

# Supporting Information

## Boron-doped carbon/iron nanocomposites as efficient oxygen reduction electrocatalysts derived from carbon dioxide

Junshe Zhang, Ayeong Byeon, J. W. Lee<sup>a\*</sup>

<sup>a</sup>Department of Chemical and Biomolecular Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon, 305-701, Korea.

\*Corresponding author: [jaewlee@kaist.ac.kr](mailto:jaewlee@kaist.ac.kr); Fax: +82-42-350-3910; Tel: +82-42-350-3940

### Experimental section

**Materials.** Argon (Ar) with a purity of > 99.9% and carbon dioxide (CO<sub>2</sub>) with a purity of > 99.8 % were purchased from Deokyang Co. LTD. Oxygen with a purity of > 99.995 % was supplied by Deokyang Co. LTD. Iron (II) chloride hydrate (FeCl<sub>2</sub>xH<sub>2</sub>O) with a purity of 99 % was supplied by Alfa Aesar. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) with a purity of 99.99 % was purchased from Fluke. Sodium borohydride (NaBH<sub>4</sub>) with a purity of > 99 % was obtained from Fluka. Methanol with a purity of 99.8 % was purchased from Merck KGaA. Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) with a purity of 99.9 % and sodium hydroxide (NaOH) with a purity of > 99 % were acquired from Fisher Scientific. Nafion® 117 solution (~5 wt. % in a mixture of lower aliphatic alcohols and water), and Pt/carbon (20 wt. %) were supplied by Sigma-Aldrich. All chemicals were used as received without further purification. Deionized (D.I.) water was produced in our lab with a resistivity of 18 MΩ cm<sup>-1</sup>.

**Fe precursor synthesis.** Fe precursor was synthesized by slowly adding 50 cm<sup>3</sup> sodium carbonate solution (0.1683 g/cm<sup>3</sup>) to 50 cm<sup>3</sup> FeCl<sub>2</sub> solution (0.1672 g/cm<sup>3</sup>) in a 200 cm<sup>3</sup> glass beaker at room temperature. The resultant suspension was continuously agitated during the addition, and the suspension was aged in open air at room temperature overnight. After the particles precipitate, the supernatant was decanted, followed by adding 150 cm<sup>3</sup> D.I. water, and a suspension of fine particles formed. The above washing procedure was repeated ten times to remove sodium and chloride ions. Finally, the suspension was filtered and the cake was kept in the open air at room temperature for several hours and subsequently dried in an oven at ca. 120 °C overnight. The Fe precursor consists of magnetite (Fe<sub>3</sub>O<sub>4</sub>, PDF #19-0629) and goethite (FeOOH, PDF #29-0713) as main crystalline phases as identified from the XRD spectrum (Figure S9).

**Preparation of boron-doped carbon/iron composites.** After loading ca. 4.4204 g NaBH<sub>4</sub> and 0.4414 g Fe precursor mixture to a 20 cm<sup>3</sup> alumina crucible boat (McDanel Advanced Ceramic Technologies LLC), and the boat was then put into a horizontal quartz tube (Ø 25 mm) mounted inside a furnace (GSL1100X, MTI Co.). After that, the quartz tube was heated to 500 °C from room temperature in 100 min, followed by maintaining at this temperature for 2 h, and finally cooled down to room temperature under 0.1 MPa CO<sub>2</sub> (gauge pressure) with a flowrate of 76 cm<sup>3</sup> STP min<sup>-1</sup>. The solid product was washed by hot D.I. water (80 °C) for ten times. After that, the solid product was dispersed in 200 cm<sup>3</sup> D.I. water, resulting in a suspension of fine particles. The suspension was filtered after one day, and then the cake was washed by ethanol, followed by dispersing it in 200 cm<sup>3</sup> ethanol. After one day, the suspension was filtered. The cake was kept in the open air at room temperature for several hours and subsequently dried overnight in an oven at ca.120 °C. The final solid product is referred to as FeBC050.

**Thermal annealing.** Around 0.12 g FeBC050 was loaded to the alumina crucible boat, which was then put into the horizontal quartz tube mounted inside the furnace. After that, the quartz tube was heated to 50 °C from room temperature in 10 min, followed by heating it to 850 °C (1050 °C) in 80 min (100 min), followed by maintaining at this temperature for 1 h, and cooled down to room temperature under 0.1 MPa Ar (gauge pressure) with a flowrate of 50 cm<sup>3</sup> STP min<sup>-1</sup>. The resultant products are referred to as FeBC850 (FeBC105).

**Physical and chemical characterization.** Powder X-ray diffraction (XRD) measurements were performed using a D/MAX-2500 X-ray (Rigaku) diffractometer for a 2θ range of 10 to 80 ° at a scan rate of 2° min<sup>-1</sup>, a step size of 0.02°, and using graphite monochromatic Cu Kα (λ=1.5406 Å) radiation with a nickel filter. The tube current was 300 mA with a tube voltage of 40 kV. Raman spectra were obtained by using an HR800 Horiba Jobin Yvon Dispersive-Raman system equipped with a CCD detector and an Olympus BX41 microscope with x 50 objective lens. Samples were placed on a cover glass and excited with 514.5 nm Ar ion laser radiation. The spectrum was obtained by multiple spectral bandpasses between 100 and 4000 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCA 2000 (Thermo VG Scientific) system equipped with Al Kα radiation (hν=1486.6 eV) as a probe under a chamber pressure of 5 × 10<sup>-10</sup> mbar. The analysis spot size was 400 μm. The spectra were referenced to C 1s peak at 284.5 eV, and the spectrum fitting was performed by using XPSPEAK 4.1. High resolution transmission electron microscope (TEM) images were obtained with a Tecnai G2 F30 (FEI) field emission microscope operating at 300 kV. The samples for TEM were prepared by drop-casting a suspension of carbon materials in ethanol on a copper grid and then drying them under ambient

conditions. Scanning electron microscope (SEM) images were taken with Magellan 400 (FEI) field emission microscope.

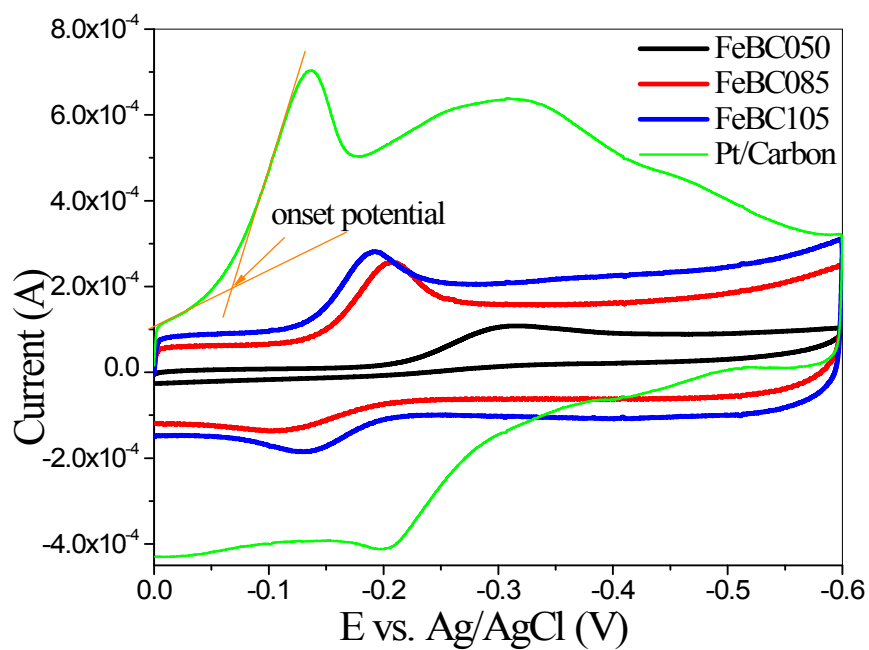
**Electrochemical measurements.** Electrochemical measurements, including cyclic voltammetry (CV) and linear sweeping voltammetry (LSV), were performed at room temperature on a RRDE-3A rotating ring disk electrode rotator (ALS Co.). The Ag/AgCl and platinum wire were served as reference and counter electrodes, respectively. The working electrodes are glassy carbon (GC) rotating disk electrodes. The potential at the working electrode was controlled through a CHI 600D analyzer (CH Instrument). To deposit the catalyst on the disk, inks were prepared by dispersing 5.0 mg catalyst in 1.0 mL solutions of water, methanol, and Nafion® with a volume ratio of 3:1:0.1 by ultrasonication for 10 min. For CV measurements, about 7.5  $\mu\text{L}$  of the catalyst ink was loaded onto the polished carbon disk electrode ( $\text{\O} 5$  mm, Pine Research Instruments), followed by leaving it in open air overnight. And, the working electrode was scanned at a rate of  $50 \text{ mV s}^{-1}$ . For LSV measurements, about 7.5  $\mu\text{L}$  of the catalyst ink was loaded onto the polished carbon disk electrode ( $\text{\O} 3$  mm, ALS Co.), followed by leaving it in open air overnight. And, the working electrode was scanned at a rate of  $10 \text{ mV s}^{-1}$  with different rotating speeds.

**Oxygen reduction reaction (ORR) activity.** The transferred electron number ( $n$ ) per oxygen molecule involved in ORR over FeBC105 was calculated from the Koutecky-Levich equation (Eq.1):<sup>1</sup>

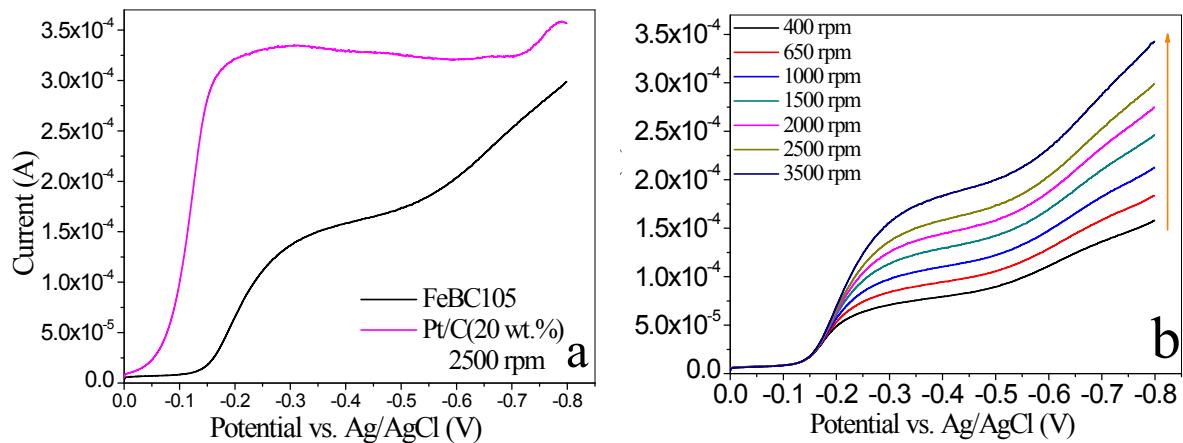
$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_d} = \frac{1}{nFAk(E)C_o^*} + \left( \frac{1}{0.62nFAD_o^{2/3}C_o^*v^{-1/6}} \right) \left( \frac{1}{\omega^{1/2}} \right) \quad (1)$$

$$\omega = 2\pi N / 60 \quad (2)$$

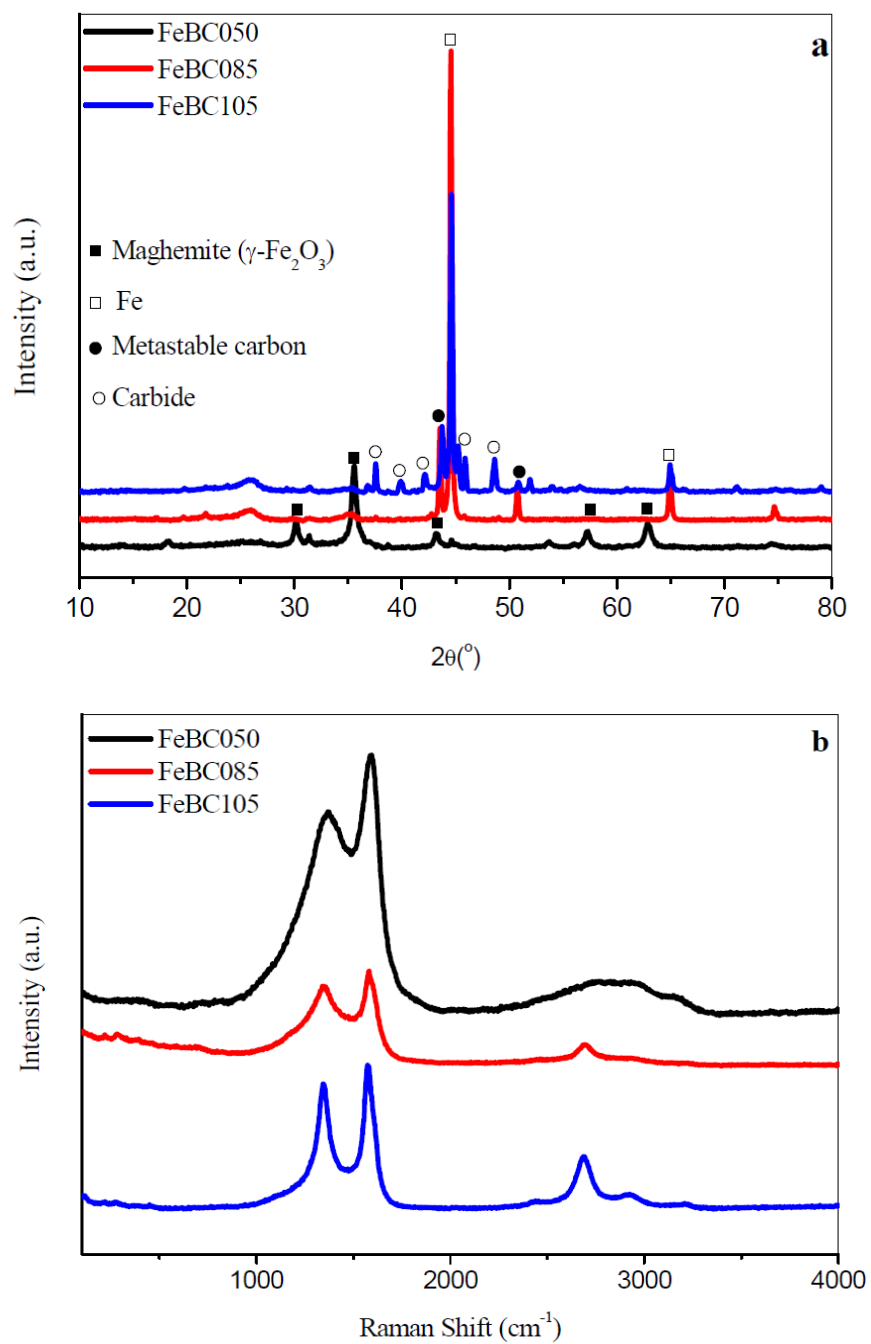
in which  $j$  is the measured current (A) with the charging current correction ( $7.05 \mu\text{A}$ ),  $j_K$  is the kinetic limiting current (A),  $j_d$  is the diffusion limiting current (A),  $n$  is the electron transfer number per oxygen molecule involved in ORR,  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $k(E)$  is the electron-transfer rate constant ( $\text{cm s}^{-1}$ ),  $E$  is the potential (V),  $A$  is the cross-section area of GC electrode ( $7.07 \times 10^{-2} \text{ cm}^2$ ),  $D_o$  is the diffusion coefficient of  $\text{O}_2$  in 1.0 M NaOH ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),<sup>2</sup>  $C_o^*$  is the bulk concentration of  $\text{O}_2$  in 1 M NaOH ( $9.698 \times 10^{-7} \text{ mol cm}^{-3}$ ),<sup>3</sup>  $v$  is the kinetic viscosity of 1 M NaOH ( $1.087 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ ),<sup>4</sup>  $\omega$  is angular velocity of the disk ( $\text{s}^{-1}$ ), and  $N$  is the rotating rate (rpm). According to Eq.1,  $n$  can be obtained from the slope of  $j^{-1}$  vs.  $N^{-1/2}$  plots.



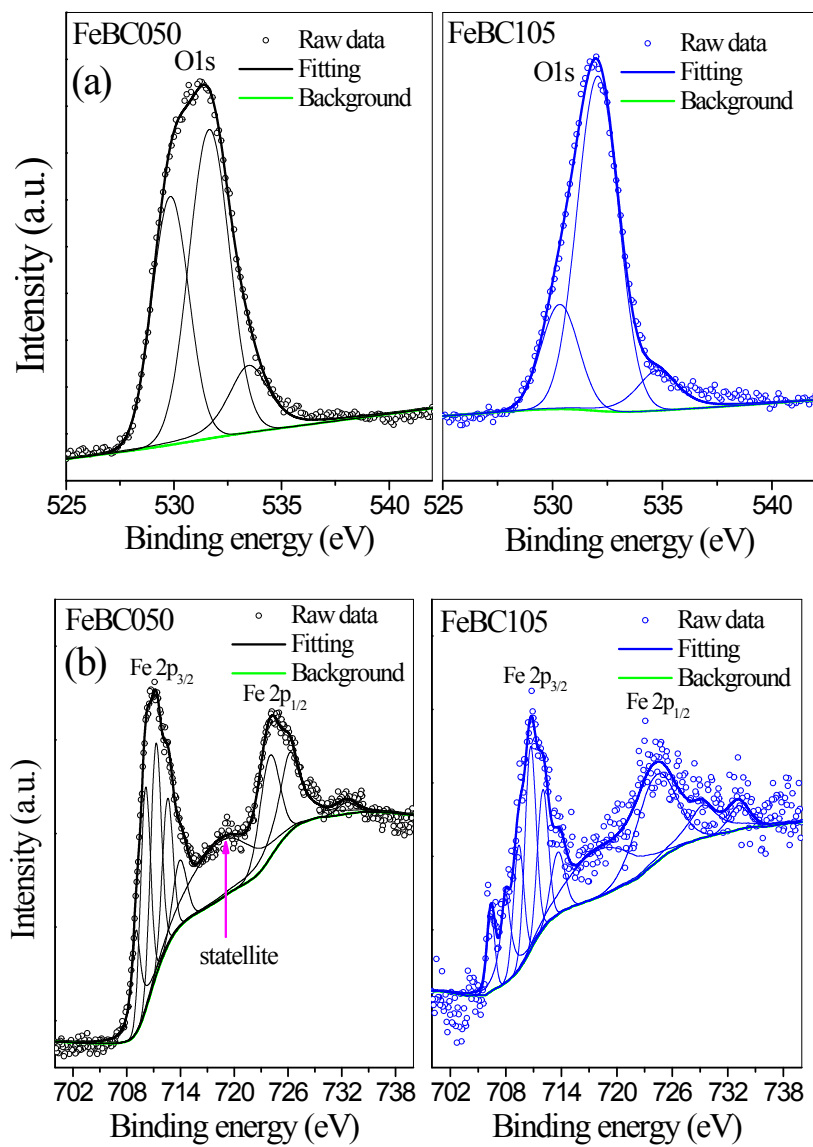
**Figure S1.** Cyclic voltammograms for Pt/Carbon and iron-carbon composites O<sub>2</sub>-saturated 1.0 M NaOH solution.



**Figure S2.** a) Linear sweep voltammograms for Pt/carbon and annealed composite (FeBC105) in  $O_2$ -saturated 1 M NaOH solution at a scan rate of  $10 \text{ mV s}^{-1}$  and rotating rate of 2500 rpm; b) Linear sweep voltammograms for annealed composite (FeBC105) in  $O_2$ -saturated 1 M NaOH solution at a scan rate of  $10 \text{ mV s}^{-1}$  and a rotating rate ranging from 400 to 3500 rpm.



**Figure S3.** XRD spectra (a) and Raman (b) spectra of untreated (FeBC050) and annealed (FeBC085 and FeBC105) composites



**Figure S4.**

and Fe 2p (b) spectra for untreated and annealed FeBC composites.

XPS O 1s (a)

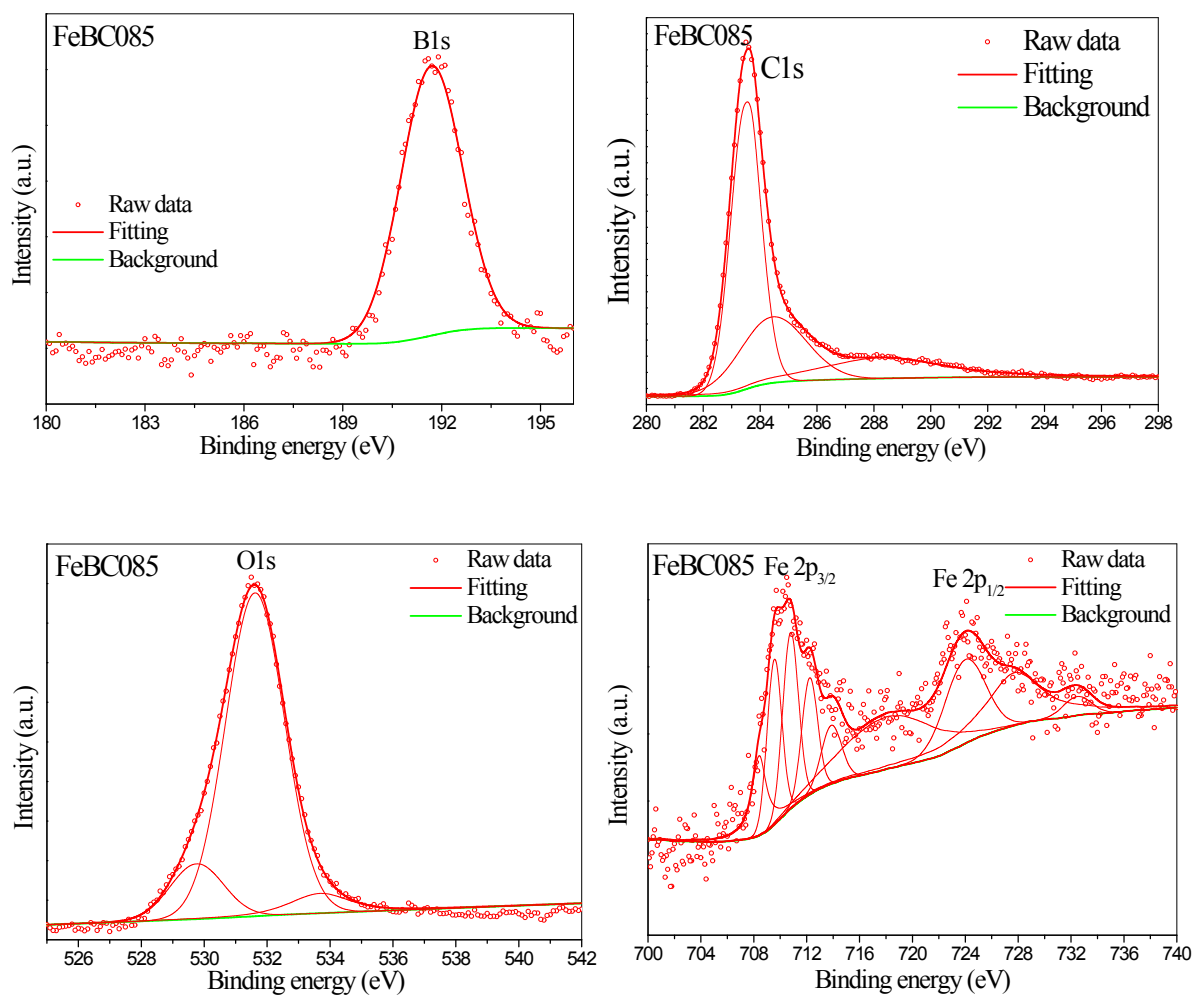
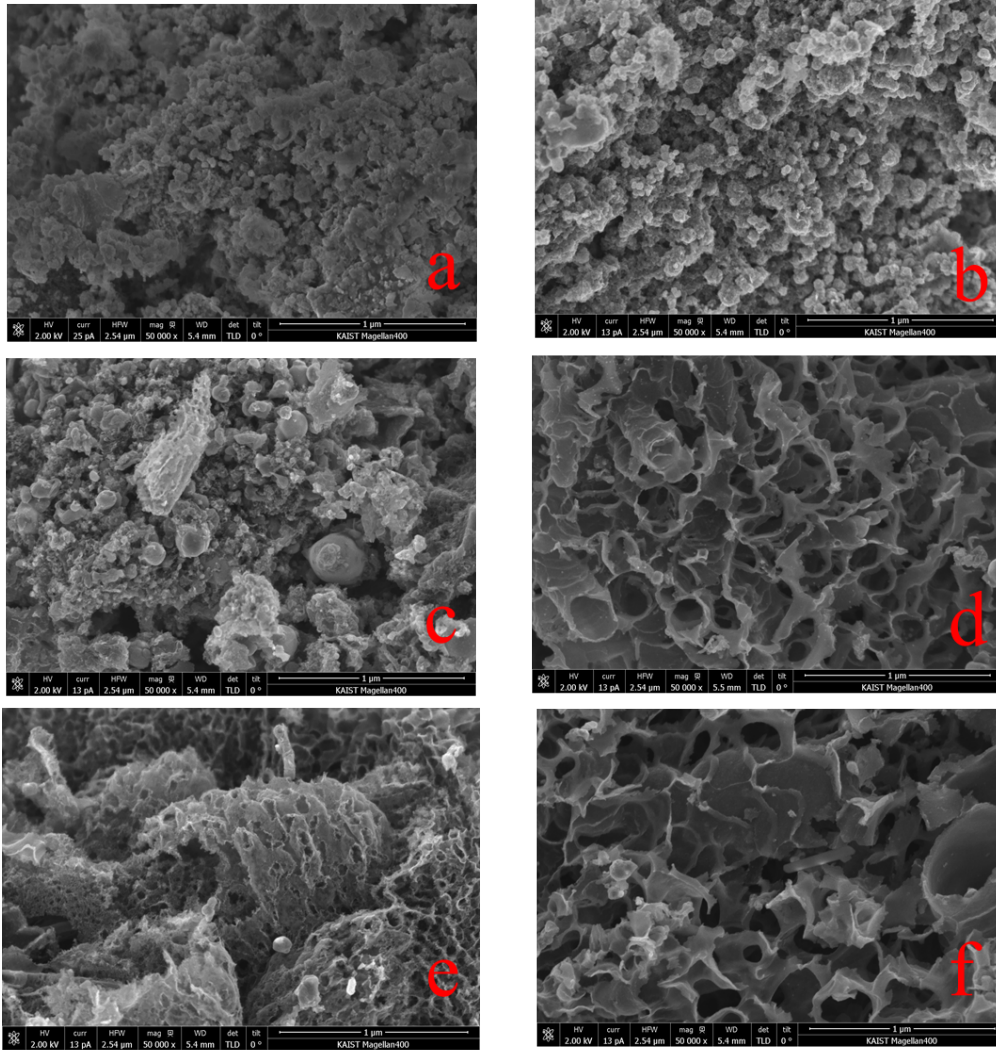
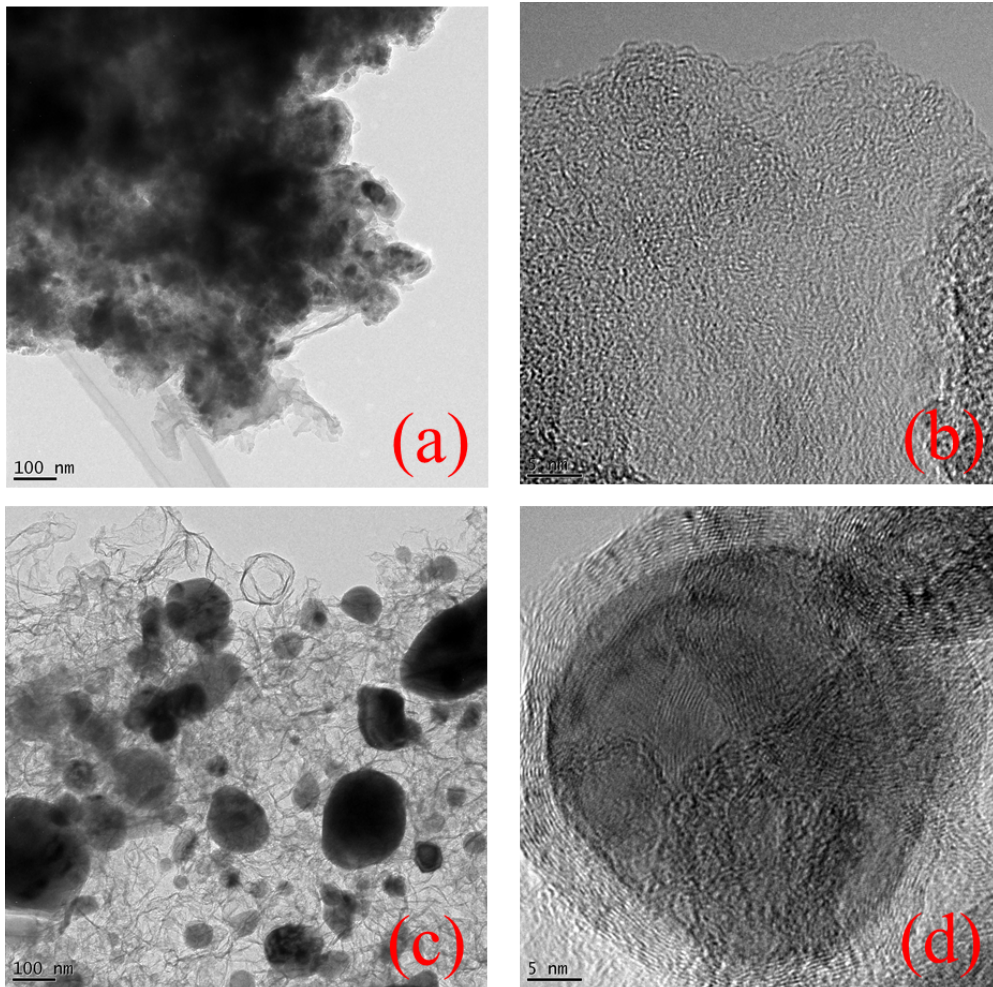


Figure S5. XPS spectra for FeBC085.

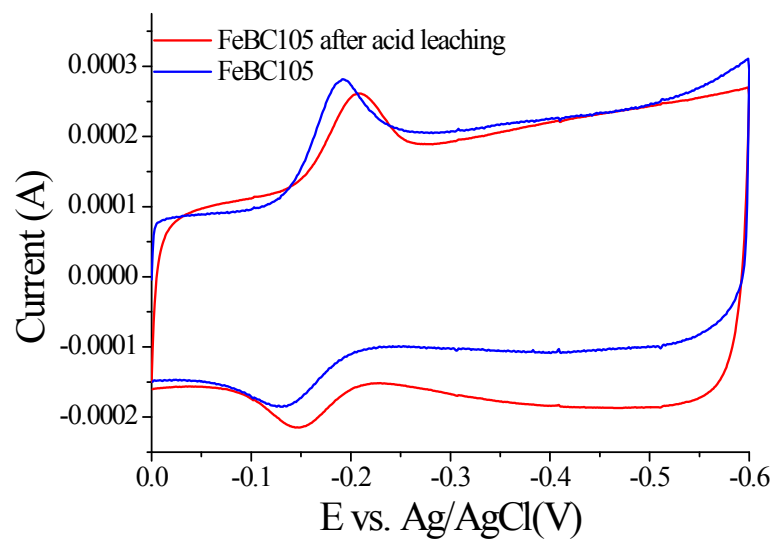




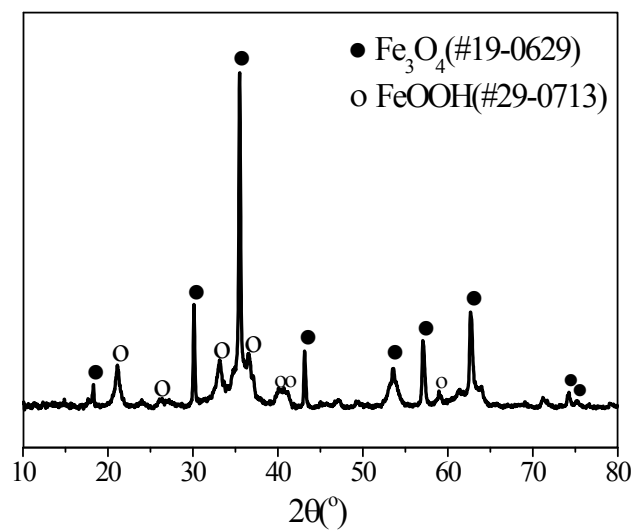
**Figure S6.** Representative SEM images of untreated composite, FeBC050 (a,b) and annealed composites, FeBC085 (c,d), FeBC105 (e,f).



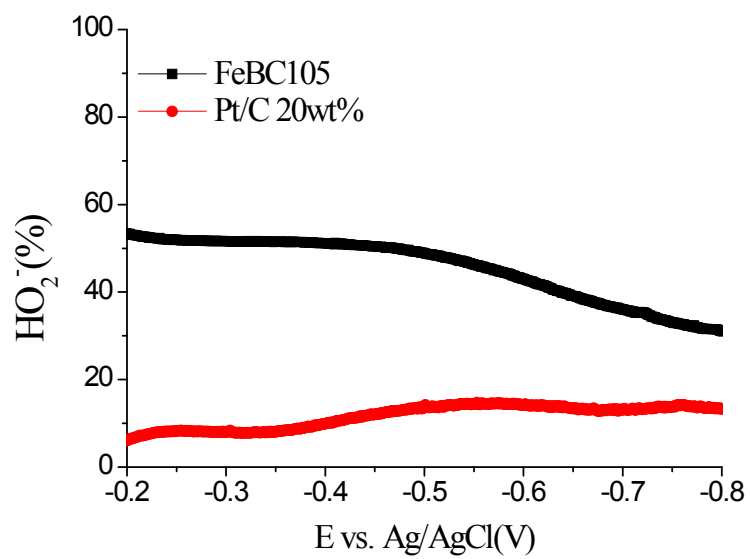
**Figure S7.** Representative TEM images of untreated composite, FeBC050 (a,b) and annealed composites, FeBC105 (c,d).



**Figure S8.** CV curve of FeBC105 and acid-leached FeBC105 at 50 mVs<sup>-1</sup>.



**Figure S9.** XRD spectrum of the Fe precursor.



**Figure S10.** Generation of peroxide in FeBC105 relative to the Pt/C catalyst.

[References]

1. A. J. Bard and L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2001, Chapter 9.
2. C. Zhang, F. F. Fan and A. J. Bard, *J. Am. Chem. Soc.* **2009**, 131,177-181.
3. D. Tromans, *Ind. Eng. Chem. Res.* **2000**, 39, 805-812.
4. P. M. Sipos, G. Hefter and P. M. May, *J. Chem. Eng. Data* **2000**, 45, 613-617.