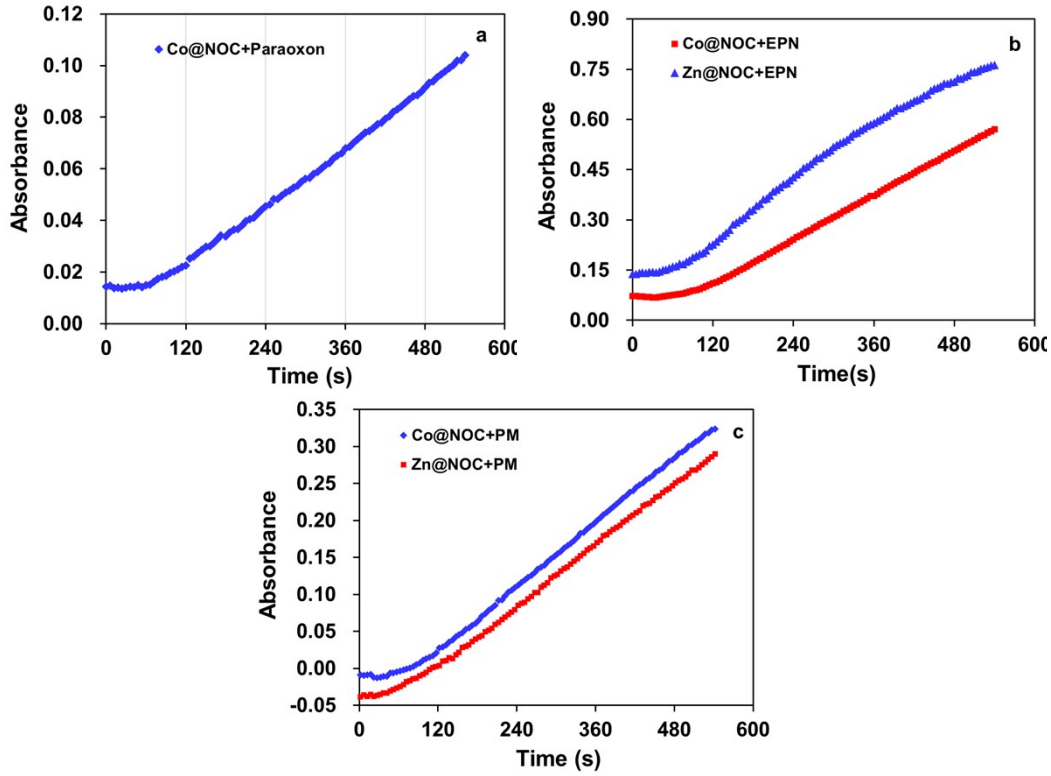


Figure S5. Initial kinetic reaction progresses of Co@NOC with paraoxon (**a**), Co@NOC and Zn@NOC with PM (**b**), Co@NOC and Zn@NOC with PM (**c**) at 40°C. Buffer： pH, 9.0, 0.15 M sodium carbonate; [Co@NOC] = [Zn@NOC]: 0.44 mg/mL; [Paraoxon] = [EPN] = [PM]: 147 μM.

6. UV-vis spectra of the supernatants after incubation of EPN with ZIF-67 and ZIF-90 at 40°C.

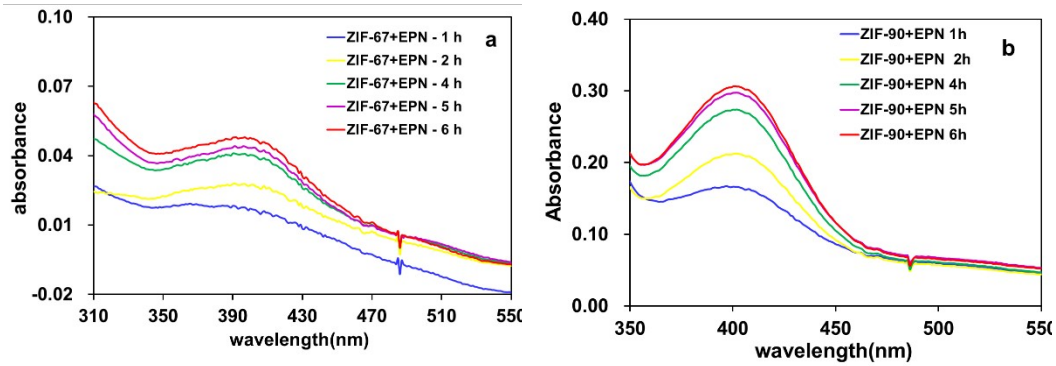


Figure S6. UV-vis spectra of the supernatants after incubation of EPN with ZIF-67 (**a**) and ZIF-90 (**b**) at 40°C for up to 6 hours. Buffer： pH, 9.0, 0.15 M sodium carbonate; [ZIF-67] =[ZIF-90] =: 0.44 mg/mL; [EPN]: 147 μM.

7. Reusability of Co@NOC and Zn@NOC

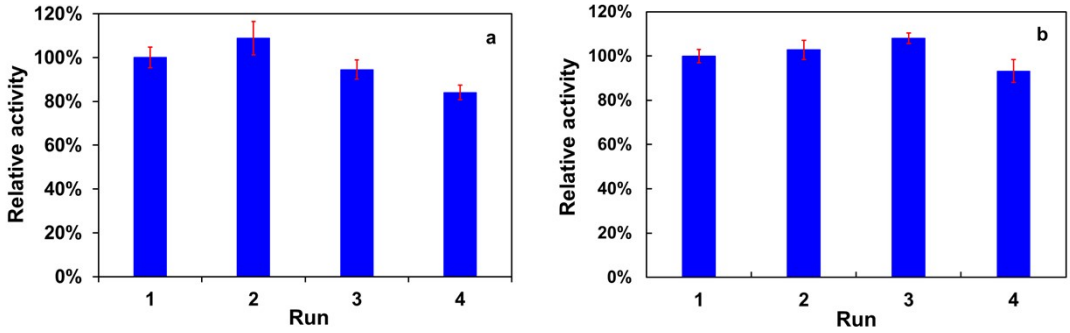


Figure S7. Reusability of Co@NOC and Zn@NOC with PM as the substrate. Co@NOC (**a**) and Zn@NOC (**b**) was repeatedly incubated with PM after each use in pH, 9.0, 0.15 M sodium carbonate at 40°C for 12 min. [Co@NOC] = [Zn@NOC]: 0.44 mg/mL; [PM]: 147 μM.

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