

## Supporting information

### **Fast Magnetically Driven Electrodeposition of Amorphous Metal Oxides Water Oxidation Catalysts from Carbon-coated Metal Carbide Nanoparticles**

**Jing Zhu,<sup>a,c</sup> François Lambert,<sup>a</sup> Clotilde Policar,<sup>a</sup> François Mavré,<sup>\*,b</sup> and Benoit Limoges<sup>\*,b</sup>**

<sup>a</sup> *École Normale Supérieure - PSL Research University, Département de Chimie, Sorbonne Universités - UPMC Univ Paris 06, CNRS UMR 7203 LBM, 24 rue Lhomond, F-75005 Paris, France.*

<sup>b</sup> *Laboratoire d'Electrochimie Moléculaire, UMR 7591 CNRS, Université Paris Diderot, Sorbonne Paris Cité, 15 rue Jean-Antoine de Baïf, F-75205 Paris Cedex 13, France.*

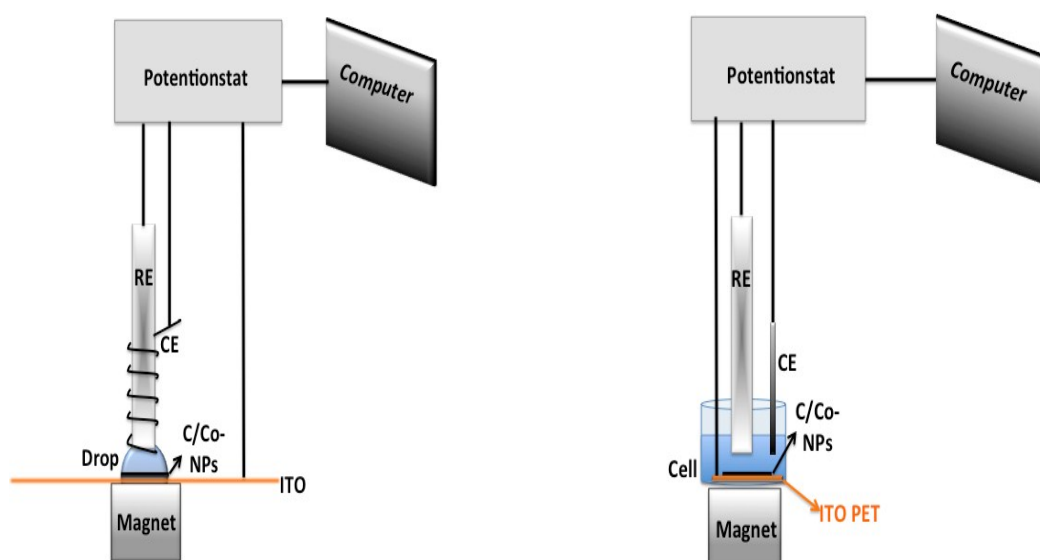
<sup>c</sup> *East China Normal University, Department of Chemistry, 500 Dongchuan Road, Shanghai 200241, China.*

#### **EXPERIMENTAL SECTION**

Carbon-coated cobalt nanoparticles (Sigma-Aldrich, Ref-697745, or TurboBeads, Ref-1008), carbon-coated nickel nanoparticles (US Research nanomaterials, Inc.; 20 nm, US1125, synthesized by laser evaporation), and cobalt oxide nanoparticles (Co<sub>3</sub>O<sub>4</sub>, Sigma, Ref-637025) were used as received. For electrochemical experiments, the magnetic powder of nanoparticles was dispersed in water (concentrations ranging from 0.5 to 50 mg/mL) in the presence of a 0.1% wt Tween 20 and ultrasonicated for less than < 5 min in such a way to obtain a homogenous colloidal suspension. The colloidal suspension was then half-to-half mixed with a buffered solution (NaPi) buffer solution (NaPi, 0.2 M, pH 7.0 or Borate, 0.2 M, pH 9.2) and a droplet of 40 µL then deposited on the surface of a flat ITO electrode delimited by an insulating eyelet (allowing to define a small circular electrochemical cell with a working disk ITO area of ~0.2 cm<sup>2</sup>). ITO-coated glass (surface resistivity 8-12 Ω/sq, 25 mm × 25 mm × 1.1 mm, slide) and ITO-coated polyethylene terephthalate films (ITO-PET surface resistivity 60 Ω/sq, L × W × thickness 1 ft × 1 ft × 5 mil, sheet) were purchased from Sigma. They were used as conducting transparent substrates after they were thoroughly rinsed with water.

Using a cylindrical magnet (rare-earth neodymium magnet, whose diameter is similar to the working ITO disk electrode) positioned underneath the electrode, the magnetic particles were rapidly collected at the working electrode/solution interface. After the magnetic particulate film is formed in the presence of a magnet applied below the ITO electrode surface, a saturated calomel reference electrode (SCE) as well as a counter electrode (platinum wire or mesh) are dipped in the 40 µL (Scheme S1, left) electrolytic solution (0.1 M sodium phosphate buffer, pH 7.0) and all were connected to a potentiostat in order to polarize the ITO electrode at a controlled potential. In this

configuration, the ITO on glass substrate was preferentially used. An alternative electrochemical set-up allowing to work with higher volume of solution was also used (Scheme S1, right). In that case, the ITO electrode was placed at the bottom of a 15 mL glassware electrochemical cell. Again a 40  $\mu$ L droplet of the half-to-half mix between the colloidal suspension and the appropriate buffer was then deposited on the surface of the ITO electrode delimited by an insulating eyelet. Polyester films coated with ITO, which exhibit transmittance and resistance similar to those of ITO on glass substrates, were preferred in that case for their lower thickness and higher flexibility, allowing thus an easier magnetic collection of the particles through the walls of the glassware electrochemical cell. After the magnetic film was formed, the electrochemical cell was carefully filled with 5 mL of the appropriate buffer solution (NaPi, 0.1 M, pH 7.0 or Borate, 0.1 M, pH 9.2) in which a saturated calomel reference electrode (SCE) as well as a counter electrode (platinum wire or mesh) were dipped. This second configuration was preferred for experiments involving long term polarization because it surely avoids any buffer depletion or reaction products concentration.

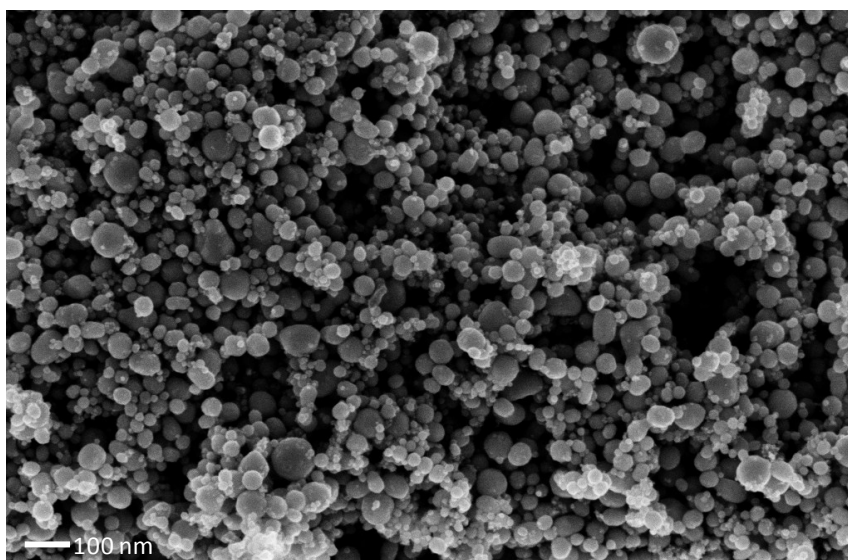


**Scheme S1. Electrochemical cell configurations**

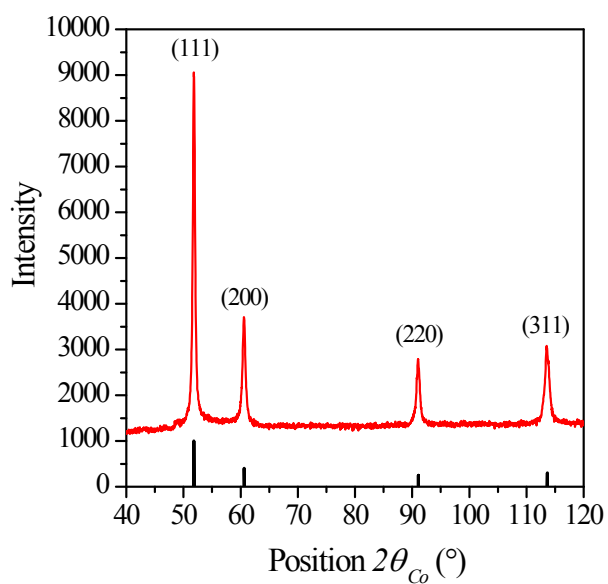
The potentiostat used in these experiments is a CHI 900 (CHI Instruments, Inc.). Although a SCE reference was always used for the experiments, all electrochemical potentials were converted relative to the normal hydrogen electrode (*vs.* NHE). Ohmic drop was not compensated. Overpotentials are expressed using the following expressions:  $\eta(j) = E(j) - (E_{\text{O}_2/\text{H}_2\text{O}}^0 - 0.059 \times \text{pH})$  where  $j$  is the current density,  $E_{\text{O}_2/\text{H}_2\text{O}}^0$  is the standard potential of the  $\text{O}_2/\text{H}_2\text{O}$  couple (1.23 V *vs.* NHE). When willing to consider a cell solution resistance  $R$ , an alternative estimation of the overpotential can be made through the following expression:  $\eta(j) = E(j) - jSR - (E_{\text{O}_2/\text{H}_2\text{O}}^0 - 0.059 \times \text{pH})$ , where  $S$  is the disk electrode surface area.

The rotating ring disk electrode (RRDE) was a glassy carbon disk/platinum ring RRDE tip (E7R9 Series, Pine research Instrumentation, ring-disk gap: 320  $\mu\text{m}$ , disk outer diameter: 5.61 mm, ring inner diameter: 6.25 mm, ring outer diameter: 7.92 mm, shroud outer diameter: 15.0 mm, collection efficiency: 37%, disk area: 0.2475  $\text{cm}^2$ , ring area: 0.1866  $\text{cm}^2$ ) mounted on a shaft attached to an adjustable speed rotator AFMSRX (Pine Research Instrumentation, USA). The results of the RRDE in the main text on Figure 4 are displayed in current densities. However, note that the calculation of the faradaic efficiency involves current ( $i$  in A) as the geometry of the RRDE tip is taken into account in the determination of the collection efficiency.

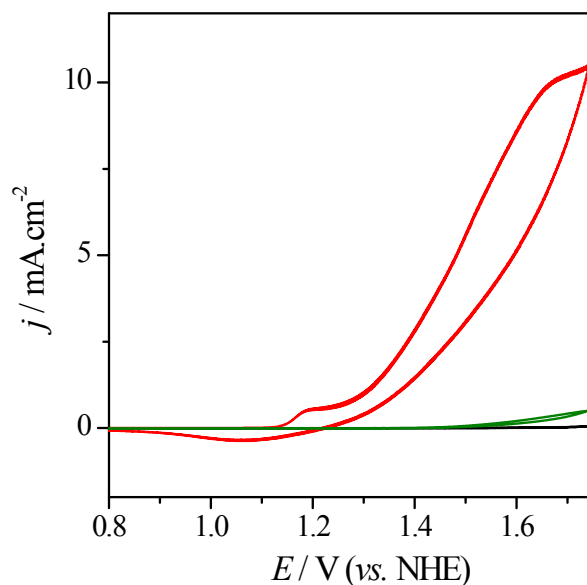
SEM images were obtained with a Zeiss Supra 40 scanning electron microscope. The images were taken at different magnifications using an in-lens detector at a low voltage (5 kV or 1 kV). The atomic composition of the deposit was analyzed using an EDX system with a JEOL 6510 scanning electron microscope.



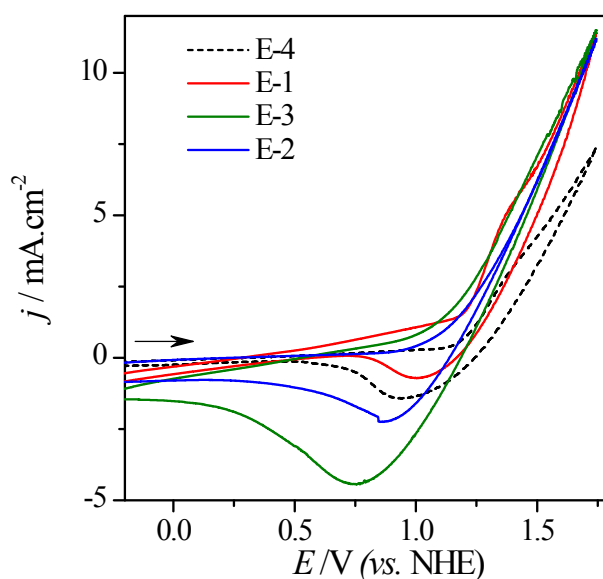
**Figure S1.** SEM image of the as received nanopowder of carbon-coated magnetic cobalt nanoparticles (< 50 nm particle size, Sigma-Aldrich ref: 697745)



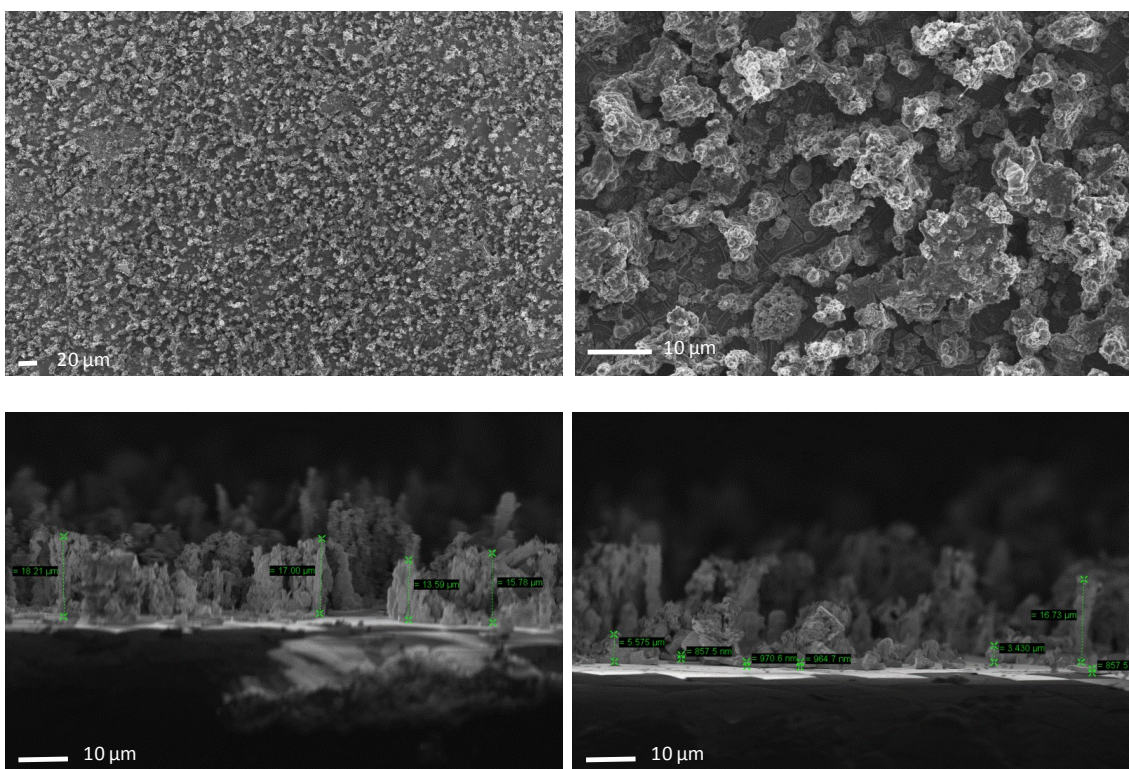
**Figure S2.** XRD pattern of the C/Co-NPs. The vertical bars represent the theoretical pattern for metallic cobalt (ref 00-015-0806).



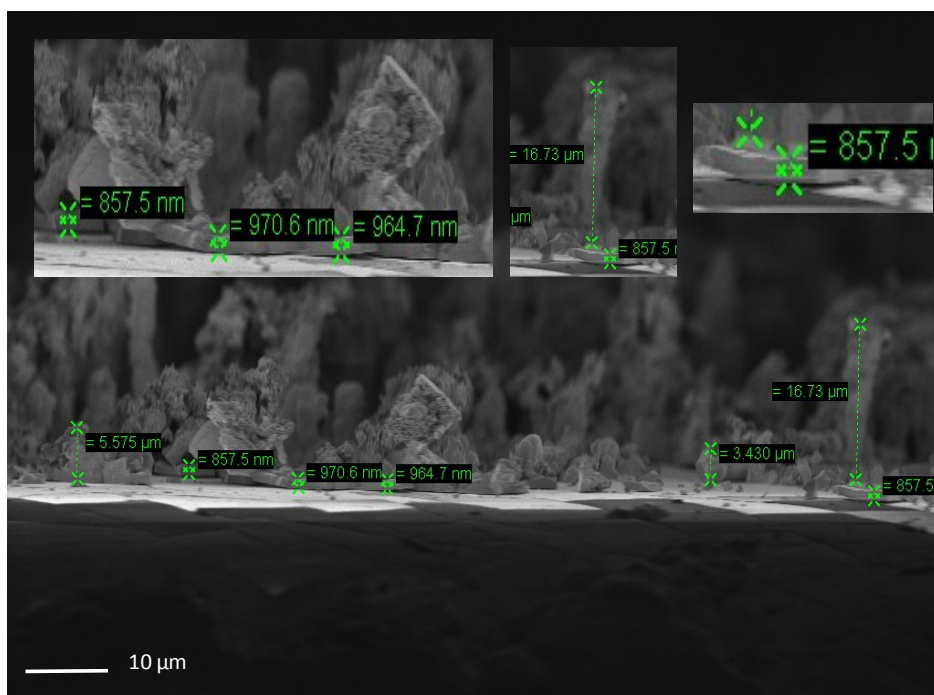
**Figure S3.** First CVs ( $\nu = 0.1$  V/s) recorded at a C/Co-NPs-coated ITO electrode ( $0.05$  mg/cm<sup>2</sup>) in a  $0.1$  M NaPi (pH 7.0), containing (red)  $0.6$  mM and (green)  $30$  mM EDTA. For comparison, the first CV recorded at an ITO electrode immersed in a  $0.5$  mM solution of  $\text{Co}^{2+}$  containing  $0.6$  mM EDTA in  $0.1$  NaPi is overlaid (black curve).



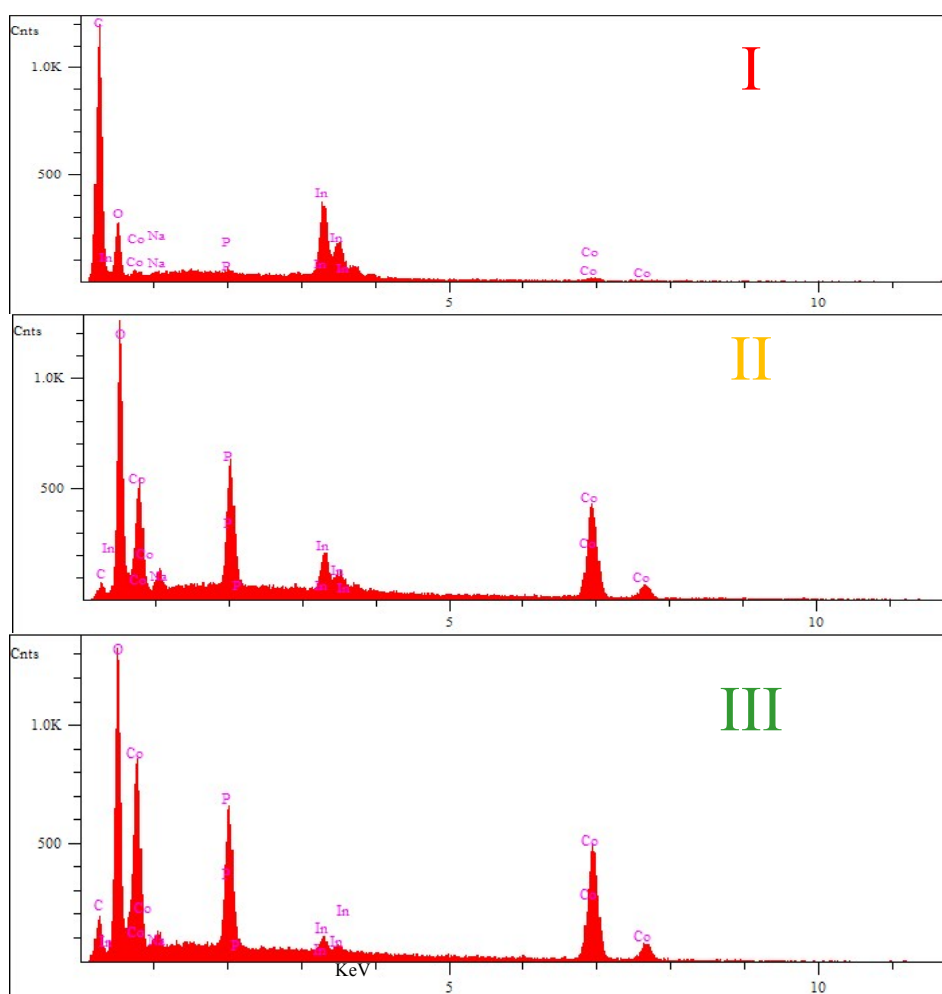
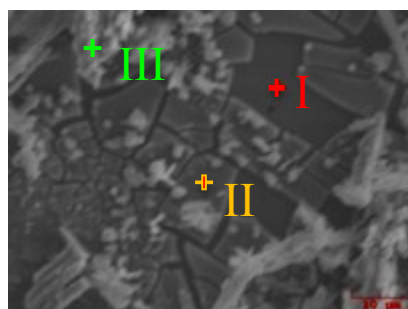
**Figure S4.** CVs ( $\nu = 0.1$  V/s) of different C/Co-NPs-coated ITO electrodes that were beforehand submitted to an anodic polarization ( $1.24$  V) for  $1$  h in a  $0.1$  M NaPi (pH 7, total volume  $5$  mL), followed by rinsing and then scanning in a  $0.1$  M NaPi (pH 7.0). The initial amount of magnetically deposited C/Co-NPs was varied as follow: (E-1)  $0.05$  mg/cm<sup>2</sup>, (E-2)  $0.5$  mg/cm<sup>2</sup> and (E-3)  $5$  mg/cm<sup>2</sup>. For comparison, the CV (E-4) of a CoPi-coated ITO electrode in a  $0.1$  M NaPi (pH 7.0) is shown. In this latter case, the CoPi coating was obtained from anodic electrodeposition at  $1.24$  V for  $1$  h in a  $0.5$  mM solution of  $\text{Co}^{2+}$  in  $0.1$  M NaPi.



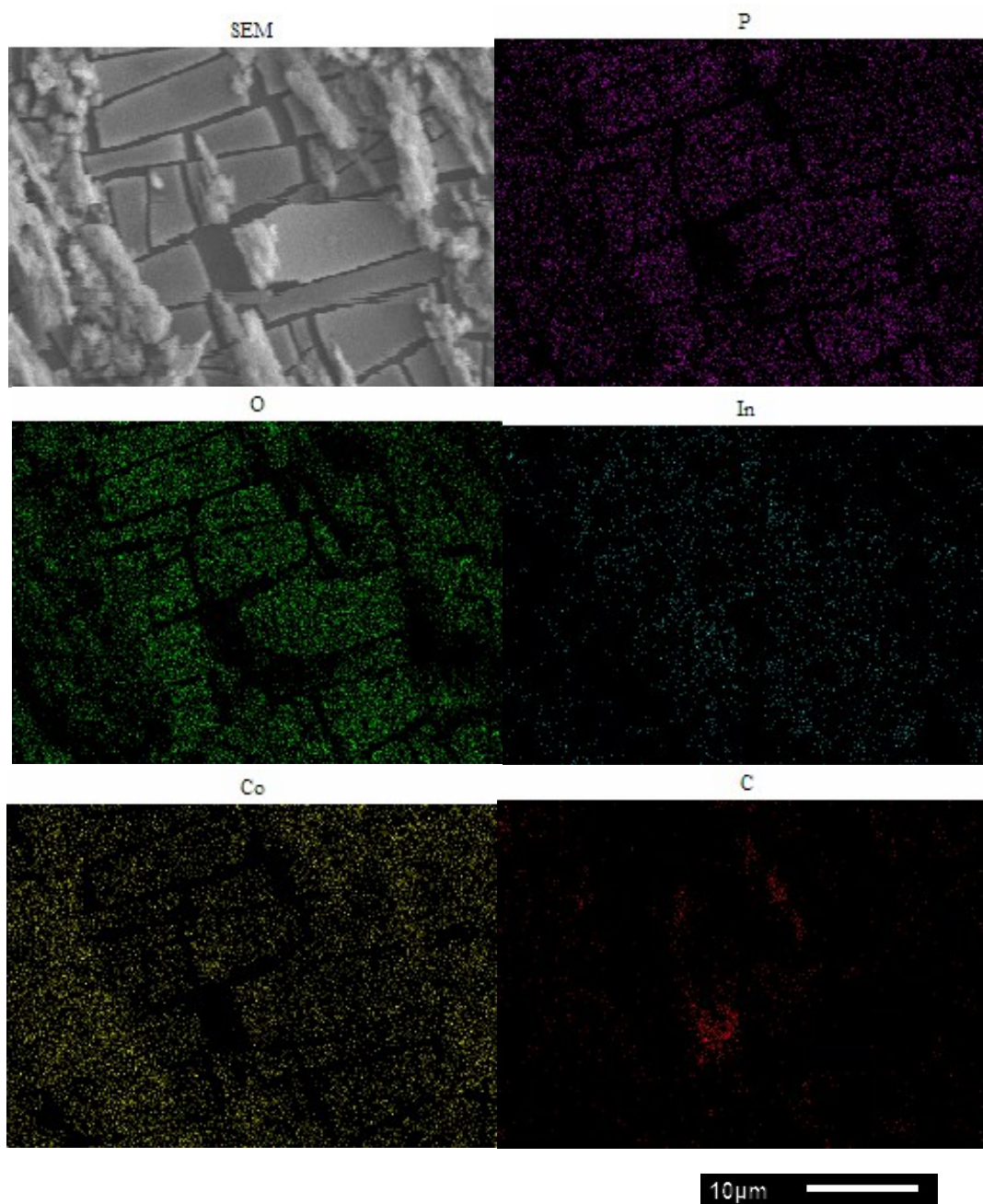
**Figure S5.** Top and side SEM views of the C/Co-NPs-coated ITO electrode E-3 prepared as described in Table 1.



**Figure S6.** Zoom of the side SEM views in Fig. S5 of the C/Co-NPs-coated ITO electrode E-3 prepared as described in Table 1.

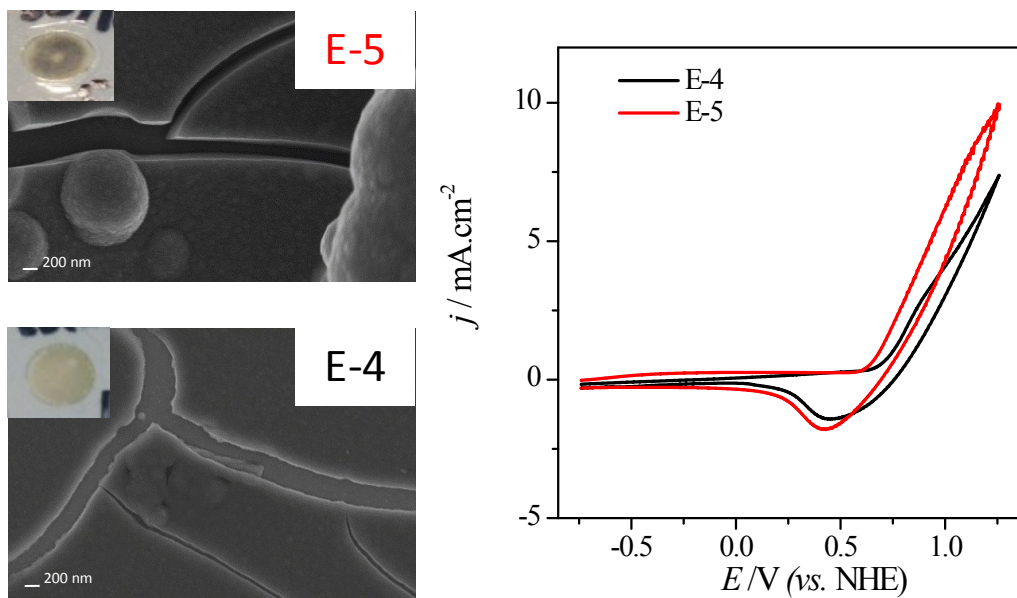


**Figure S7.** SEM image and EDX spot analysis of electrode E-8 (the selected spots are marked with a cross and the corresponding X-ray spectra identified by their numbering). The electrodeposited film was obtained upon applying an anodic potential of 1.24 V for 1800 s to a particulate film of C/Co-NPs deposited (5 mg/cm<sup>2</sup>) on an ITO electrode and immersed in a 0.1 M NaPi (pH 7, total volume: 5 mL).



**Figure S8.** SEM image and EDX elemental mapping of electrode E-8. The mapped element is mentioned at the top of each image. Other conditions are the same than in Fig. S7.





**Figure S9.** Left: SEM images of electrode E-4 and E-5 (see Table 1 for the experimental conditions used for the preparation of these films). Right: CVs ( $\nu = 0.1$  V/s) of electrodes E-4 (black) and E-5 (red) recorded in a 0.1 M phosphate buffer (pH 7, total volume: 5 mL).