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Dual Role of Borohydride Depending on Reaction Temperature: Synthesis of Iridium and Iridium Oxide

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Supporting Information

Experimental Section

$IrCl_3$ was obtained from Alfa-Aesar, Germany. Sodium borohydride, p-nitro aniline (R6G) were obtained from SD fine chemicals, India. Analytical grade ethanol, acetone, sulphuric acid and potassium hydroxide were obtained from SRL, India. All the glassware were rinsed with aqua regia followed by thorough washing with distilled water. Water with resistivity of 18 MΩ cm was used in all the experiments.

Synthesis of iridium nanofoams and iridium oxide nanoparticles

Iridium oxide

An aqueous solution of required amount of 0.1M iridium (III) chloride was stirred in an ice-bath followed by the addition of ice-cold aqueous, fresh sodium borohydride solution. The molar ratio between the $IrCl_3$ precursor and borohydride was maintained at 1:4. The colour of the solution changed to pale yellow immediately after the addition of borohydride. As the stirring continued, the ice-bath temperature slowly reaches ambient condition, 25^{o}C, and the solution was continuously stirred at 25^{o}C for 48 hours. During this process, the colour of the solution slowly changed from pale yellow to dark blue forming a colloid. The colour change became visible only after about ~ 40h. Once the colour of the colloid became dark blue, it remained as such for a long time. Even after several months, the dark blue colour colloid could

be sonicated for a short time to obtain the same characteristics as that of the colloid after 48 h. of preparation.

The preparation procedure was carried out at different temperatures to understand the formation of IrO_x and Ir. This is amplified in the manuscript.

Iridium foams

The irdium foams were synthesized by adding fresh aqueous sodium borohydride (ratio of $IrCl_3$ precursor and borohydride was maintained at 1:4) to a solution of 0.1M iridium (III) chloride kept at 80^{o}C. The stirring at this temperature was carried out for 10 minutes when a black colour, solid material was found to float on the surface. The colloidal solution was cooled down to 25^{o}C and the solid separated, washed with ethanol and water before further characterization.

Catalytic reduction of p-nitroaniline using Ir-based nanostructures

Stock solution of p-nitroaniline (p-NA) was prepared and kept in dark and solution of sodium borohydride (0.1 M) was prepared freshly before the start of the experiment. The reduction of p-NA was carried out in 1 cm path length quartz cuvette. In a typical reaction, an aqueous solution of 0.3 mM p-NA and 10 mM borohydride were taken in the cuvette. One µM concentration of Ir nanoparticles was added to the solution and the progress of the reaction was monitored with time using UV-Vis spectrophotometer. Similar experiments were carried out using IrO_2 (500 µM) as catalyst.

Characterization

Morphological and structural characterization were carried out using transmission electron microscope (TEM, JEOL 2100F) operated at 200 kV equipped with EDAX and selective

area electron diffraction (SAED**)** accessories. The sample for TEM was prepared by slow evaporation of dilute colloid in ethanol on a copper grid. The X-ray diffraction (XRD) was performed using Panalytical X-ray diffractometer equipped with graphite-monochromatized Cu-Kα radiation source. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Axis ultra multi technique X-ray photoelectron spectrometer with an MgKα as the X-ray source. Optical absorption spectra were recorded on PerkinElmer UV-Vis-NIR spectrophotometer. IR spectroscopy was recorded under ambient conditions using thermo scientific FTIR instrument. Dynamic light scaterring (DLS) measurements were carried out using Malvern Zetasizer Nanoseries ZS (ZEN 3690) instrument at 25^{o}C in water with a He-Ne laser **(**wavelength 633 nm).

Electrochemical Characterization

Working electrodes for oxygen evolution reactions (OER) on IrO_2 based nanostructures were fabricated as follows. Briefly, 3 mg of catalyst (Ir) was dispersed in water followed by the addition of 10 µL of nafion solution. The mixture was sonicated to obtain a homogeneous dispersion and 5 µL aliquot of the dispersion was uniformly spread onto a polished GC electrode of 3 mm diameter. The electrode was then dried under ambient conditions and used for electrochemical studies. Large area Pt foil as the auxiliary electrode and saturated calomel electrode (SCE) and mercury/mercuric oxide (Hg/HgO, 1 M KOH) were used as reference electrodes in acidic and alkaline solutions, respectively. Prior to electrochemical measurements, the electrolyte was completely deaerated by using high purity N_2 gas to remove dissolved oxygen.

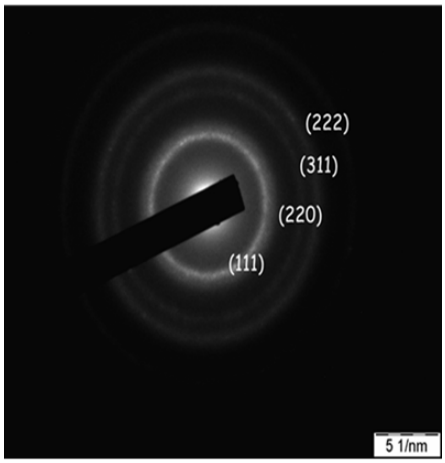

Figure S1. Selected area electron diffraction pattern of as-prepared Ir foam.

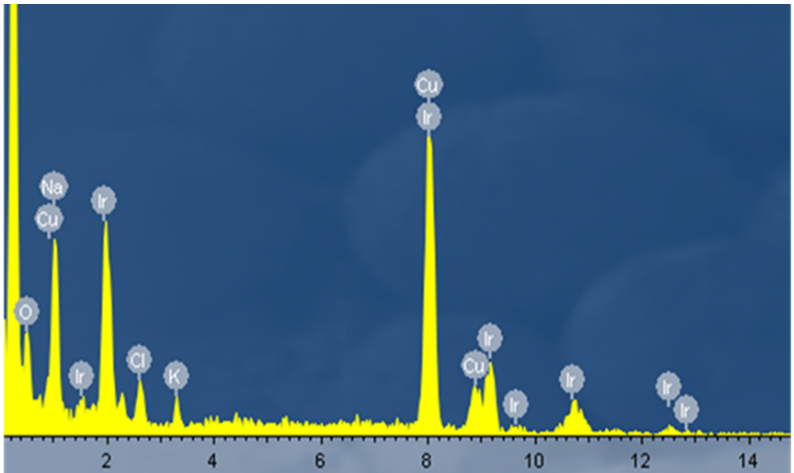

Figure S2. EDS spectrum of Ir nanofoam prepared at 80^{o}C using Ir^{3+} and $NaBH_4$. Ir nanofoam is drop-cast on carbon grid for recording the TEM image and the EDS spectrum.

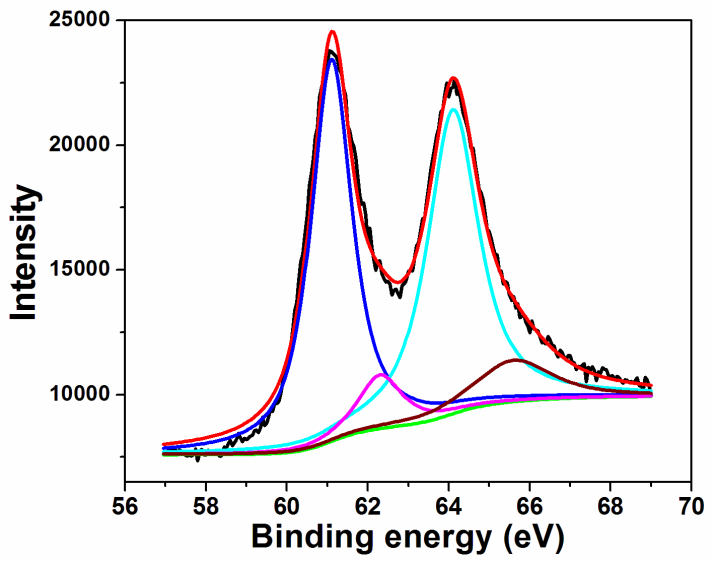

Figure S3. Deconvoluted XPS spectrum of Ir 4f region of Ir nanofoams.

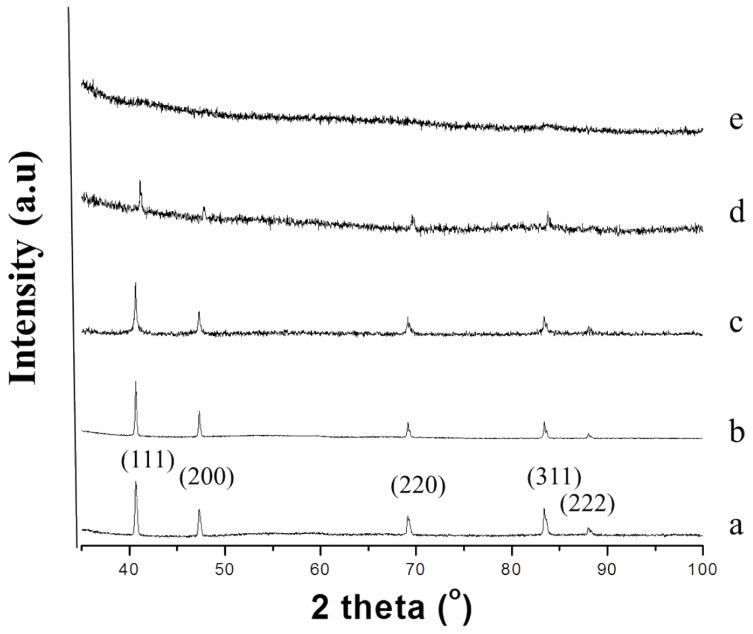

Figure S4. XRD patterns of (a-d) Ir and (e) IrO_2 (e) prepared by reacting Ir^{3+} using borohydride at (a) 70°C (b) 60 °C (c) 50 °C (d) 40°C for 15 minutes and (e) room temperature for 48 hours.

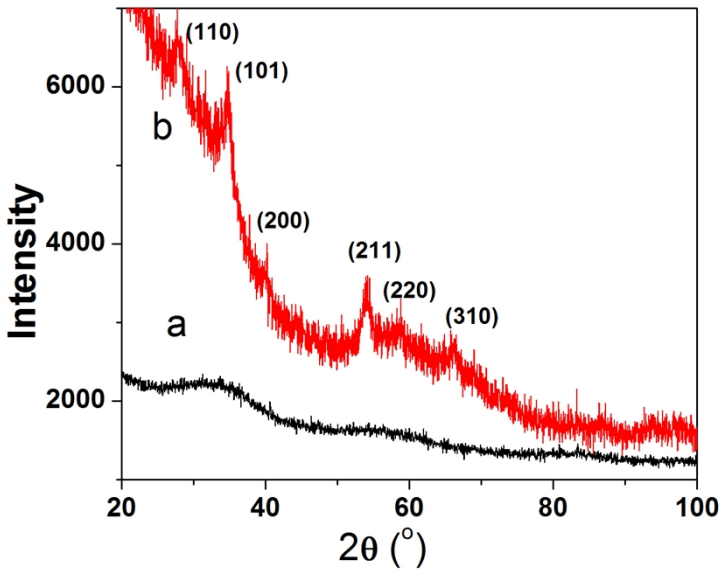

Figure S5. X-ray diffraction patterns of IrO_2 (a) before and (b) after annealing at 400°C.

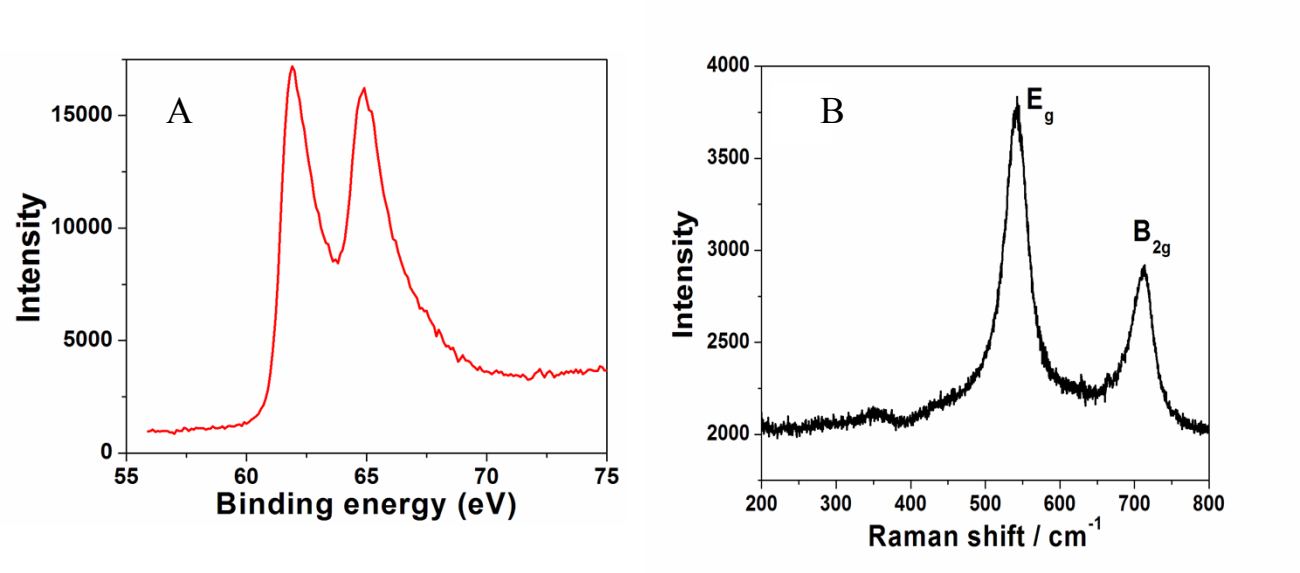

Figure S6. (A) XPS spectrum and (B) Raman spectrum of IrO_2 prepared at 25^0 C by treating Ir^{3+} with borohydride.

Formation of Ir and IrO_2 at different temperatures.

The standard reduction potentials for the reactions,

$Ir^{3+} + 3e$ -----→ Ir 0.86 V

$NaBH_4 + 8\ OH^-$ -----→ $NaBO_2 + 6\ H_2O + 8\ e^-$ - 1.24 V vs. SHE)

Though the potentials suggest that the reduction of Ir (III) to Ir (0) should be feasible, the observations are different.

The following is a brief summary of certain papers that deal with the reaction of Ir (III) ions (reduction as well as hydrolysis) using various (strong reducing) agents including sodium borohydride. It is quite well documented that the borohydride undergoes hydrolysis to form various complex species and no zerovalent Ir is formed under ambient conditions when Ir (III) or Ir (VI) are used. It has been observed by various researchers that use of strong reducing agents such as Cu, Mg, Zn and also borohydride *(Anal. Chem., 32, 486, **1960**; Talanta, 18, 841, **1971**; Hydrometallurgy, 3, 297, **1978**; J. Chem. Soc. Dalton Trans., **1979**, 1415; Int. J. Hydrogen Energy, 36, 224, **2011**; J. Phys. Chem. C, 112,* 13837, **2008** *and several others)* does not help in reducing Ir ions under ambient conditions.

- The Anal. Chem. paper mentions, " -- although the recorded potential for the iridium system (reduction potential is 0.76 V) indicates that copper (reduction potential is 0.34 V) would serve as a precipitant of iridium metal, it has been the experience in this laboratory that the expected reduction does not take place under certain conditions, whereas it does for rhodium (reduction potential is 0.45 V)".

  "--------- When magnesium and zinc metal, commonly used as strong reducing agents, were applied as precipitants of iridium metal in 1N hydrochloric acid, they precipitated only part of iridium, even though the solution was boiled up to 1 hour and subsequently warmed on a steam bath for 24 hours".

  The authors go on to say that "It is possible that the resistance to reduction by iridium is the result of unusually stable dissolved complexes".

- The J. Chem. Soc. Dalton Trans. paper mentioned the hydrolysis of iridium ions and various complexes formed.

- The Int. J. Hydrogen Energy paper deals with hydrolysis of borohydride under harsh conditions of different temperatures (30 to 80^{o}C) and at different pH values of the solution.
  The authors have concluded that the hydrolysis reaction leads to the formation of BH_4^- / $BH_3(OH)^-$; $BH_3(OH)^-$ / $BH_2(OH)_2^-$; $BH_2(OH)_2^-$ / $BH(OH)_3^-$ and $BH(OH)_3^-$ / $B(OH)_4^-$ simultaneously.

  One important aspect that needs to be mentioned here is that there is simultaneous production of hydrogen in the system during the above process.

- The J. Phys. Chem. C paper mentions during the preparation of dendrimer supported Ir catalysts from Ir(III) that no discernible reduction of Ir^{3+} to form zerovalent nnaoparticles was observed after adding $NaBH_4$.

Hence, it is clear that though the redox potentials are favourable, the reduction of Ir ions in presence of sodium borohydride under ambient conditions does not proceed.

The reduction of metal ions using borohydride should take in to account the redox potentials of the species formed as mentioned above. Additionally, the formation of hydrogen possibly play a role in the formation of IrO_x and Ir at different temperatures.

It has been reported that the hydrolysis of Ir (III) in presence of base resulted in the formation of Ir_2O_3 which is oxidized by O_2 to iridium(IV) oxide. Without oxygen, the reaction of the precursor to IrO_2 cannot occur. If oxygen is added to the reaction, a rapid formation of a blue colloidal solution is the result. Even in the case of iridium(IV) chloride, where an oxidation should not be involved, O_2 is reported to be needed.

This observation matches with the assumption of *Witzmann* in 1908 (*L. Wöhler, W.Witzmann, Zeitschrift für anorganische Chemie* ***1908****, 57, 323*) and the results of *Harriman* (*A. Harriman, J. M. Thomas, G. R. Millward, New Journal of Chemistry* ***1987****, 11, 757*) that both, the base and oxygen are necessary to accomplish an oxidation reaction to iridium(IV)oxide. In this context the chemical equation is assumed to be:

$$2\ IrCl_3 + 6\ KOH \longrightarrow Ir_2O_3 + 3\ H_2O + 6KCl$$
$$2\ Ir_2O_3 + O_2 \longrightarrow 2\ IrO_2$$

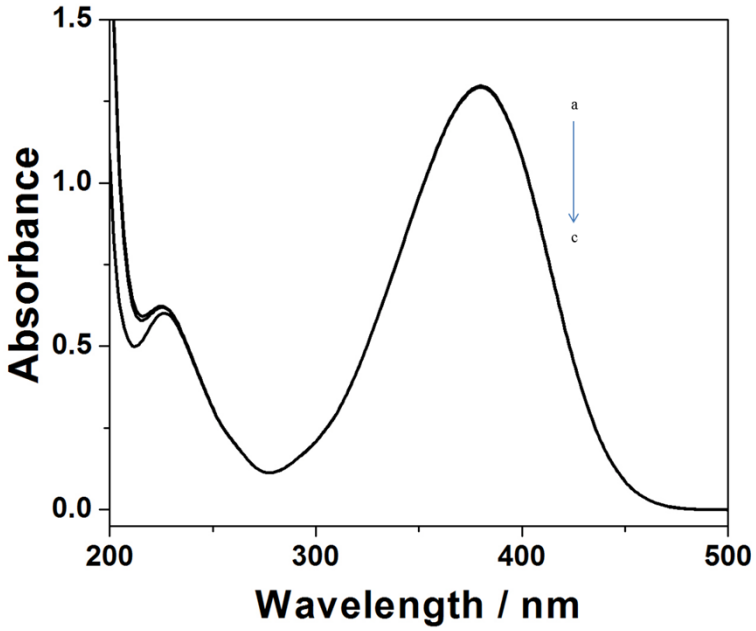

Figure S7. UV-Vis spectra for p-NA reduction in presence of only $NaBH_4$ at different time intervals. a-c correspond to 5 minutes, 6 hours and 12 hours respectively.

Additional figures

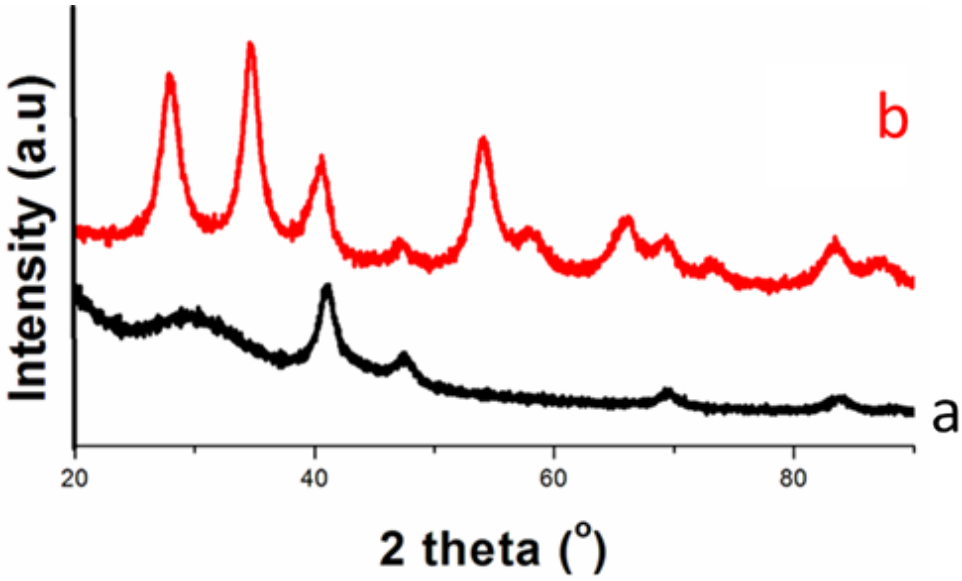

Figure S8. XRD patterns of Ir foams (a) before annealing and (b) IrO_x (after annealing at 500°C).

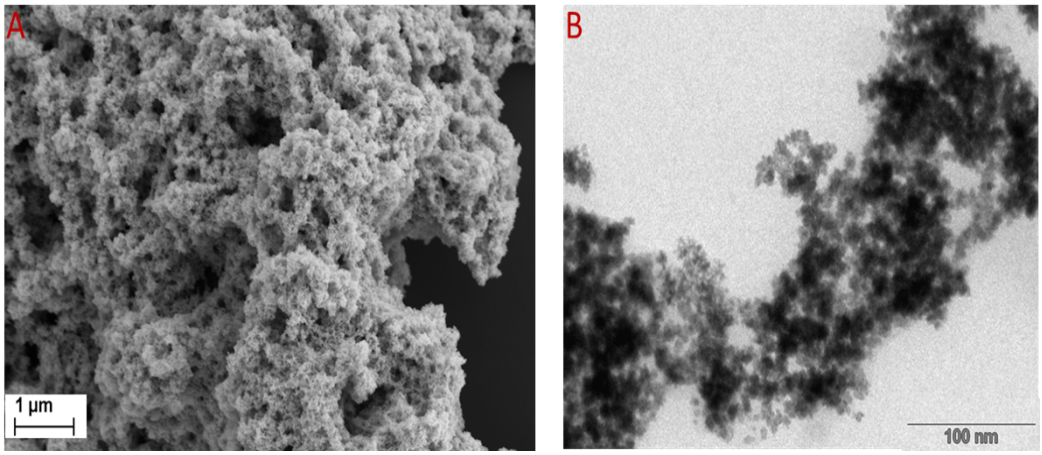

Figure S9. (A) SEM and (B) TEM images of IrO_x foams. The foams are prepared by annealing the Ir foams at 500^{o}C.

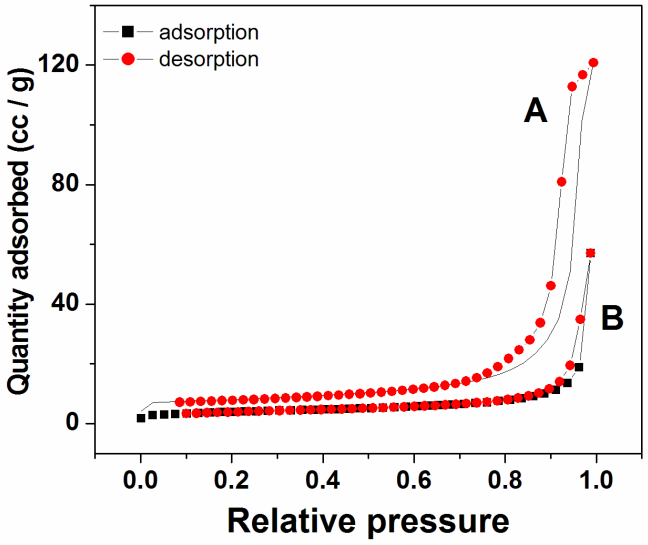

Figure S10. N_2 adsorption-desorption isotherms (77 K) of (A) IrO_x nanofoams and (B) IrO_x particles using BET method.

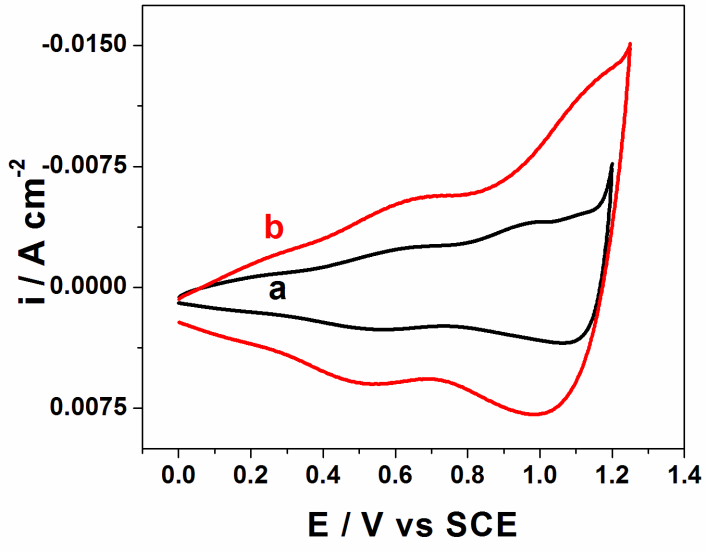

Figure S11. Cyclic voltammograms of (a) IrO_x particles and (b) IrO_x foams in 0.5 M H_2SO_4 at a scan rate of 50 mV/s. The currents are normalized with respect to geometric area.

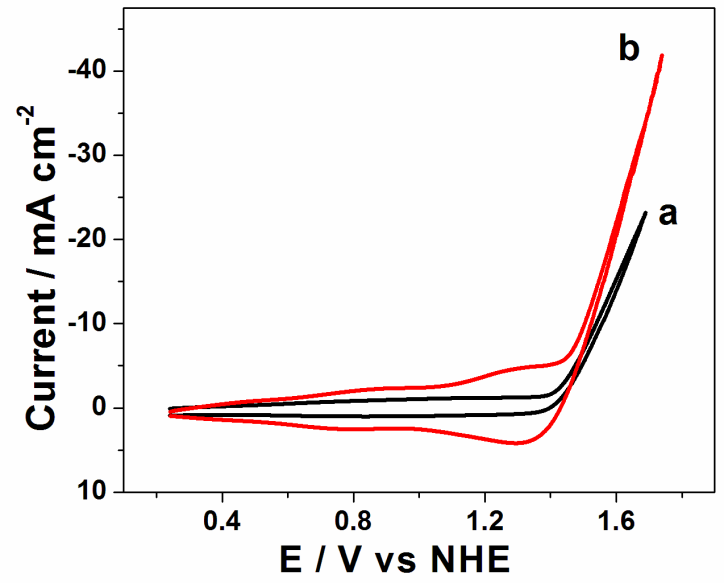

Figure S12. Cyclic voltammograms of (a) IrO_2 particles and (b) IrO_2 foams for oxygen evolution reaction (OER) in 0.5 M H_2SO_4 at a scan rate of 10 mV/s.