

## Supporting Information

### **Exfoliated graphite with spinel oxide as an effective hybrid electrocatalyst for water splitting**

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## Table of contents

Experimental .....	3
Synthesis of $\text{MnCo}_2\text{O}_4$ .....	3
Synthesis of hybrid nanostructures .....	3
Material characterization .....	3
Electrochemical measurements .....	4
References .....	8

## **Experimental**

### **Synthesis of MnCo<sub>2</sub>O<sub>4</sub>**

In the method used, MnCo<sub>2</sub>O<sub>4</sub> was synthesized by co-precipitation using oxalic acid as a precipitating agent. First, 3 mmoles of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and 3 mmoles of Mn(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O were dissolved in 25 mL of distilled water. The resulting mixture was added to a solution containing 22.5 mmoles of oxalic acid, 25 mL of ethyl alcohol, and 25 mL of distilled water and left on a magnetic stirrer for 2 h. After this time, the mixture was placed in a laboratory dryer at 50°C for 6 hours. Then the obtained suspension was filtered on a Büchner funnel and dried in a laboratory dryer at 80°C for 12 hours. In the final step, the obtained mass was subjected to an annealing process conducted in an atmosphere of inert gas N<sub>2</sub>, at 900°C with a heating rate of 3.14°C min<sup>-1</sup>, and after reaching the set temperature, the sample was annealed for 8 hours.

### **Synthesis of hybrid nanostructures**

In the first step, the carbon material was obtained by electroexfoliation of graphite sheet in 0.5 M H<sub>2</sub>SO<sub>4</sub> at +5 V until the graphite sheet was completely disintegrated, and the material obtained after exfoliation was washed with distilled water, drained on a slow funnel, and then dried at 80°C for 24 h and was denoted as EG. In the next step, EG material was suspended in 10 mL of ethyl alcohol and 10 mL of distilled water and mixed with a mass of spinel-type metal oxide before annealing. The hybrid nanostructures based on MnCo<sub>2</sub>O<sub>4</sub> and EG (MnCo<sub>2</sub>O<sub>4</sub>/EG) were obtained by three different mass ratios of reagents 2:1, 1:1, 1:2, 1:3, and 3:1, then the materials were annealed the same way as MnCo<sub>2</sub>O<sub>4</sub>. The obtained samples were labeled MnCo<sub>2</sub>O<sub>4</sub>/EG (2/1), MnCo<sub>2</sub>O<sub>4</sub>/EG (1/1), MnCo<sub>2</sub>O<sub>4</sub>/EG (1/2), MnCo<sub>2</sub>O<sub>4</sub>/EG (1/3), and MnCo<sub>2</sub>O<sub>4</sub>/EG (3/1).

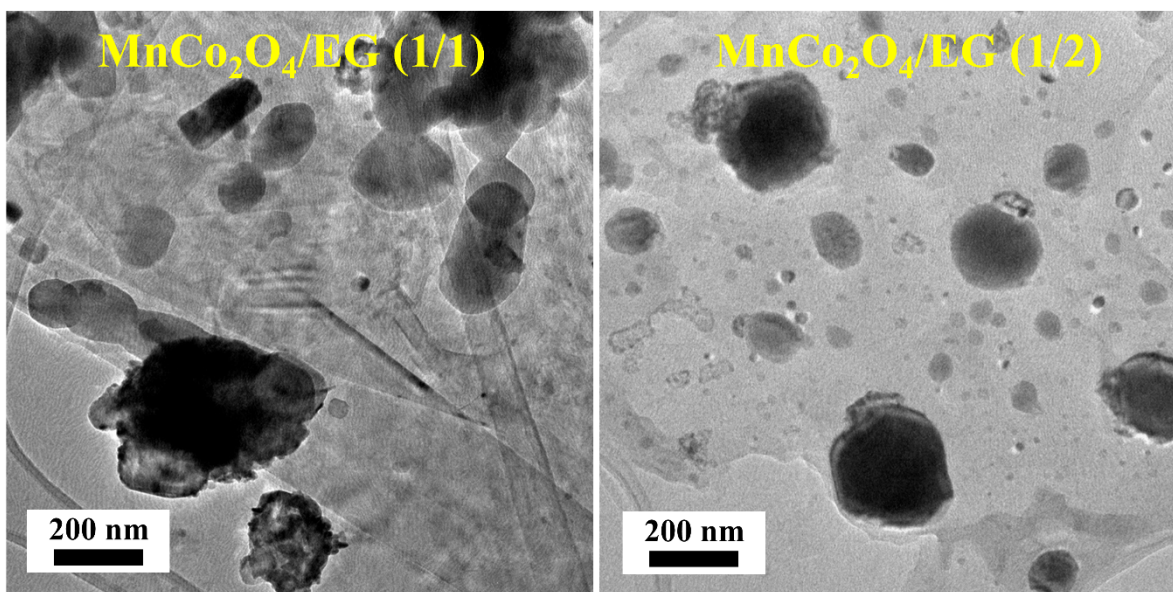
### **Material characterization**

Information on the crystallographic structure of the studied materials at the atomic level was provided using images obtained using high-resolution transmission electron microscopy (HRTEM) produced by FEI Europe, model Tecnai F20 X-Twin, operating at an accelerating voltage of 200 kV. X-ray diffractographic (XRD) analysis of the materials obtained was performed using a Philips X'Pert X-ray diffractometer, with an X'Celerator Scientific detector employing Cu K $\alpha$  radiation ( $\lambda=0.15406$  nm), angles ranging from 10° to 80° with step size

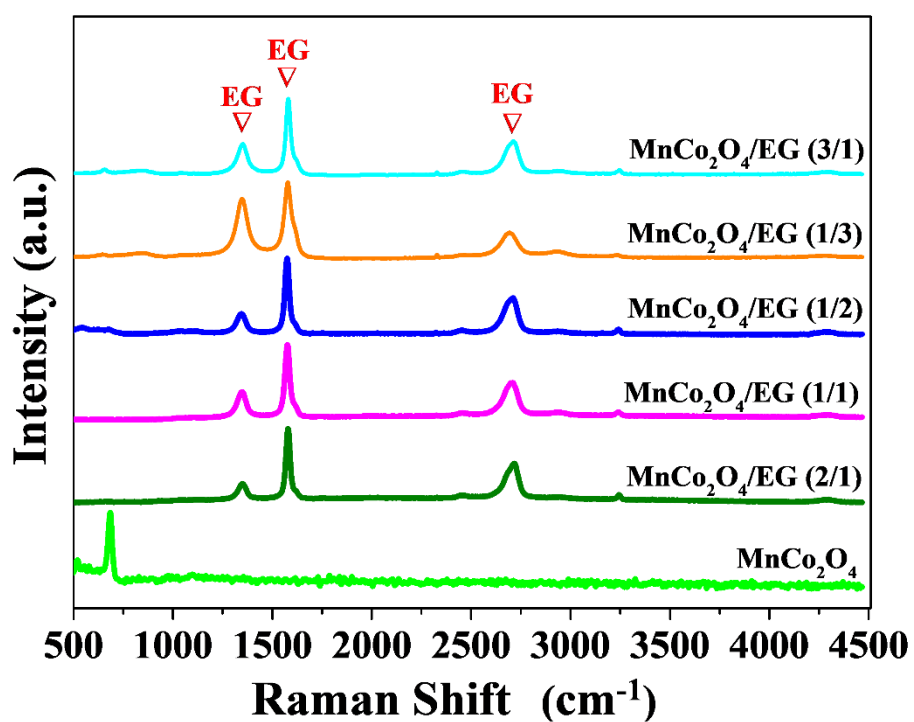
0.02. Raman spectra were obtained by a Renishaw InVia Raman analyzer (laser wavelength 532 nm, Renishaw Company). X-ray photoelectron spectroscopy (XPS) analysis was performed with a PHI5000 VersaProbe II Scanning XPS Microprobe spectrometer (ULVAC-PHI, Chigasaki), using a monochromatic Al K $\alpha$  radiation source.

### **Electrochemical measurements**

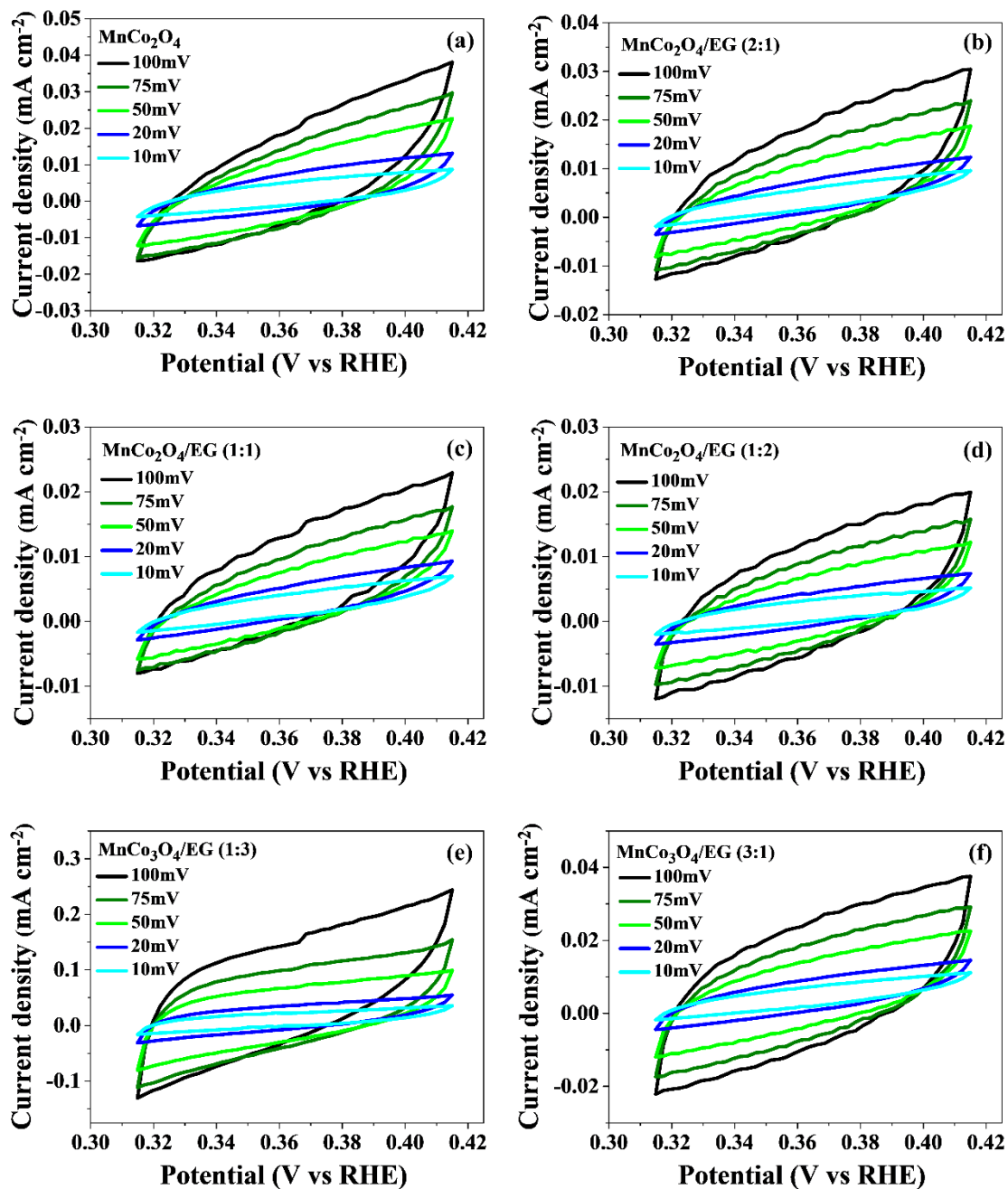
To check the potential application of the electrocatalytic activity of the obtained hybrid materials in the H<sub>2</sub> evolution reaction and the O<sub>2</sub> evolution reaction samples were investigated using linear sweep voltammetry (LSV). Electrochemical measurements were performed with an Autolab electrochemical analyzer (PGSTAT128, the Netherlands) using a three-electrode system. The reference electrode was Ag/AgCl (saturated KCl), a platinum plate was used as the counter electrode, and hybrid catalysts applied to a glassy carbon electrode (GCE) with a diameter of 3 mm were used as the working electrode. The catalytic ink was prepared by suspension of 3 mg of the samples in 0.75 mL of distilled water, 0.2 mL of isopropanol, and 0.05 mL of 5% aqueous Nafion solution. The obtained suspension was sonicated in an ultrasonic bath for 60 minutes. In the next step, the prepared catalytic ink was placed on the polished surface of the glassy carbon electrode, then left to dry oven for a few minutes at 60°C. The catalytic activity of reference materials such as Pt/C catalyst (20 wt% Pt) for the hydrogen evolution reaction (HER) and a mixture of ruthenium (IV) oxide and iridium (IV) oxide in a 1:1 ratio for the OER reaction were also measured. The potential measurements carried out were recalculated against a reversible hydrogen electrode (RHE). The activity of the samples in the OER and HER reactions was tested at a scan rate of 1 mV s<sup>-1</sup> in aqueous electrolyte of 1 M KOH. Stability for the best samples from LSV measurements was performed at the constant potential to achieve a current density of 10 mA cm<sup>-2</sup>. In order to characterize the obtained catalysts, cyclic voltammetry measurements were also performed before and after the HER and OER tests. Moreover, the electrochemically active surface area (ECSA) was estimated through the cyclic voltammetry method. Under a non-Faradaic region, a series of CV scans were performed at different scan rates. The double-layer capacitance (CDL) was found by obtaining the slope of the linear fit. The ECSA of obtained electrodes was determined on the basis of the equation:  $ECSA = C_{DL}/C_s$ , where  $C_s$  is the specific capacitance. The  $C_s$  used for our calculations was 0.040 mF cm<sup>-2</sup>.<sup>1</sup>



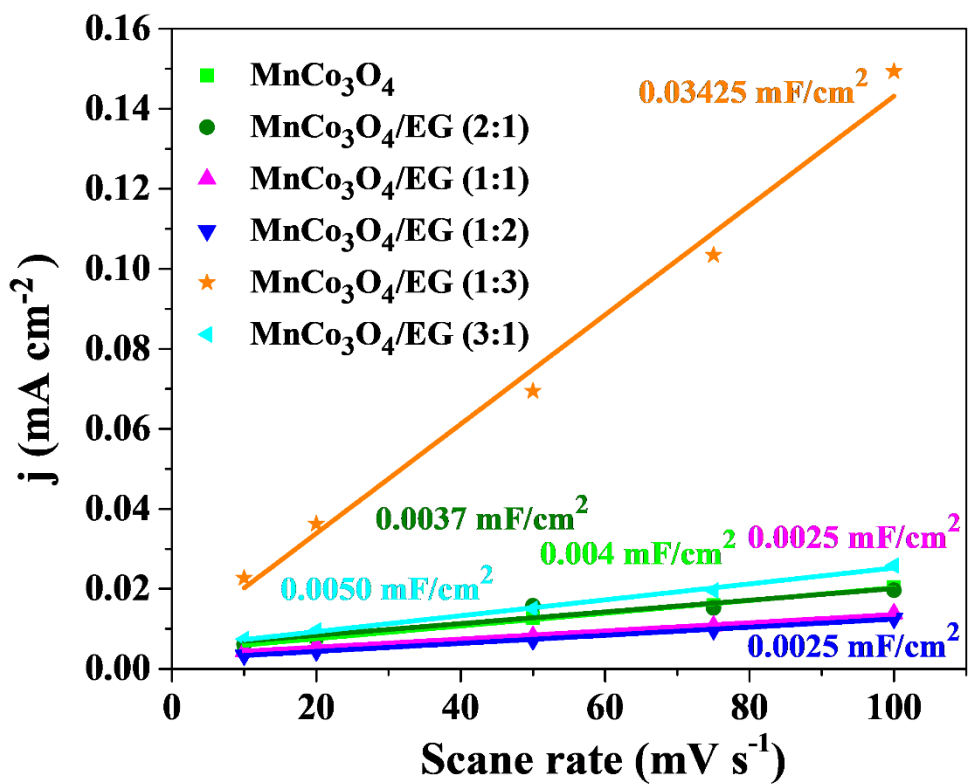
**Figure S1.** HRTEM images of MnCo<sub>2</sub>O<sub>4</sub>/EG (1/1) and MnCo<sub>2</sub>O<sub>4</sub>/EG (1/2).



**Figure S2.** Raman spectra of MnCo<sub>2</sub>O<sub>4</sub> and MnCo<sub>2</sub>O<sub>4</sub>/EG series at different place of sample than for spectra presented on Figure 2(b).



**Figure S3.** Cyclic voltammograms of obtained electrodes used to determine the electrochemical double-layer capacitance (Cdl) and estimate the electrochemically active surface area (ECSA). CV were performed on between 0.31 V and 0.42 V vs RHE at different scan rates (10, 20 50 75, 100 mV s<sup>-1</sup>).



**Figure S4.** Calculated double-layer capacitance (CDL) used to estimate the electrochemically active surface area of the obtained catalysts.

**Table S1.** The ECSA parameters for the obtained catalysts.

<b>Electrode</b>	<b>Estimated ECSA (cm<sup>2</sup>) (0.04 mF cm<sup>-2</sup>) in 1 M KOH</b>
<b>MnCo<sub>2</sub>O<sub>4</sub></b>	0.1
<b>MnCo<sub>2</sub>O<sub>4</sub>/EG (2:1)</b>	0.093
<b>MnCo<sub>2</sub>O<sub>4</sub>/EG (1:1)</b>	0.063
<b>MnCo<sub>2</sub>O<sub>4</sub>/EG (1:2)</b>	0.063
<b>MnCo<sub>2</sub>O<sub>4</sub>/EG (1:3)</b>	0.856
<b>MnCo<sub>2</sub>O<sub>4</sub>/EG (3:1)</b>	0.125

## References

1. P. Connor, J. Schuch, B. Kaiser and W. Jaegermann, *Zeitschrift für Physikalische Chemie*, 2020, **234**, 979-994.