Supporting Information

Organic-Inorganic Hybrids of Fe-Co Polyphenolic Networks Wrapped Fe₃O₄ Nanocatalysts for Significantly Enhanced Oxygen Evolution

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Materials and Methods

Chemicals and materials: Iron (III) chloride hexahydrate (AR, ≥98%), Cobalt(II) nitrate hexahydrate (AR, ≥98%), anhydrous sodium acetate (AR, ≥98%), 2-methylimidazole (AR, ≥98%), tannic acid (AR, ≥98%), iridium oxide (AR, ≥98%) were purchased from Aladdin, China. Perfluorosulfonic acid-PTEE copolymer (Nafion solution, 5%wt) was from Alfa Aesar. All the reagents were used as received without further purification. Nanopure water purified through a Millipore water purification system was used for all experiments.

Synthesis of Fe₃O₄ colloidal particles: In a typical protocol, 1.9 g of FeCl₃·6H₂O and 5.6 g of CH₃COONa were dissolved in 70 ml of ethylene glycol. The solution was transferred to a 50 ml Teflon-lined stainless steel autoclave container and reacted at 200 °C for 12 h. Afterwards the container was cooled to room temperature naturally and the produced solids were isolated from the solution via centrifugation at 5000 rpm for 10 min, and were washed with ethanol for 3 times and dried at 70 °C for 12 h.

Synthesis of ZIF-67@Fe₃O₄ composite: 70 mg of the as-synthesized Fe₃O₄ NPs were dispersed in 25 ml methanol by sonication for 15 min. 330 mg of 2-methylimidazole was then dissolved in this solution and form the solution A. In a separate glass vial, 300 mg of Co(NO₃)₂·6H₂O was dissolved in 25 ml methanol to form the solution B. Solutions B was slowly injected to solution A and the remaining solution was stirred for 5 min, and ZIF-67@Fe₃O₄ particles were obtained after aging at room temperature for 24 h. The produced solids were collected by centrifugation at 5000 rpm for 10 min and washed with ethanol 3 times, and dried at 70 °C for 12 h. These experiments were all performed in air.
Formation of CoFe-phenolic networks@Fe₃O₄ Core-Shell Structure: 20 mg of the as-synthesized ZIF-67@Fe₃O₄ polyhedrons were placed in 50 ml tannic acid solution (5 g/l, dissolved in methanol) and were aged under stirring for 30 min. Hybrid nanoparticles with core-shell structure were formed during this process and were collected by centrifugation at 5000 rpm for 10 min and washed with ethanol 3 times, and dried at 70 °C for 12 h. These experiments were all performed in air.

Materials characterization: Powder XRD patterns were collected on an Empyrean X-ray diffractometer equipped with a Cu Ka radiation source (λ = 0.154178 nm). XPS measurements were performed using a Thermo Fischer ESCALAB 250Xi spectrophotometer with the excitation source of monochromatic aluminum. The structure and composition of the samples were studied by scanning electron microscopy (Merlin Compact SEM operated at 10-20 kV) and transmission electron microscopy (Tecnai G2 F30 TEM operated at 200 kV), along with energy dispersive X-ray (EDX) spectroscopy for both SEM and TEM. Fourier transform infrared spectroscopy (FTIR) spectra were acquired using a Nexus system. UV-vis absorption spectra were recorded using a METASH Model 8000 UV-vis spectrophotometer. The electrical conductivity was measured at room temperature using a Hall Effect Measurement System equipped with a four-point probe with the pattern of 5 mm × 5 mm (SwimHALL 8800, Chinese Taipei). Samples were prepared by compressing the powders at 15 MPa using a die-set to thin discs. The BET surface area and pore size distribution were investigated by a Micromeritics TriStar II 3020 analyzer.

Electrochemical measurements: Linear sweep voltammetry (LSV), chronopotentiometric measurements and cyclic voltammetry (CV) measurements were carried out in 1 M KOH (pH 13.7) using a potentiostat (CHI660D, CH Instruments). All measurements were performed in a
three-electrode configuration at room temperature, using a saturated calomel electrode as the reference electrode and a graphite rod as the counter electrode. The working electrode was a glassy carbon electrode cased with the 20 µl of the catalyst ink, which was prepared by dispersing 5.0 mg catalyst in 1 ml methanol containing 0.1% Nafion and was sonicated for 2 h to form a homogeneous mixture. The catalyst loading was about 1.4 mg cm\(^{-2}\). All potential measurements were converted to the RHE based on the following formula:

\[ E_{\text{RHE}} = E_{\text{SCE}} + 0.242 + 0.059 \, \text{pH} \] (in volts).

The overpotentials for oxygen evolution reaction were calculated according to the following formula:

\[ \eta = E_{\text{RHE}} - 1.23 \, \text{V} \]

The electrochemical double-layer capacitance was determined from CV curves measured in the potential range according to the following equation:

\[ C_{\text{dl}} = \frac{I_c}{\nu} \]

where \( C_{\text{dl}} \), \( I_c \), and \( \nu \) are the double-layer capacitance (mF cm\(^{-2}\)), charging current (mA cm\(^{-2}\)), and scan rate (mV s\(^{-1}\)), respectively. For LSV, the overpotential was swept from 1.0 to 1.7 V (vs. RHE) at a scan rate of 5 mVs\(^{-1}\). EIS was recorded at 1.5 V (vs. RHE) using an AC voltage amplitude of 2 mV and a quiet time of 5 s. The frequency range investigated was from 0.1 Hz to 100 kHz. Chronopotentiometry was used to evaluate the catalytic stability; the current densities were set to 10 mA cm\(^{-2}\) and 50 mA cm\(^{-2}\), respectively, and the potential was limited to 1.4 - 2.0 V (vs. RHE).

Figure S1: High resolution SEM image of as-synthesized Fe\(_3\)O\(_4\) nanoparticles. These particles have diameters of approximately 200 nm and appeared as agglomerates of primary particles with
few nanometers.

Figure S2: a) Comparison of the conductivity of Fe$_3$O$_4$, ZIF-67@Fe$_3$O$_4$, MPN@Fe$_3$O$_4$ NPs and ZIF-67; b) nitrogen adsorption/desorption isotherms and (c) BJH pore size distribution curves of MPN@Fe$_3$O$_4$, ZIF-67@Fe$_3$O$_4$, Fe$_3$O$_4$ NPs and ZIF-67.

Figure S3. TEM image of the MPN@Fe$_3$O$_4$ nanoparticles. The presence of thin MPN shells and Fe/Co cations were clearly resolved for each particle.
Figure S4: Structural characterization of FeMPN@Fe₃O₄ prepared by dispersing 20 mg Fe₃O₄ and 250 mg tannic acid in 50 ml methanol. The reaction time was 30 min. The results show formation of thin Fe-MPN layers (FT-IR and SEM) and the reduced crystallinity (XRD) after reaction with TA.

Figure S5: UV-Vis absorption spectrum of the aqueous solution of FeCl₃/CoCl₃ and tannic acid (Fe³⁺: Co³⁺: TA=1:1:6, pH=2)

Figure S6: Comparison of the FT-IR spectra of MPN@Fe₃O₄ hybrid catalyst, ZIF-67@Fe₃O₄, Fe₃O₄, 2-methylimidazolate and tannic acid.
Figure S7: a) XPS survey spectra and (b) elemental concentration of ZIF-67@Fe$_3$O$_4$ and MPN@Fe$_3$O$_4$ hybrid particles. High-resolution XPS spectra of c) Fe 2p and d) Co 2p in MPN@Fe$_3$O$_4$

Figure S8: Comparison of the hybrid catalysts presented in this work with representative catalysts described in the literature. The comparison was based on their overpotential at the benchmark current density of 10 mA cm$^{-2}$. 
Figure S9: CV curves of a) MPN@Fe$_3$O$_4$, c) ZIF-67@Fe$_3$O$_4$ and e) Fe$_3$O$_4$ particles acquired at scan rates from 20 to 100 mV s$^{-1}$ in 1.0 M KOH; b), d), and f) are the relationship between the differences in current density vs scan rate from a), c) and e), respectively.

Figure S10: EIS of MPN@Fe$_3$O$_4$, ZIF-67@Fe$_3$O$_4$, Fe$_3$O$_4$ NPs and IrO$_2$. 
Figure S11: LSV and Tafel plot of MPN@Fe$_3$O$_4$ electrocatalysts prepared by varying the reaction time between tannic acid and ZIF-67@Fe$_3$O$_4$ as specified.
Figure S12. CV curves (left) and current-scan rate relationship (right) of MPN@Fe$_3$O$_4$ catalysts prepared by varying the reaction time between tannic acid and ZIF-67@Fe$_3$O$_4$. 

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Figure S13: a) LSV and b) Tafel plot of pristine Fe$_3$O$_4$ and FeMPN@Fe$_3$O$_4$. The presence of FeMPN significantly improve the OER activity of Fe$_3$O$_4$.

Figure S14: a) CV curves and b) current-scan rate relationship of FeMPN@Fe$_3$O$_4$ electrocatalysts.
Figure S15: a) LSV and b) Tafel plot of pristine ZIF-67 and CoMPN@ZIF-67. The presence of CoMPN significantly improve the OER activity of ZIF-67. C) XRD pattern and SEM images, and d) FT-IR spectra of ZIF-67 and CoMPN@ZIF-67, the presence of thin organic MPN layers were evident.

Figure S16: left) CV curves and right) current-scan rate relationship of a-b) ZIF-67 and c-d)
CoMPN@ZIF-67 electrocatalysts.

Figure S17: LSV of MPN@Fe$_3$O$_4$ hybrid catalysts before and after the durability test.

Figure S18: a) SEM image and b) FT-IR spectrum of MPN@Fe$_3$O$_4$ particles after the stability tests. No obvious morphological/spectral changes were observed.
Figure S19: a) XRD pattern and high resolution XPS spectra of b) Fe 2p$_{3/2}$, c) Co 2p$_{3/2}$, and d) O 1s of MPN@Fe$_3$O$_4$ after durability test.

Reference