A facile synthesis of Fe_3C@mesoporous carbon nitride nanospheres with superior electrocatalytic activity

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1. Materials

Dopamine (DA), iron nitrate ($Fe(NO_3)_3$ $9H_2O$), ammonia aqueous solution (28%), copper(I) bromide (CuBr), trimethylamine (TEA), phenol, formalin (37% in water), Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) ($EO_{106}PO_{70}EO_{106}$, Pluronic F-127 with an average molecular weight of 12.6 kg/mol), monomethoxy poly(ethylene oxide) with molecular weight (M_n) of 5 kg/mol (PEO_{114}), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), 3-(trimethoxysiyl)propyl methacrylate (TMSPMA), anisole, dichloromethane (CH_2Cl_2), *n*-hexane and ethanol were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. Deionized water (High-Q, Inc. 103S Stills) with a resistivity of >10.0 MΩ was used in all experiments. All chemical reagents were used without further purification unless otherwise noted.

2. Synthesis of block copolymer of PEO-*b*-PTMSPMA

Amphiphilic BCP of PEO-*b*-PTMSPMA was prepared *via* atom transfer radical polymerization (ATRP) followed our previous report.[1] The macroinitiator of PEO_{114}-Br was synthesized according to our reported procedure.[2] Typically, CuBr (58 mg, 0.4 mmol), TMSPMA (10 g, 40.3 mmol), PEO_{114}-Br (1g, 0.2 mmol), PMDETA (0.167 mL, 0.8 mmol) and anisole (10 mL) were added into a 50 mL two-necked flask. The reaction mixture was degassed by three freeze-pump-thaw cycles and then filled with nitrogen. The flask was then placed in a pre-heated oil bath at 65 ^oC for 100 mins. After polymerization, the reaction was stopped by adding CH_2Cl_2 and the reaction mixture then cooled to room temperature. Then the mixture was passed through a silica column using CH_2Cl_2 as an eluent to remove the catalyst. The polymer solution was then concentrated and precipitated in cooled *n*-hexane three times. $M_{n,NMR}$ estimated from ^1H NMR was 73.9 kg mol^{-1}, giving the degree of polymerization for two blocks as, PEO_{114}-*b*-$PTMSPMA_{298}$.

From gel permeation chromatography (GPC) measurement, the polymer has a polydispersity index (PDI) of 1.28.

3. Synthesis of Fe_3C@*m*CN Catalysts

3.1 Formation of mCN nanospheres

In a typical experiment, 1 g of dopamine was dissolved in the 20 mL of ethanol, followed by the addition of 40 mL of water. Then, 500 mg of BCP of PEO-*b*-PTMSPMA in ethanol (20 mL) was added dropwise into the above solution under stirring. After further stirring for 30 mins, 2.5 mL of ammonia aqueous solution (28%) was injected into the solution to induce self-polymerization of dopamine. Continually stirring for 20 hrs, the as-made CAM@polydopamine (CAM@PDA) nanospheres were collected by washing and centrifugation with water and ethanol for three times, and dried at 60 ^{o}C overnight (See Figure S1a,b for details). The sample then was calcined under nitrogen atmosphere at 800 ^{o}C (See Figure S1c,d for details) and treated with 2 M of NaOH to remove the residual silica, to synthesize nitrogen-doped mesoporous carbon (*m*CN-800) nanospheres (See Figure S1e,f for details).

3.2 Synthesis of Fe_3C@mCN nanospheres

About 100 mg of as-made CAM@PDA nanospheres (see section 3.1 for details) were dissolved into 50 mL of ethanol, and sonicated for 30 mins. Then 50 mg of $Fe(NO_3)_3\ 9H_2O$ was added into the above solution. Then the mixture was stirred at room temperature until totally dry powders were obtained. After that the black powders were calcined under nitrogen atmosphere at elevated temperature (550-900 ^{o}C) to grow nanosized Fe_3C nanoparticles and nitrogen-doped graphitic carbon nanospheres. All samples then were treated with 2 M of NaOH to remove the residual silica, and washed three times with water. The final samples were dried at 60 ^{o}C overnight to form Fe_3C@ *m*CN nanospheres.

3.3 Synthesis of mCN-800@Fe_3C nanospheres

About 100 mg of *m*CN-800 nanospheres (see section 3.1 for details) were dissolved into ethanol, and sonicated for 30 mins. Then 20 mg of $Fe(NO_3)_3\ 9H_2O$ was added into the above solution. Then the mixture was stirred at room temperature until totally dry powders were obtained. After that the black powders were calcined under nitrogen atmosphere at 800 ^{o}C to obtain *m*CN-800@Fe_3C nanospheres (see Figure S5 for details).

4. Synthesis of Fe_3C@*m*C Catalysts

Mesoporous nitrogen-free carbon was prepared using previously reported method.[3] Typically, 1 g of F-127 was dissolved in 15 mL of water, and then 10 mL of resol precursor was added by stirring for 30 min. The obtained mixture was stirred at 70 ^{o}C for 2 h. After that, 50 mL of water was added to dilute the solution. The reaction was stirred for another 20 h. The mixture was then centrifuged to collect as-made carbon. After that, 100 mg of *m*C and 50 mg of $Fe(NO_3)_3$ $9H_2O$ were mixed in 50 mL of ethanol. Then the mixture was stirred at room temperature until dry powders were left. The powders were subsequently calcined under nitrogen at 800 ^{o}C to obtain Fe_3C@*m*C-800.

5. ORR evaluation

The electrocatalytic activities of Fe_3C@*m*CN nanocatalysts and commercial Pt/C (20 wt% Pt on Vulcan XC72) towards ORR were recorded in O_2-saturated 0.1 M KOH solution with a rotating disc working electrode (RDE) configuration at room temperature. Pyrolytic graphite was used as a working electrode, and a standard calomel electrode (SCE) was used as reference electrode. Typically, an ink of the nanocatalyst was prepared by mixing 2 mg of catalysts with 1 mL of water/EtOH (4:1). After sonication for 15 min, 25 µL of Nafion solution was further mixed and sonicated for 30 min. Then 10 µL of the above-prepared solution was dropped on the working electrode and dried before use. The same procedure was used with the commercial Pt/C, but without the addition of carbon black.

The number of electrons transferred (n) was calculated according to the Koutecky-Levich (K-L) equation by rotating the electrode at different rates:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k} \qquad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \qquad (2)$$

$$J_k = nFkC_0 \qquad (3)$$

where j is the measured current density, j_k is the kinetic current, j_L is the diffusion limiting current, respectively. ω is the rotation speed of the electrode in rad/s, k is the electron transfer rate constant, B is the reciprocal of the slope of the K-L plots, F is the Faraday constant (96485 C/mol), C_0 is the saturated concentration of oxygen in 0.1 M KOH (1.2×10^{-6} mol/cm^3), D_0 is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2/s), and v is the kinematic viscosity of the electrolyte (0.01 cm^2/s).

6. Characterizations

Scanning electron microscope (SEM) images of the nanocatalysts were recorded using an FEI Nova NanoSEM 450 with an accelerating voltage of 10 kV and a beam current of 10 mA. SEM samples were prepared by casting the suspension of the materials on silicon wafers. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) studies were carried out using a JEOL 2010 transmission electron microscope with an accelerating voltage of 200 kV. Scanning TEM (STEM) mapping and high angle annular dark-field scanning TEM (HAADF-STEM) were performed using a Talos F200X Atomic Resolution Analytical Microscope. TEM and STEM samples were prepared by casting a suspension of the materials on a carbon coated copper grid (300 mesh). The wide-angle X-ray diffraction (WXRD) patterns were recorded using a Rigaku Ultima IV diffractometer (Cu Kα radiation, λ=1.5406 Å) with an operating voltage of 40 kV and a current of 44 mA. WXRD were collected over a 2θ range of $10\sim85^{o}$ with a continuous scan rate of 1^{o} min^{-1}. The Brunauer-Emmett-Teller (BET) surface areas of catalysts were measured using a Quantachrome Autosorb-1-C automated N_2 gas adsorption system. The X-ray photoelectron spectroscopy (XPS) experiments were recorded on a PHI model 590 spectrometer with multi-probes using Al Kα (λ = 1486.6 eV) as the radiation source. The XPS samples were prepared on carbon tape using adhesive copper tape struck to a sample stage placed in the chamber. GPC measurements were performed using a Waters GPC-1 (1515 HPLC Pump and Waters 717Plus Autoinjector) equipped with a Varian 380-LC evaporative light scattering detector and a Waters 2487 dual absorbance detector, three Jordi Gel fluorinated DVB columns (1-100 K, 2-10 K and 1-500 Å). The molecular weight was calibrated using standard polystyrene samples. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance 300 MHz spectrometer. Elemental analysis (C and N) of the catalysts was measured using a PerkinElmer elemental analyzer (NA 1500) equipped with a VARIO micro software.

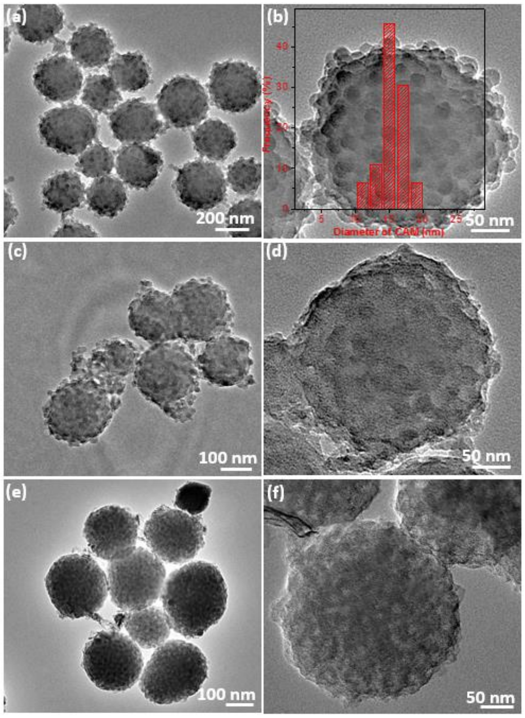
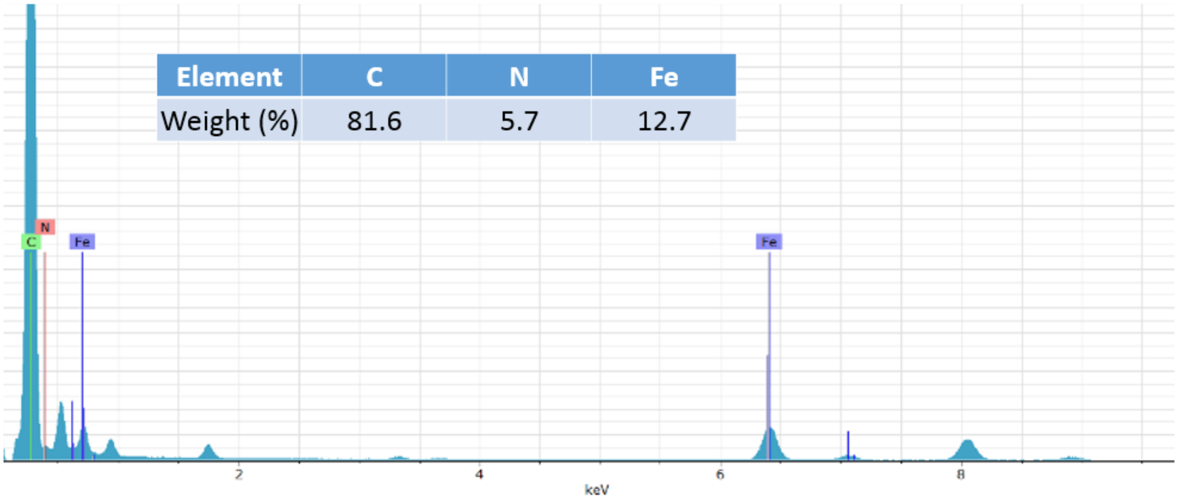


Figure S1. Nanostructures of CAM@PDA and *m*CN-800 nanospheres. TEM images of as-made CAM@PDA (a,b), calcined CAM@PDA (c,d) and *m*CN-800 (e,f). The insert in (b) is the size distribution of CAMs.



Element	C	N	Fe
Weight (%)	81.6	5.7	12.7

Figure S2. STEM-EDX spectra and corresponding elemental compositions (inserted) of Fe_3C@*m*CN-800.

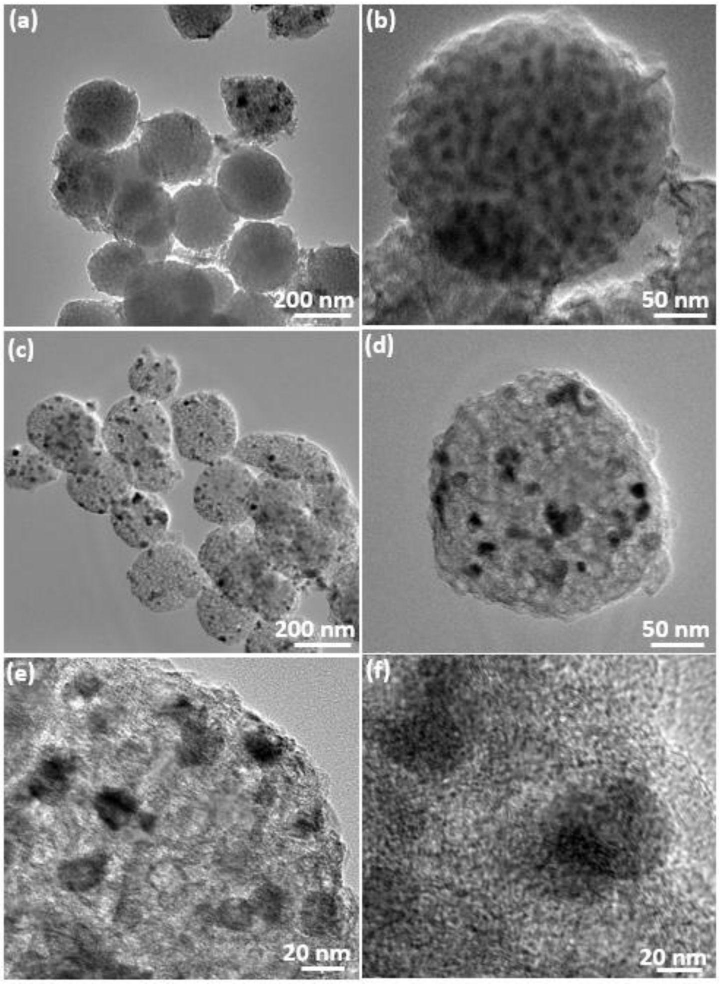


Figure S3. TEM images of Fe_3C@*m*CN-550 (a,b) and Fe_3C@*m*CN-700 (c-f). From TEM, it is obvious that no Fe_3C nanocrystals are presented in Fe_3C@*m*CN-550; while the Fe_3C@*m*CN-700 is not highly crystalline for both Fe_3C and carbon supports.

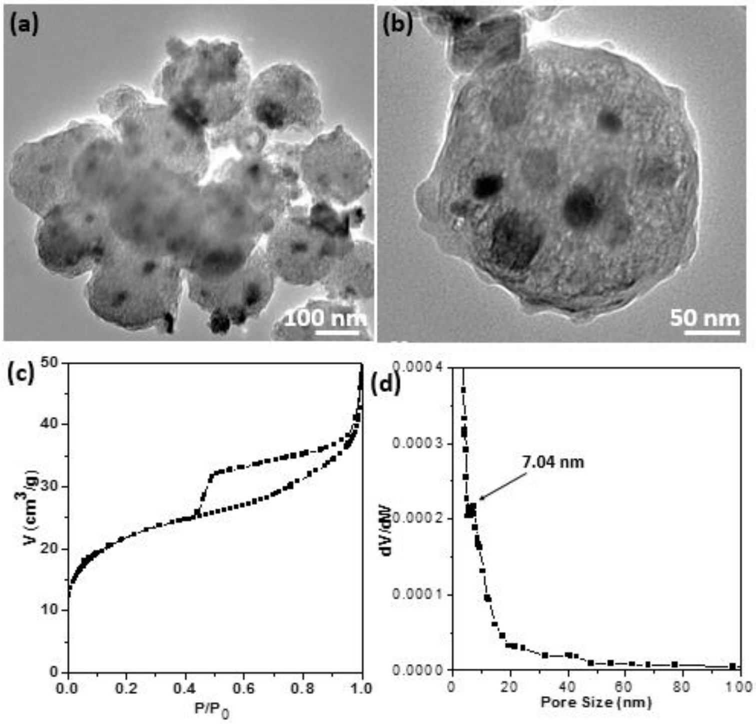


Figure S4. TEM images (a,b), N_2 sorption isotherms (c), pore size distribution (d) of Fe_3C@*m*CN-900.

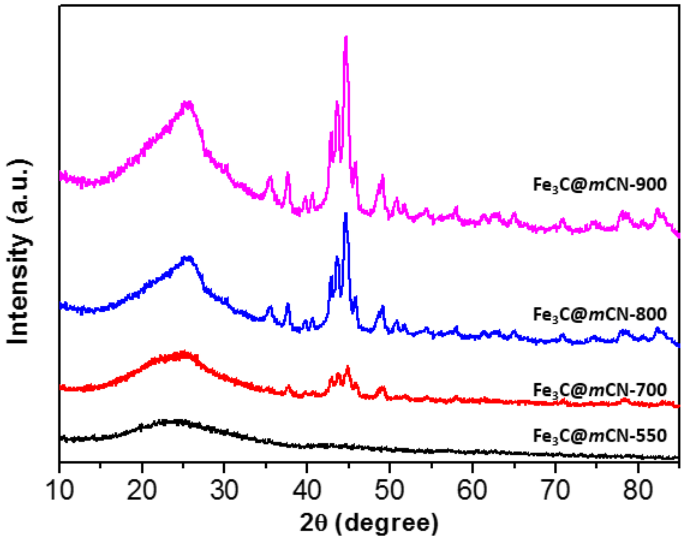


Figure S5. XRD patterns of Fe_3C@*m*CN catalysts obtained at various temperatures.

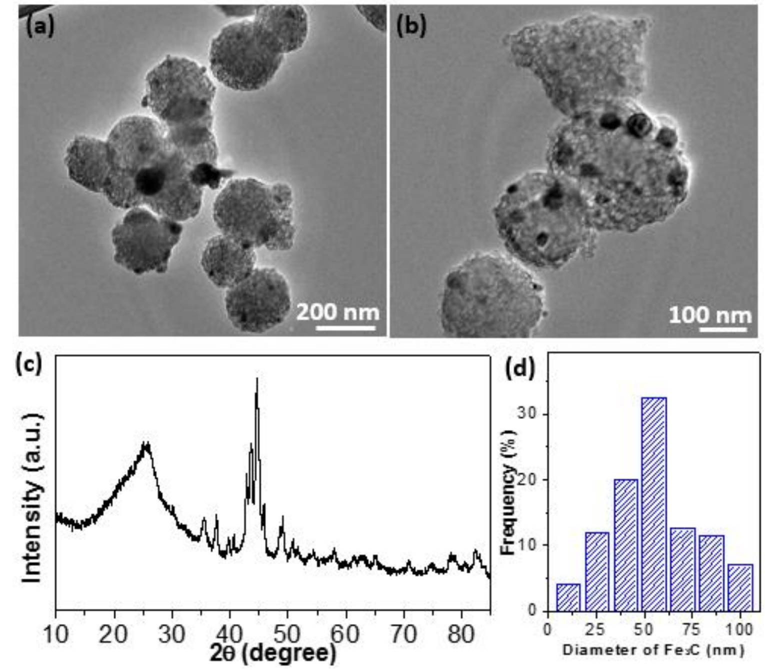


Figure S6. TEM images (a,b), XRD pattern and (c) Fe_3C size distribution (d) of *m*CN-800@Fe_3C. The post loading of ferric ions resulted in the migration of Fe_3C nanocrystals to the surface of *m*CN nanospheres.

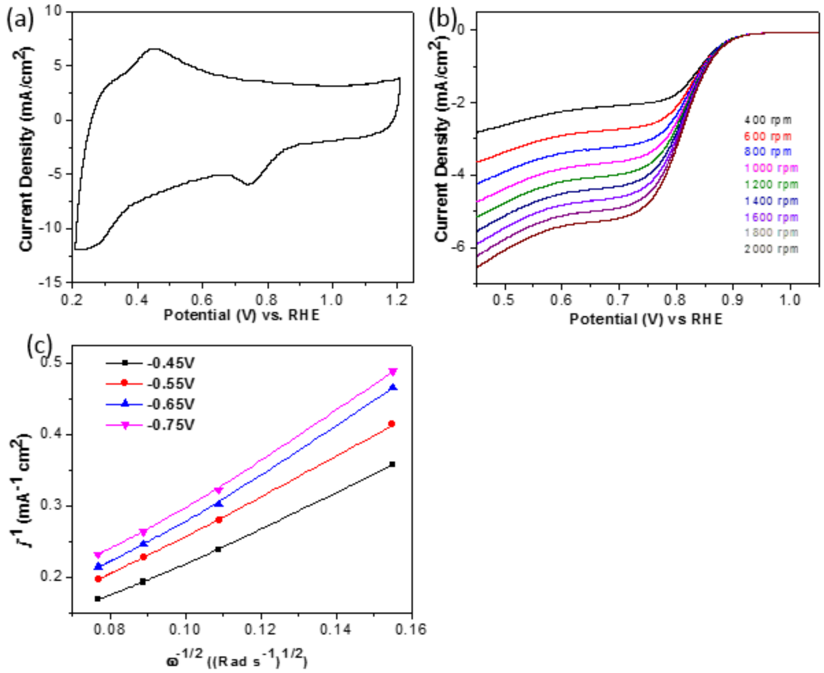


Figure S7. ORR activities of Fe_3C@*m*CN-800: (a) Cyclic voltammetry scan, (b) LSV curves at various rotation speeds, (c) K-L plots at different potentials.

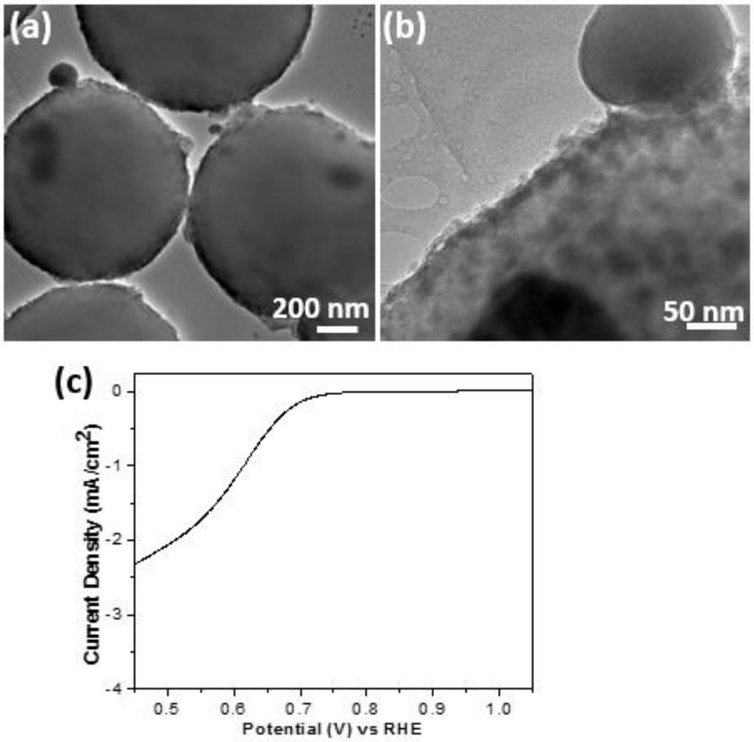


Figure S8. (a,b) TEM images and ORR activity of Fe_3C@*m*C-800. Much larger Fe_3C particles with a diameter range from 50-200 nm were obtained.

Table S1. Summary of physical properties and ORR activities of Pt/C and Fe_3C@*m*CN electrocatalysts.

Catalysts	**Surface Area (m^2 g^{-1})** [a]	**Size of Fe_3C (nm)** [b]	**E_0 (V)** [c]	**$E_{1/2}$ (V)** [c]	**$E_{j = -3\ mA/cm2}$ (V)** [d]
Pt/C	68-115	--	0.91	0.81	0.79
*m*CN	225	--	0.80	0.71	--
Fe_3C@*m*CN-700	--	5-15	0.84	0.72	0.60
Fe_3C@*m*CN-800	232	10-30	0.90	0.81	0.80
Fe_3C@*m*CN-900	76	10-50	0.90	0.80	0.76
*m*CN-800@ Fe_3C	--	20-100	0.88	0.77	0.72
Fe_3C@*m*C-800	--	50-200	0.70	0.60	--

[a] The surface area was measured by BET. The surface area of Pt/C was obtained from Ref S4.[4] [b] The size of Fe_3C nanocrystals was obtained from TEM. [c] The potentials were obtained from LSV curves collected on the RDEs at a rotation rate of 1600 rpm. E_0 is the onset potential and $E_{1/2}$ is the half-wave potential. [d] Potentials were obtained at a current density of -3 mA/cm^2.

Supporting References

1. B. Liu, Z. Luo, A. Federico, W. Song, S. L. Suib and J. He, *Chem. Mater.*, 2015, **27**, 6173.
2. W. Li, C.-H. Kuo, I. Kanyo, S. Thanneeru and J. He, *Macromolecules*, 2014, **47**, 5932.
3. Y. Fang, D. Gu, Y. Zou, Z. Wu, F. Li, R. Che, Y. Deng, B. Tu and D. Zhao, *Angew. Chem. Int. Ed.*, 2010, **49**, 7987.
4. A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini and L. Giorgi, *J. Power Sources*, 2002, **105**, 13.