Core-Shell-Structured MOF-derived 2D Hierarchical Nanocatalysts with Enhanced Fenton-like Activities

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Supporting Information

1. Materials

Natural graphite flakes (Sigma-Aldrich) were used to prepare GO via the modified Hummers method.¹ Hexadecyltrimethylammonium bromide (CTAB), 2-methylimidazole (2-MeIm), cobalt chloride hexahydrate (CoCl₂·6H₂O), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), bisphenol A (BPA), poly(sodium 4-styrene sulfonate) (PSS), phenol (Ph), biphenyl (BP), naphthalene (NP), peroxymonosulfate (PMS) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were purchased from Aladdin Reagent Co. Ltd. (China). Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and sodium hydroxide (NaOH) were obtained from KESHI chemical agent factory. All chemical reagents were analytical grade without further purification.

2. Preparation of ZIF-67@ZIF-8@GO templates

The core-shell ZIF-67@ZIF-8@GO precursor was synthesized according to previous reports with minor modifications.² Concisely, the Zn(NO₃)₂·6H₂O (200 mg) and CTAB (5 mg) were mixed with the GO suspension (10 mL, 4.5 mg/L) by stirring for 50 min to allow the uniform adsorption of Zn²⁺ ions to the surface of GO through the electrostatic interaction. Then, the 2-methylimidazole (40 mL, 2.825 g) was added to coordinate with Zn²⁺ ions and reacted for 30 min to form the core of ZIF-8@GO. The final products were treated through centrifuging, washing with anhydrous ethanol and methanol for several times, and denoted as ZIF-8@GO. The fabrication procedure of ZIF-67@GO composite is similar to that of preparing ZIF-8@GO composite but using Co(NO₃)₂·6H₂O as a metal salt.

Subsequently, the prepared ZIF-8@GO (3.9 g) was used as the core materials and dissolved in 23 mL methanol containing CoCl₂·6H₂O (190 mg) and CTAB (3 mg) by stirring for 5 min, the 3 mL methanol solution of 2-methylimidazole (895 mg) was added into above-mixed solution by stirring for 4 h at room temperature to fabricate the core-shell ZIF-67@ZIF-8@GO templates, the obtained products were collected via centrifugation and washed with methanol for several times, then air-dried for overnight and denoted as ZIF-67@ZIF-8@GO. The fabrication procedure of ZIF-67@ZIF-8 is also similar to that of making ZIF-67@ZIF-8@GO but using bare ZIF-8 seeds instead of ZIF-8@GO seeds.

3. Characterization of catalysts

The surface morphologies, sizes, and elemental compositions of catalysts were analyzed by the field emission scanning electron microscope (FE-SEM, Apreo S HiVac FEI) and high-resolution transmission electron microscope (HR-TEM, Tecnai G2 F20 S-TWIN) embedded with energy-dispersive X-ray spectroscopy (EDX). The X-ray diffraction (XRD, Ultima IV (Rigaku, Japan)) was used to analyze crystal structures of catalysts with Cu K α radiation for a 2 θ range of 20-80°. The thermal behavior was analyzed by thermogravimetry (TG, Netzsch STA 209F3) under N₂ atmosphere with a heating rate of 10 °C·min⁻¹ from 50 °C to 900 °C. The Raman spectra were performed by a LabRAM HR confocal Raman system with 633 nm diode laser excitation at room temperature. The N₂ adsorption/desorption isotherms were obtained by the Ankersmid Belsorp-Max and based on the Brunauer-Emmett-Teller (BET) to assess the surface area and pore size distribution, respectively. The surface elemental composition and all binding energies were measured by X-ray photoelectron spectroscopy (XPS, ESCAL 250) with Al K α monochromatic X-ray sources. The electron paramagnetic resonance (EPR, Bruker EMXplus) measurements of radicals trapped by DMPO were recorded on with a center field at 3500 G, and a sweep width of 140 G.

4. Supporting data and results



Fig. S1 The SEM images of (a) ZIF-8@GO, (b) ZIF-67@GO, and (c) ZIF-67@ZIF-8.



Fig. S2 The XRD patterns of different precursors.



Fig. S3 The SEM images of (a) C-ZIF-8@GO-900, (b) C-ZIF-67@GO-900, and (c) C-ZIF-67@ZIF-8-900. (d, e) TEM images of C-ZIF-67@ZIF-8-900 and (f) corresponding size distributions of Co nanoparticles in (d).



Fig. S4 The SEM images, TEM images, and corresponding size distributions of Co nanoparticles of (a, d, g) C-ZIF-67@ZIF-8@GO-800, (b, e, h) C-ZIF-67@ZIF-8@GO-900, and (c, f, i) C-ZIF-67@ZIF-8@GO-1000, respectively.



Fig. S5 The TEM images from different random CNTs to reveal the hollow part of multiwalled CNT nanostructures.



Fig. S6 The EDX spectrum of C-ZIF-67@ZIF-8@GO-900.



Fig. S7 The Raman spectra of different precursors after carbonization.

Table S1. The atomic ratios of the C, Co, and N species and weight ratios of the Co species in the ZIF-67@ZIF-8@GO obtained at different carbonization temperatures. The higher C ratio in the C-ZIF-67@ZIF-8@GO-900 is supposed to be caused by the in-situ growth of CNT structures.

Samples	C (At.%)	Co (At.%)	Co (Wt.%)	N (At.%)
C-ZIF-67@ZIF-8@GO-800	84.14	2.25	9.81	5.94
C-ZIF-67@ZIF-8@GO-900	88.61	1.48	6.72	4.91
C-ZIF-67@ZIF-8@GO-1000	87.24	1.53	6.90	5.07



Fig. S8 High-resolution C1s XPS spectra of ZIF-67@ZIF-8@GO obtained at different carbonization temperatures.



Fig. S9 The kinetic linear fitting and k_{obs} of different catalysts for the removal of BPA.



Fig. S10 The (a) kinetic linear fitting and (b) k_{obs} of C-ZIF-67@ZIF-8@GO obtained at different carbonization temperatures for the removal of BPA.

References:

- 1. X. Fan, F. Yang, J. Huang, Y. Yang, C. Nie, W. Zhao, L. Ma, C. Cheng, C. Zhao and R. Haag, *Nano Lett.*, 2019, **19**, 5885-5896.
- 2. Z. L. Chen, R. B. Wu, Y. Liu, Y. Ha, Y. H. Guo, D. L. Sun, M. Liu and F. Fang, *Adv. Mater.*, 2018, **30**, 1802011.