

Supporting Information

Monodisperse $M_xFe_{3-x}O_4$ ($M = Fe, Cu, Co, Mn$) Nanoparticles and Their Electrocatalysis for Oxygen Reduction Reaction

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Experimental Section

Chemicals and Materials. $Fe(acac)_3$, $Cu(acac)_2$, $Co(acac)_2$, $Mn(acac)_2$ ($acac$ = acetylacetonate), oleylamine (OAm, >70%), oleic acid (OA), benzyl ether (BE, >98%), 1,2-tetradecanediol, hexane, ethanol and Nafion (5%) were all purchased from Sigma Aldrich. C-Pt catalyst (20% mass loading with Pt particle diameter of 2.5-3.5 nm) was obtained from Fuel Cell Store.

Instrumentation. TEM and HRTEM samples were prepared by depositing a drop of diluted nanoparticle (NP) dispersion in hexane on amorphous carbon coated copper grids. TEM images were obtained from a Philips CM 20 operating at 200 kV. High-resolution TEM (HRTEM) images were obtained from a JEOL 2010 with an

accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were collected from a Bruker AXS D8-Advanced diffractometer with Cu K α radiation (λ = 1.5418 Å). Metal components within NPs were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a JY2000 Ultrace ICP Atomic Emission Spectrometer equipped with a JY AS 421 autosampler and 2400g/mm holographic grating, and the mass ratios were converted into atomic ratios. Electrochemical measurements were carried out on a Autolab potentiostat from Metrohm Instrument Company (Autolab 302). A three-electrode system consisting of a glassy carbon (GC) working electrode (5-mm in diameter), an Ag/AgCl reference electrode (in 4 M KCl) and a platinum wire counter electrode, was used. Magnetic properties were measured on a Lakeshore 7404 high sensitivity vibrating sample magnetometer (VSM) with fields up to 1.5 T.

Synthesis of $M_xFe_{3-x}O_4$ NPs. A solution of 25 ml BE, 0.96 ml OA, 1 ml OAm, 1.15 g 1,2-tetradecandiol and 1 mmol Fe(acac)₃ in a four-necked flask was heated to 120 °C under nitrogen flow and magnetic stirring and was kept at this temperature for 1 h. The solution was heated up to 210 °C at a rate of 8 °C/min and kept at this temperature for 2 h. Under a blanket of nitrogen atmosphere and at a slow heating rate (3 °C/min), the solution was further heated to 300 °C and kept at this temperature for 1 h. After cooled down to room temperature, the NPs were collected and washed by addition of ethanol (20 ml) and subsequent centrifugation at 10000 rpm for 8 min. The product was redispersed into hexane and precipitated out by addition of ethanol

and centrifugation to remove all residual impurities. Final product, 7 nm Fe₃O₄ NPs, was dispersed in hexane for further use.

Similarly, other M_xFe_{3-x}O₄ NPs with M = Cu, Co, or Mn were synthesized by adding 0.5 mmol Cu(acac)₂/Co(acac)₂/Mn(acac)₂ in the beginning of the reaction. Specifically, 5 nm Mn_xFe_{3-x}O₄ NPs with different x were synthesized by varying the amount of Mn(acac)₂, OA and OAm. To synthesize Mn_{0.4}Fe_{2.6}O₄ NPs, 0.35 mmol Mn(acac)₂, 1 ml OA and 1.1 ml OAm were added in the reaction mixture. To prepare MnFe₂O₄ NPs, 0.67 mmol Mn(acac)₂, 0.92 ml OA and 1 ml OAm were added. However, our efforts in preparing M_xFe_{3-x}O₄ with x > 1 failed. For example, when 1 mmol Mn(acac)₂ was used in the synthesis, we obtained Mn_{1.4}Fe_{1.6}O₄ NPs. But these NPs were irregular in shape and had an average size larger than 10 nm (**Figure S2**).

Catalyst Preparation. The as-synthesized NPs were mixed with Ketjen-300 J carbon at a weight ratio of 4:6 in 20 ml mixture of hexane and acetone (V/V=1:1) and sonicated for 1 h. The C-NPs were separated from the solvents by centrifugation and washed with hexane. The C-NPs were annealed in air at 165 °C for 12 h to remove the surfactant.¹ The C-NPs (both as-made C-NPs and commercial C-Pt) were suspended in a mixture of deionized water, isopropanol and Nafion (V/V/V=4/1/0.05) to form a catalyst ink (2 mg/ml) for electrochemistry measurements.

GC electrode was polished by 0.1 μm and 0.05 μm alumina powder and rinsed with deionized water, followed by sonication first in ethanol and then in deionized water. 20 μl catalyst ink was deposited on the GC working electrode and dried at ambient condition.

Electrochemical Measurements. Cyclic voltammograms (CVs) were obtained by scanning between 0.2 V to -0.8 V vs Ag/AgCl at a scan rate of 50 mV/s in N₂-saturated 0.1 M KOH solution. CVs were also obtained by scanning between 0 V to -0.8 V vs Ag/AgCl at a scan rate of 50 mV/s in O₂-saturated 0.1 M KOH solution. ORR polarization curves were obtained by linear sweep voltammetry scanning from 0.2 V to -0.8 V vs Ag/AgCl at a scan rate of 10 mV/s in O₂-saturated 0.1 M KOH with RDE at different rpms (400-2500 rpm). Chronoamperometric was performed to evaluate the catalyst durability at -0.3 V vs Ag/AgCl with the electrode rotating at 200 rpm in O₂-saturated 0.1 M KOH. The electron transfer number (n) was calculated from the slopes of the Koutecky-Levich plots² according to:

$$\frac{1}{I} = \frac{1}{I_L} + \frac{1}{I_K} = \frac{1}{I_K} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nAF C_{O_2} D_{O_2}^{2/3} \nu^{-1/6}$$

where I, I_K and I_L are measured current, kinetic current and diffusion-limiting current respectively, ω is the angular velocity, F is the Faraday constant (96485 C•mol⁻¹), A is the electrode surface area, C_{O₂} is the concentration of dissolved O₂ (1.2 × 10⁻⁶ mol•cm⁻³), D_{O₂} is the diffusion coefficient of O₂ (1.9 × 10⁻⁵ cm²•s⁻¹) and ν is kinetic viscosity of the electrolyte (0.01 cm²•s⁻¹).³ The constant 0.62 is applied when the rotation speed is expressed in radius per second (rad/s).²

References

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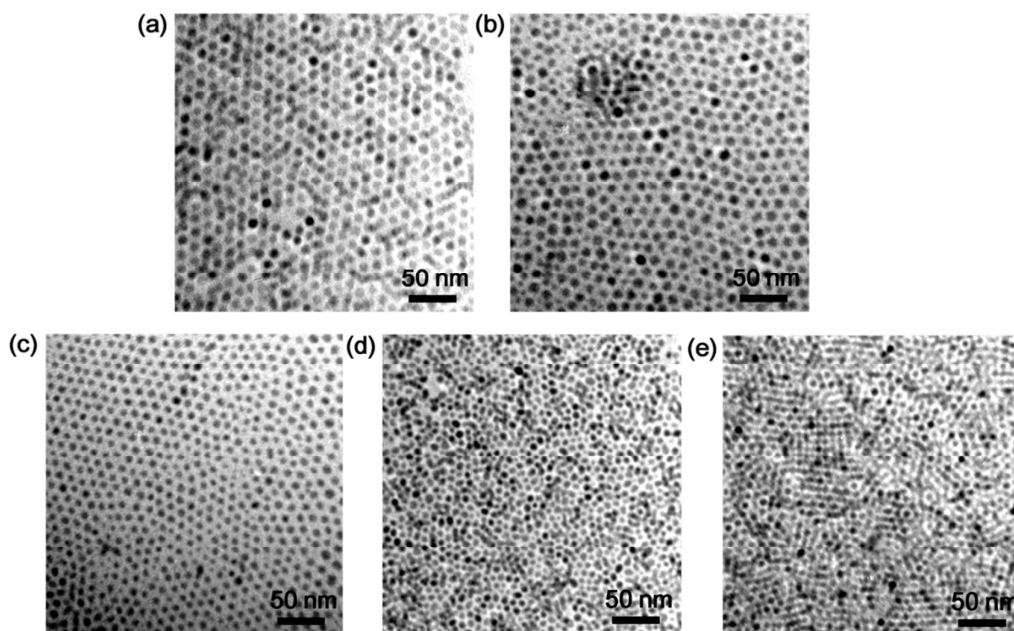


Figure S1. TEM images of the as-synthesized (a) 7 nm Fe_3O_4 , (b) 8 nm $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4$, (c) 5 nm $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ and (d) 5 nm $\text{Mn}_{0.4}\text{Fe}_{2.6}\text{O}_4$ NPs and (e) $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ NPs.

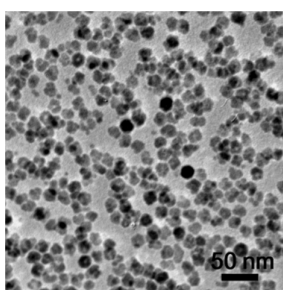


Figure S2. TEM image of as-synthesized $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$ NPs

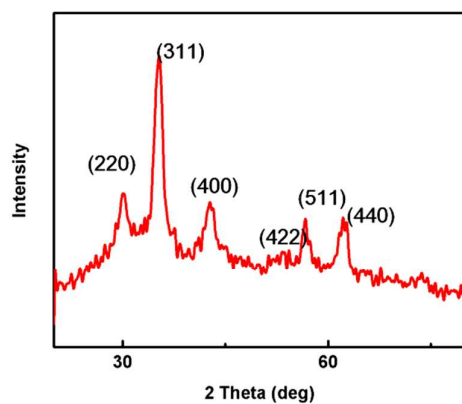


Figure S3. XRD pattern of the MnFe₂O₄ NPs.

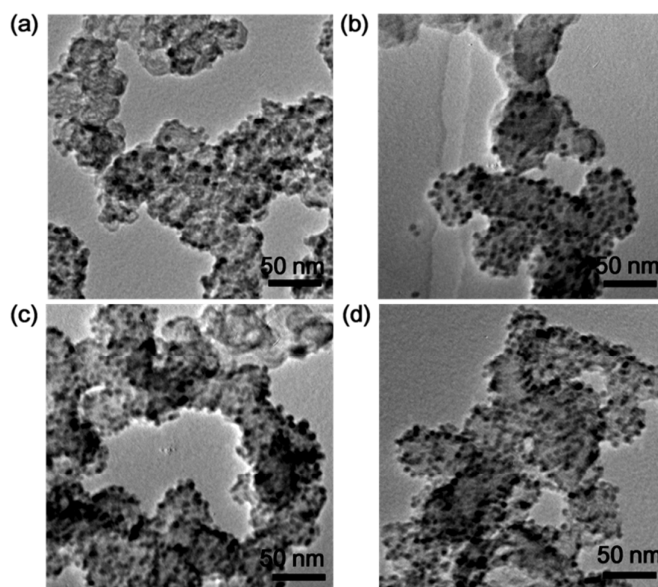


Figure S4. TEM images of (a) C-Fe₃O₄, (b) C-Cu_{0.7}Fe_{2.3}O₄, (c) C-Co_{0.8}Fe_{2.2}O₄, (d) C-Mn_{0.6}Fe_{2.4}O₄ NPs after air annealing at 165 °C for 12 h.

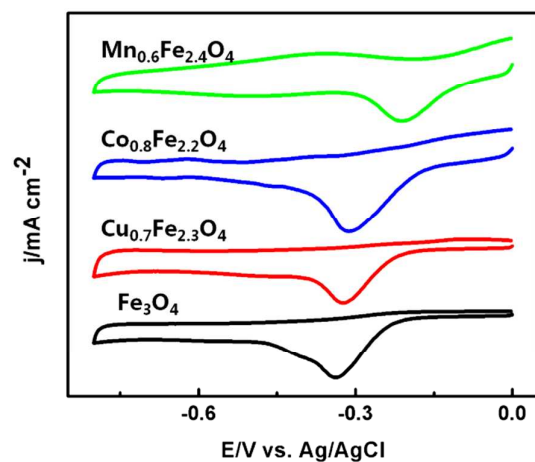


Figure S5. CV's of the C- Fe_3O_4 , C- $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4$, C- $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ and C- $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ NPs in O_2 -saturated 0.1 M KOH at a scan rate of 50 mV/s.

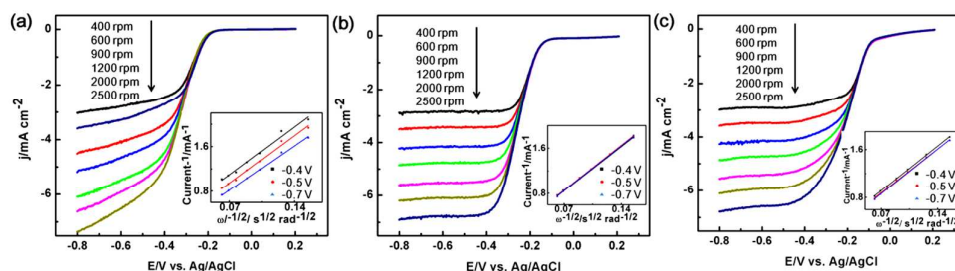


Figure S6. ORR polarization curves of (a) C- $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4$, (b) C- $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ and (c) C- $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ NPs at different rpm (400 rpm -2500 rpm) in O_2 -saturated 0.1 M KOH at a scan rate of 10 mV/s. **Insets:** Koutecky-Levich plots at different potentials (-0.4 V, -0.5 V and -0.7 V).

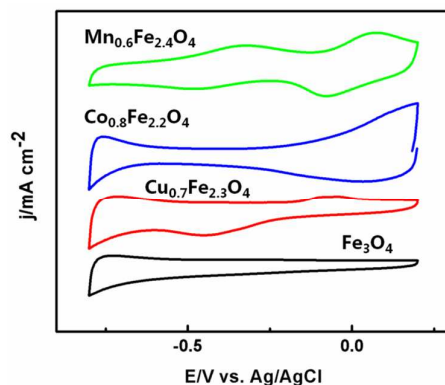


Figure S7. CV's of the C-Fe₃O₄, C-Cu_{0.7}Fe_{2.3}O₄, C-Co_{0.8}Fe_{2.2}O₄ and C-Mn_{0.6}Fe_{2.4}O₄ NPs in N₂-saturated 0.1 M KOH at a scan rate of 50 mV/s.