

**One-step synthesis of nitrogen-doped few-layer graphene structures decorated with  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$  nanoparticles for highly efficient electrocatalysis of oxygen reduction reaction**

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**1. Experimental**

Samples for scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) were prepared by drop-casting of ultra-sonicated nanocomposite suspension onto the surface of a conductive substrate followed by air-drying at ambient temperature. SEM images were taken with a Zeiss SUPRA 25 microscope (Carl Zeiss, Germany) equipped with an EDS detector for energy dispersive X-ray (EDX) analysis. XPS spectra were obtained using a Specs PHOIBOS 150 MCD electron spectrometer (Specs, Germany) with a Mg cathode ( $h\nu = 1253.6$  eV). The vacuum in the spectrometer chamber did not exceed  $4 \cdot 10^{-8}$  Pa. The spectra were recorded in a mode of constant transmission energy (40 eV for survey spectra and 10 eV for individual lines). The survey spectrum was recorded in 1.00 eV increments, while the spectra of individual lines were recorded in 0.03 eV increments. Background subtraction was carried out according to the Shirley method and spectra deconvolution was performed using the CasaXPS processing software (version 2.3.19). Quantification of atomic content was carried out using the sensitivity factors from the elemental library of CasaXPS. The studied area was 300–700  $\text{mm}^2$  while the information depth, 1–2 nm. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEM-2100 Electron Microscope (JEOL Ltd., Japan). The samples for TEM were prepared via ultrasonication of the  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$  powder in ethanol and drop-casting of the obtained suspension on a carbon-coated TEM grid. XRD pattern was recorded using an Aeris (Malvern PANalytical B.V.) XRD powder diffractometer with a Cu  $K\alpha$  radiation ( $\lambda = 1.5406$  Å). Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA (PerkinElmer, USA) in air. The sample was heated up to 800 °C at a constant heating rate of 10 °C/min.

The linear-sweep voltammetry (LSV) measurements were performed in a three-electrode cell using a RRDE-3A ring rotating disk electrode setup (ALS Co., Ltd, Japan) with an Elins P-20X potentiostat (Elins, Russia). The glassy carbon (GC) disc 3 mm in diameter pressed in a PEEK polymer was used as a working electrode; platinum coil, as a counter electrode; and the Ag/AgCl (sat. KCl) electrode as a reference to which all values of potential ( $E$ ) were referred. 7

$\mu\text{L}$  of the aqueous suspension of the catalyst (ca.  $0.4 \text{ mg}\cdot\text{mL}^{-1}$ ) containing ca. 0.1 wt % of Nafion polymer were drop-cast onto the glassy carbon electrode and dried at ambient temperature. As a result, the catalyst loading was ca.  $400 \text{ }\mu\text{g}\cdot\text{cm}^{-2}$ . The surface of the initial GC electrode was polished with a  $0.3 \text{ }\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder. The LSV measurements were performed in air-saturated aqueous solution of 0.1 M KOH, potential scan rate  $v$  was  $10 \text{ mV}\cdot\text{s}^{-1}$ , electrode rotation rate was 640–4900 rpm. Number of electrons  $n$  in the electrode reaction was calculated from the LSV curves using the Koutecký–Levich equation:<sup>S1</sup>

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \quad (\text{S1})$$

$$j_k = nFkc^0 \quad (\text{S2})$$

$$j_d = 0.62nFD^{2/3}\omega^{1/2}v^{-1/6}c^0, \quad (\text{S3})$$

where  $j_k$  and  $j_d$  are densities of the kinetic and limiting diffusion current, respectively,  $[j] = \text{mA}\cdot\text{cm}^{-2}$ ;  $k$  is a rate constant of oxygen reduction reaction,  $[k] = \text{cm}\cdot\text{s}^{-1}$ ;  $\omega$  is angular velocity of electrode rotation,  $[\omega] = \text{rad}\cdot\text{s}^{-1}$ ;  $F$  is the Faraday constant,  $F = 96.485 \text{ C}\cdot\text{mol}^{-1}$ ;  $D$  is oxygen diffusivity in 0.1 M KOH,  $D = 1.9\cdot 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ ;  $v$  is kinematic viscosity of 0.1 M KOH,  $v = 0.01 \text{ cm}^2\cdot\text{s}^{-1}$ ;  $c^0$  is bulk concentration of dissolved oxygen,  $c^0 = 0.24\cdot 10^{-3} \text{ mol L}^{-1}$  in 0.1 M KOH solution.<sup>S2,S3</sup>

For the Tafel plots, the kinetic current was calculated from the mass-transport correction of RDE current:

$$j_k = \frac{j_d j}{j_d - j} \quad (\text{S4})$$

Catalyst stability was probed by the chronoamperometry at  $-0.3 \text{ V}$  at the electrode rotation rate of 2000 rpm in air-saturated 0.1 M KOH solution at room temperature. Furthermore, accelerated durability test was performed as a potential cycling at a scan rate of  $100 \text{ mV/s}$  in the  $E$  region from 0 to  $-1300 \text{ mV}$  in air-saturated 0.1 M KOH. The LSVs for  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$  at 2000 rpm were collected before and after 500 and 1000 potential cycles.

## References

- S1 A. J. Bard and L. R. Faulkner, *Electrochemical methods: Fundamentals and applications*, 2nd ed., Wiley, New York, 2001.
- S2 L. T. Qu, Y. Liu, J. B. Baek and L. M. Dai, *ACS Nano*, 2010, **4**, 1321.
- S3 G. Jürmann and K. Tammeveski, *J. Electroanal. Chem.*, 2006, **597**, 119.

## 2. Composition of Mn<sub>1.5</sub>Co<sub>1.5</sub>O<sub>4</sub>/N-FLGS sample

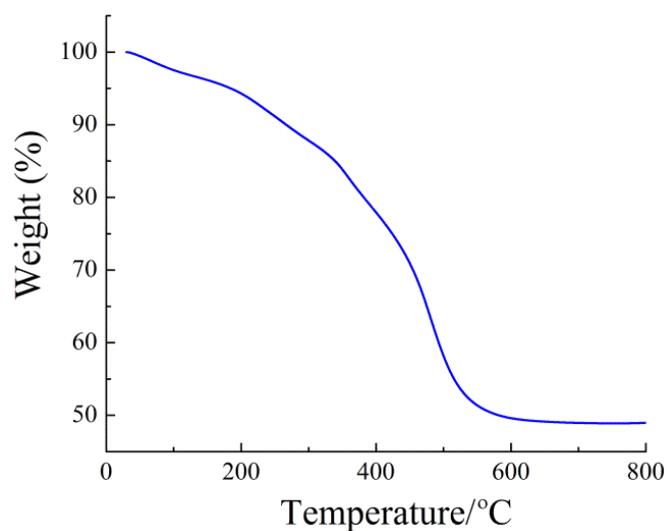
**Table S1** Elemental composition of the surface layer of Mn<sub>1.5</sub>Co<sub>1.5</sub>O<sub>4</sub>/N-FLGS (according to XPS results).

C, at. %	O, at. %	N, at. %	S, at. %	Co, at. %	Mn, at. %
57.1	32.8	5.8	0.8	1.8	1.7

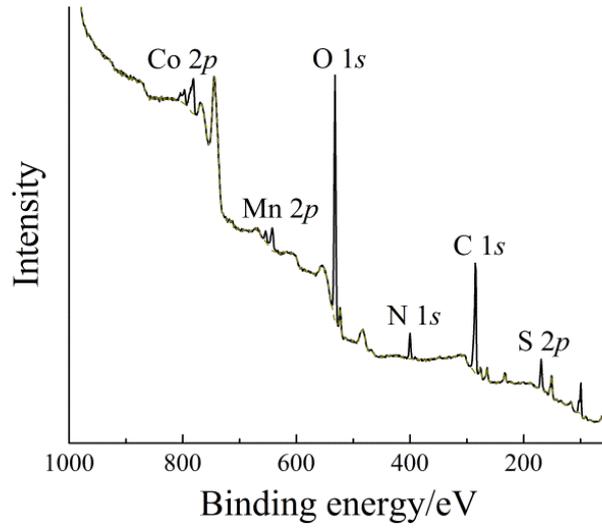
**Table S2** Elemental composition of the bulk Mn<sub>1.5</sub>Co<sub>1.5</sub>O<sub>4</sub>/N-FLGS material (as determined by EDX).

C, at. %	O, at. %	N, at. %	S, at. %	Co, at. %	Mn, at. %
50.5	30.7	4.0	1.0	7.0	6.8

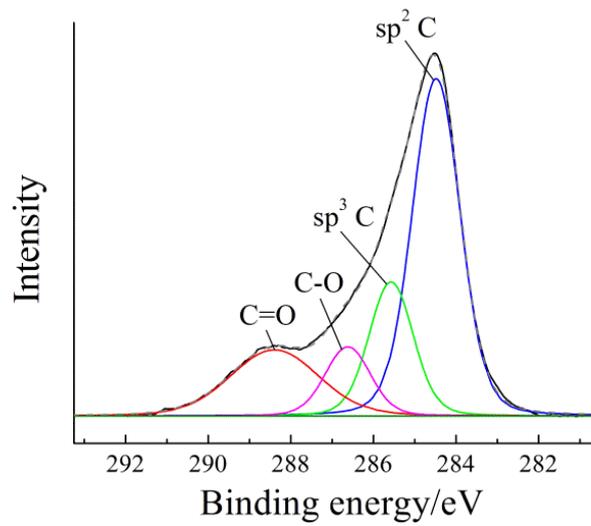
A significant difference between Co and Mn content determined by XPS and EDX is apparently conditioned by various concentration of metals in the bulk and on the surface of the sample.



**Figure S1** TGA curve for Mn<sub>1.5</sub>Co<sub>1.5</sub>O<sub>4</sub>/N-FLGS obtained in air in the temperature range from 25 to 800 °C.



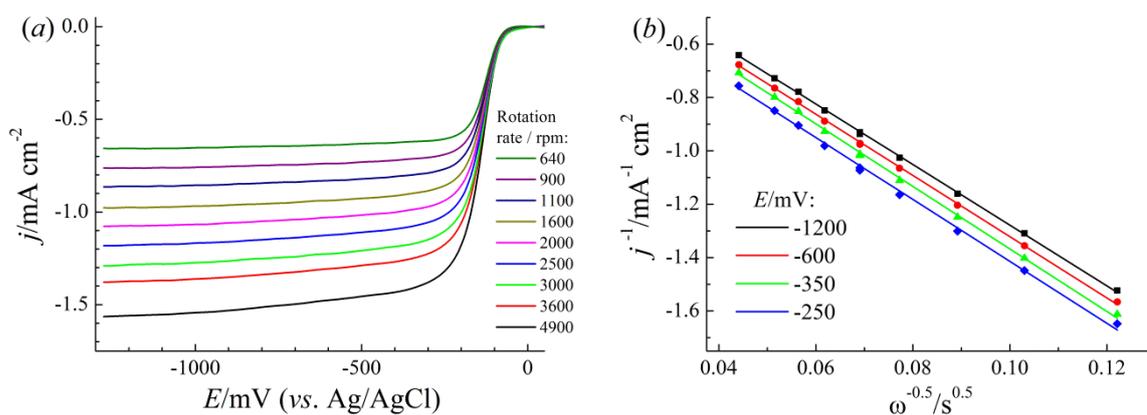
**Figure S2** Survey XPS spectrum of  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$ .



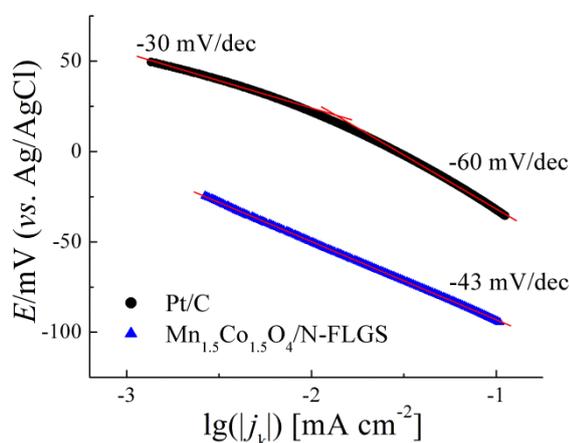
**Figure S3** C 1s high resolution XPS spectrum of  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$  composite.

### 3. Oxygen reduction reaction on $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$ in air-saturated 0.1 M KOH

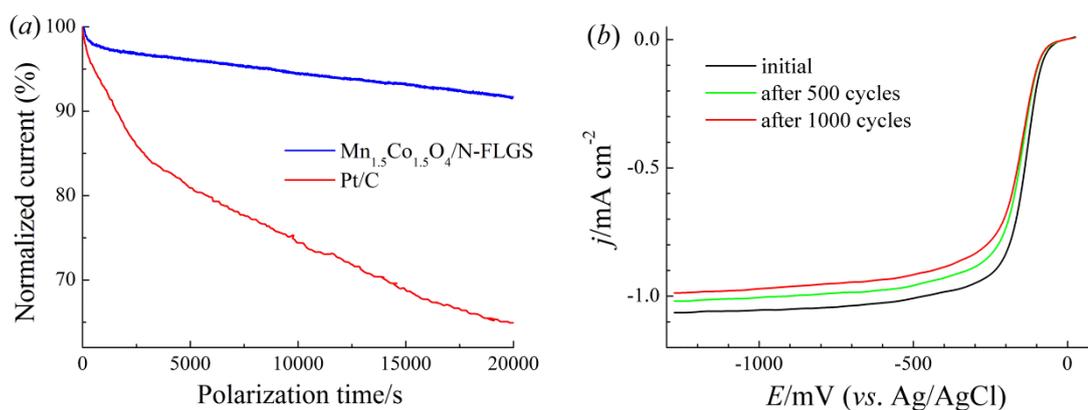
solution



**Figure S4** (a) LSVs on a GC electrode coated with  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$  at different electrode rotation rates; (b) relevant Koutecký-Levich plots at selected potentials.



**Figure S5** Tafel plots for  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$  and Pt/C catalysts.



**Figure S6** (a) Chronoamperograms in air-saturated 0.1 M KOH at  $E = -0.3$  V for the  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{N-FLGS}$  nanocomposite and Pt/C catalyst; (b) LSVs before and after 500 and 1000 potential cycles. Electrode rotation rate is 2000 rpm.