Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Co_3O_4 Nanoparticles/Cellulose Nanowhiskers-Derived Amorphous Carbon Nanoneedles: Sustainable Materials for Supercapacitors and Oxygen Reduction Electrocatalysis

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Thermal treatment procedure for making the Co_3O_4/CNN materials in a temperature programmable furnace

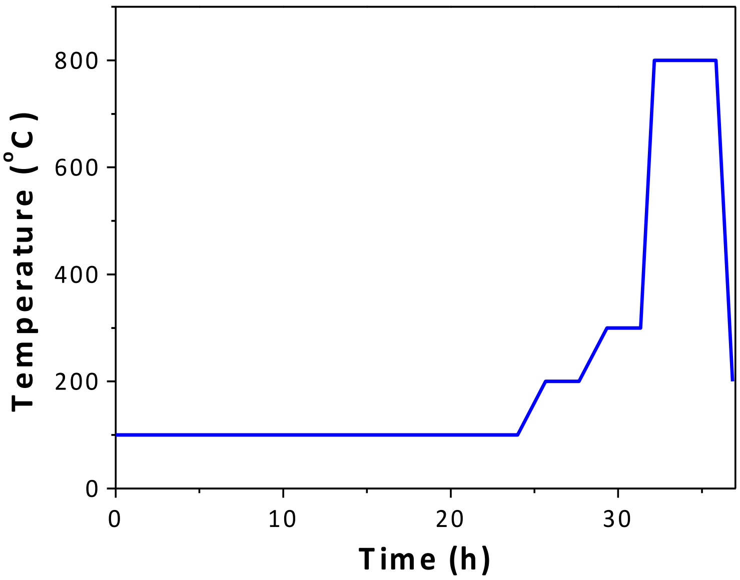

Figure S1. Thermal treatment procedure used for the synthesis of carbon nanoneedles-supported Co_3O_4 nanoparticles (Co_3O_4-CNN) from their parent materials, *i.e.*, Co^{2+}/Cellulose@SiO_2 core-shell-sell materials. The thermal treatment protocol was divided in three stages according to the events occurring in the samples. In the first stage, the samples were kept at 100 °C for 24 h. This allowed physically adsorbed water to be removed from them. The longer heating time also promoted the condensation reaction between the silanols groups of the SiO_2 shells in the parent materials and the formation of a robust silica framework. This, in turn, helped the silica shells to have less permeability and prevent the carbonaceous species from escaping during the subsequent carbonization stages. In the second stage, the temperature was increased at a low ramp of 1 °C/min, reaching two temperature plateaus (200 and 300 °C). The time span in each plateau was 2 h. During this stage the cellulose nanowhiskers in the materials undergo slow degradation as this temperature favors further dehydration of cellulose nanowhiskers without making their C-C bonds to cleave.[16] The third and last stage starts with heating the material from 300 °C to 800 °C at a ramp of 10 °C/min up. Finally, the materials were kept at 800 °C for 3 h to let their carbon precursors undergo complete carbonization.

Electrochemical Measurements

Cyclic Voltammetry. Cyclic voltammetry analyses of the samples and electrocatalysis tests using the Co_3O_4-CNN materials as electrocatalysts were conducted using a Versastat-3 from PAR (Princeton Applied Research) instrument. A three-electrode configuration consisting of a saturated calomel electrode as the reference electrode, a platinum wire (diameter: 0.1 mm) as the counter electrode and the powdered Co_3O_4-CNN samples supported on glassy carbon as the working electrode was employed. The voltammograms were obtained at a scan rate of 20 mV s^{-1}. The CV was performed in 0.1 M KOH solution saturated with oxygen (O_2) or nitrogen (N_2).

Working electrodes preparation. 10 mg of the catalyst was added in 2 mL of propanol/water solution (1:3 v/v) with 210 μL of 5% Nafion solution. The catalyst was dispersed by sonication for 30 min to form "a catalyst ink". The electrodes were prepared by carefully drop casting 4 μL onto a glassy carbon electrode with 5 mm of diameter. The final catalyst loading was 100 μg/cm^2. The current presented in all electrochemical measurements and corresponding *i-V* graphs were all normalized to the geometrical area of the electrodes.

Electrochemical experiments using rotating disc electrode (RDE). The kinetics of the ORR over the Co_3O_4-CNN materials were analyzed using a rotating disk electrode (RDE, Pine Research Instrumentation) that is connected to a Pine Bipotentiostat (Pine Research Instrumentation) assembled with a rotator (Pine Research Instrumentation). For the experiments, a three-electrode configuration consisting of a saturated calomel electrode as the reference electrode, a platinum wire (diameter: 0.25 mm) as the counter electrode and powdered sample supported on glassy carbon as the working electrode was employed. The working electrode was scanned cathodically at a rate of 5 $mV\cdot s^{-1}$ at RDE experiment with varying rotating speed from 400 rpm to 2,400 rpm. The working electrode was prepared using the method described above.

The number of electrons transferred (n) in the oxygen reduction reaction (ORR) was determined using Koutecky–Levich (K-L) equation:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFC_o(D_o)^{2/3}v^{-1/6}$$

where j_k is kinetic current, j_l is diffusion-limiting current, n is the overall number of transferred electrons during O_2 reduction, F is Faraday constant (96,500 $C \cdot mol^{-1}$), k is rate constant for oxygen reduction, C_0 is the saturated O_2 concentration in the electrolyte, D_O is the diffusion coefficient of O_2 in the electrolyte, v is the kinetic viscosity of the solution, and ω is the angular frequency of the rotation in terms of $rad \cdot s^{-1}$.

The RDE experiment was performed using 0.1 M KOH solution saturated with O_2. The number of electrons transferred (n) and the value of j_k were obtained from the slope and the intercept on the Koutecky−Levich plots ($1/j$ vs $\omega^{-0.5}$), respectively, by using $C_0 = 1.2 \times 10^{-3}$ M, $D_0 = 1.9 \times 10^{-5}$ cm s^{-1}, and $v = 0.1$ m^2 s^{-1}.

Reference electrode calibration. All electrochemical measurements were carried out using a saturated calomel electrode as reference. The SCE reference electrode is calibrated in the electrolyte solution used in the present work (0.1 M KOH) using the inter-conversion point between the hydrogen oxidation reaction and hydrogen evolution reaction. In this experiment, linear sweep voltammetry was carried out in a three-electrode setup, in which a platinum foil was used as working electrode (1 cm^2 dipped in the solution), a platinum wire (0.25 mm diameter) was used as a counter electrode, and the saturated calomel electrode was used as a reference electrode. The solution (0.1 M KOH) was purged with hydrogen gas prior the analysis for approximately 30 minutes.

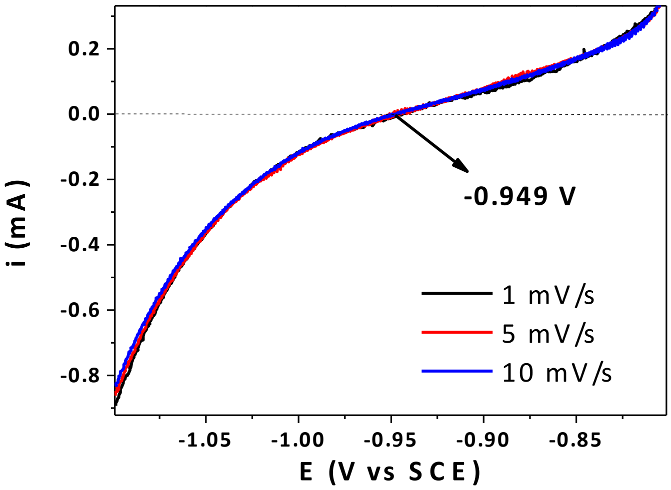

Figure S2. Linear sweep voltammograms obtained at different scan rates for 0.1 KOH solution saturated with hydrogen (H_2).

In Figure S2, the linear sweep voltammograms of a H_2-saturated 0.1 M KOH solution at different scan rates is presented. The system was swept in a cathode direction. It is observed that at -0.949 V vs SCE reference occur as the inter-conversion point between the hydrogen oxidation reaction and the hydrogen evolution reaction.

The result above indicates that the following relation between SCE reference and reversible hydrogen electrode scale can hold true:

$$E_{RHE} = E_{SCE} + 0.949\,V$$

Accordingly, all the electrochemical results presented in this work were presented with respect to RHE.

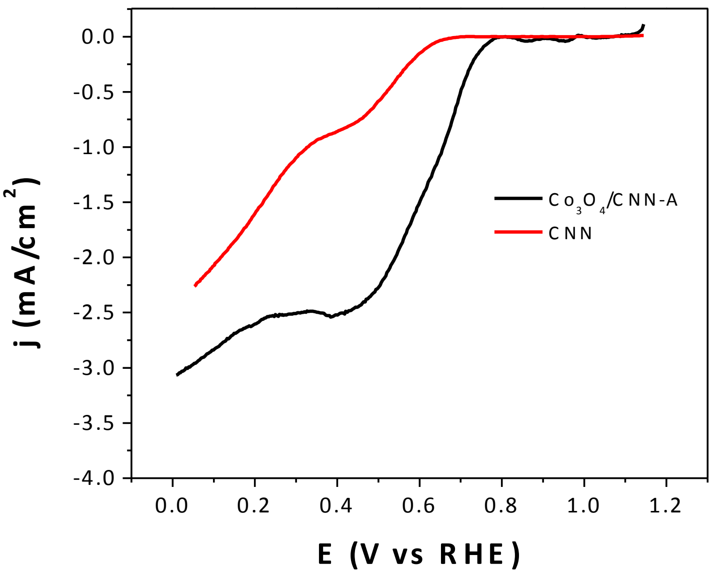

Figure S3. RDE steady-state polarization curve at 900 rpm for the ORR using Co_3O_4/CNN-A and CNN catalysts in oxygen-saturated KOH (0.1 M). The sample, named CNN, is prepared using 0.1 mM $FeCl_3$ (5 mg) to promote the formation of silica coating around the cellulose nanowhiskers through in the nanoreactor synthetic method. The residual Fe species were removed during removal of silica coating afterwards.