

Electrode materials based on α -NiCo(OH)₂ and rGO for high performance energy storage devices

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Electronic Supplementary Information

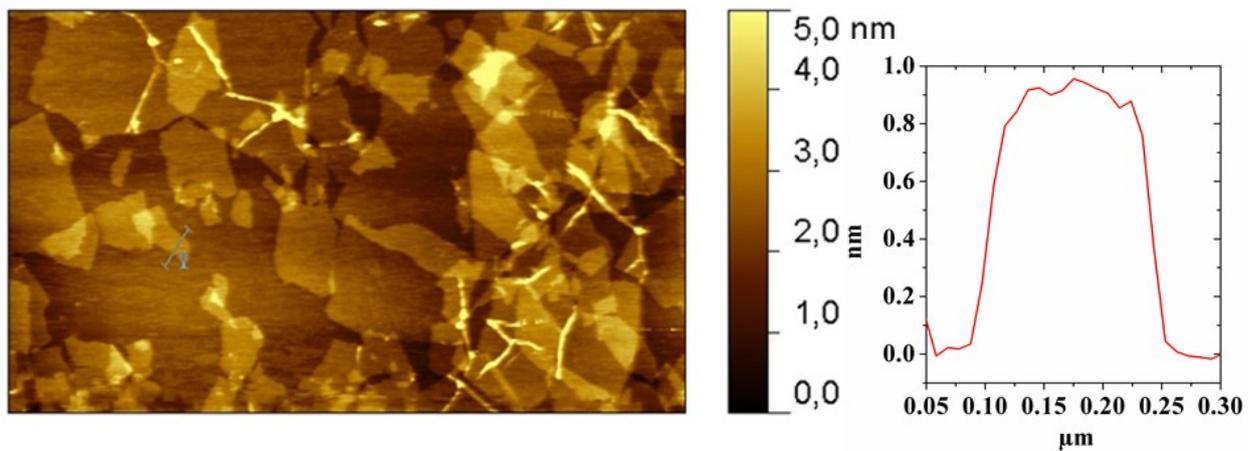


Fig. S1. Tapping mode AFM topographic image and height profile of GO on mica.

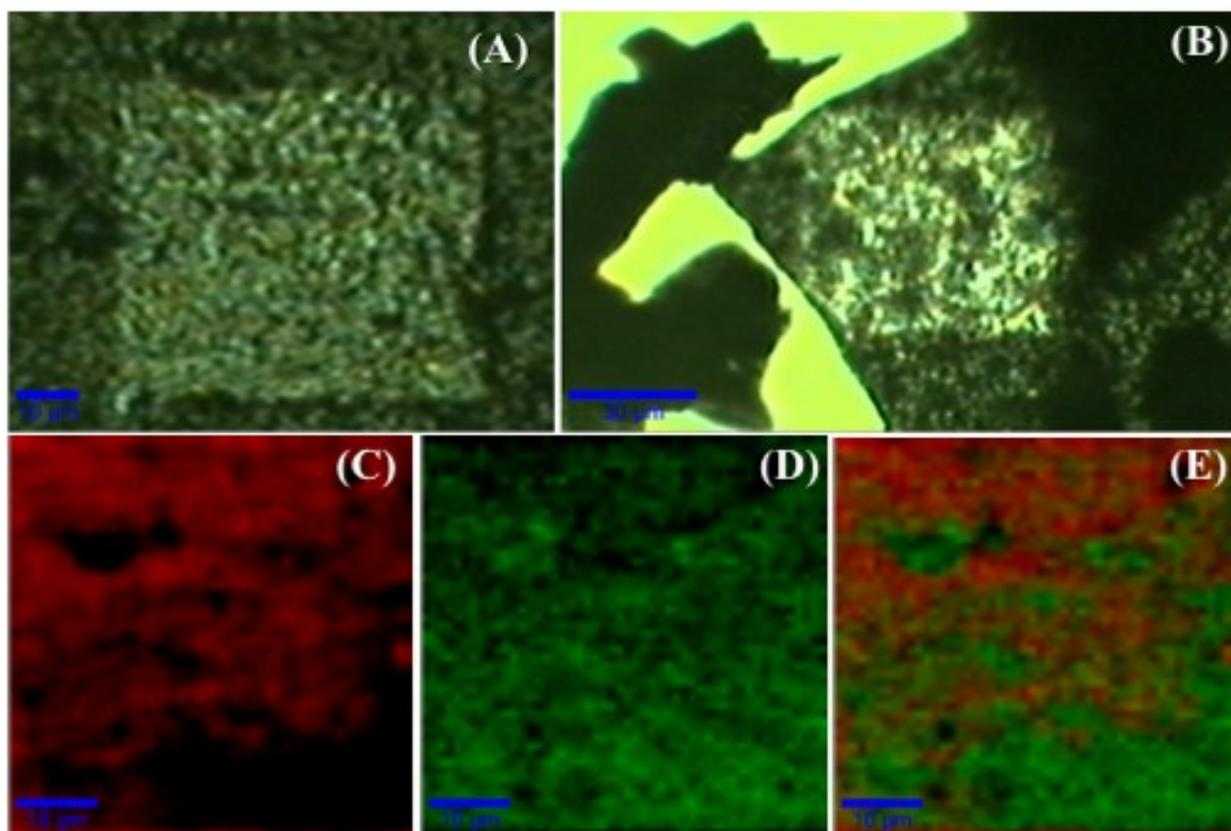


Fig. S2. Optical image of (A) Ni@rGO, (B) NiCo@rGO powder after a confocal Raman microscopy scan in the lighter square area, and confocal Raman image of (C) rGO, (D) NiO and (E) combination image of rGO + NiO in the Ni@rGO nanocomposite.

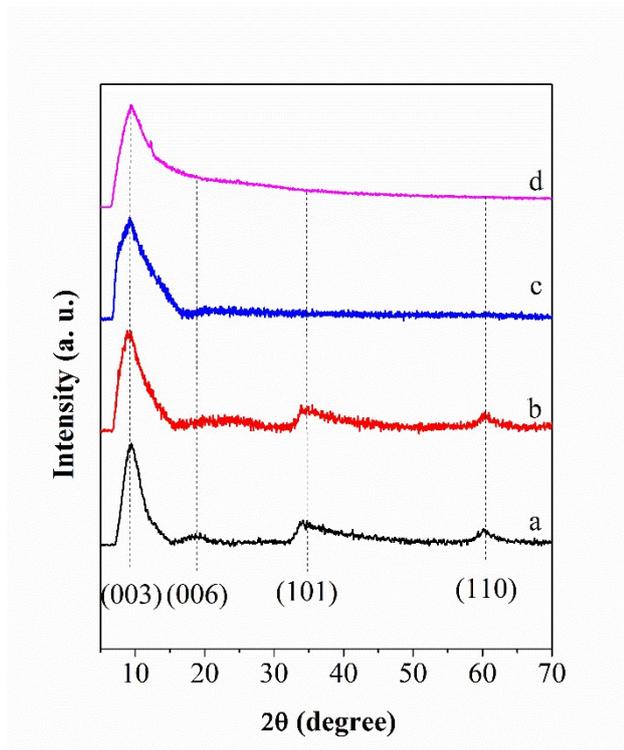


Fig. S3. X-ray diffractograms of a) α -Ni(OH)₂, b) Ni@rGO, c) NiCo and d) NiCo@rGO. The main reflection planes were indicated in the figure.

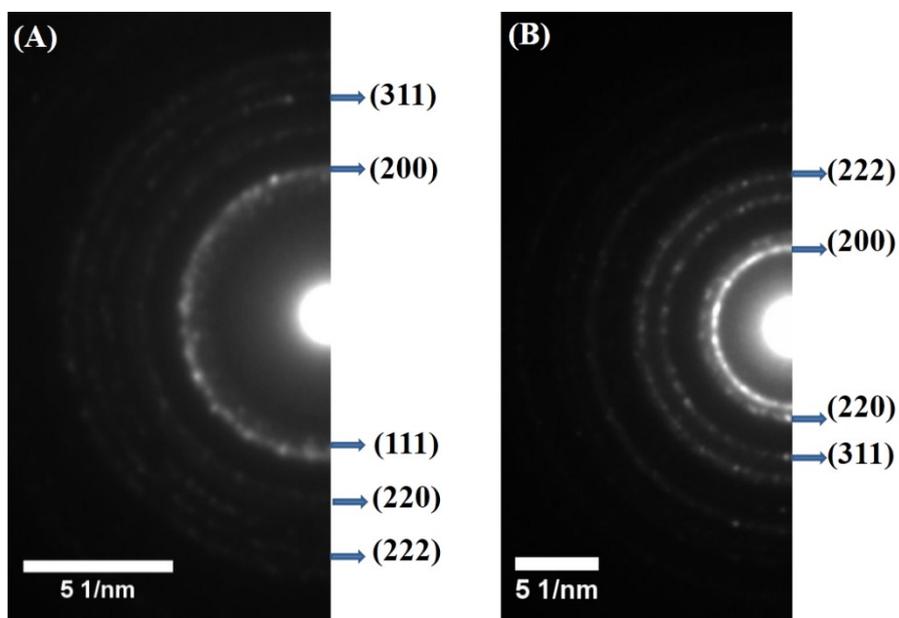


Fig. S4. Selected area diffraction pattern of (A) NiO e (B) (NiCo)O generated *in situ* by the local heating induced by the electron beam.

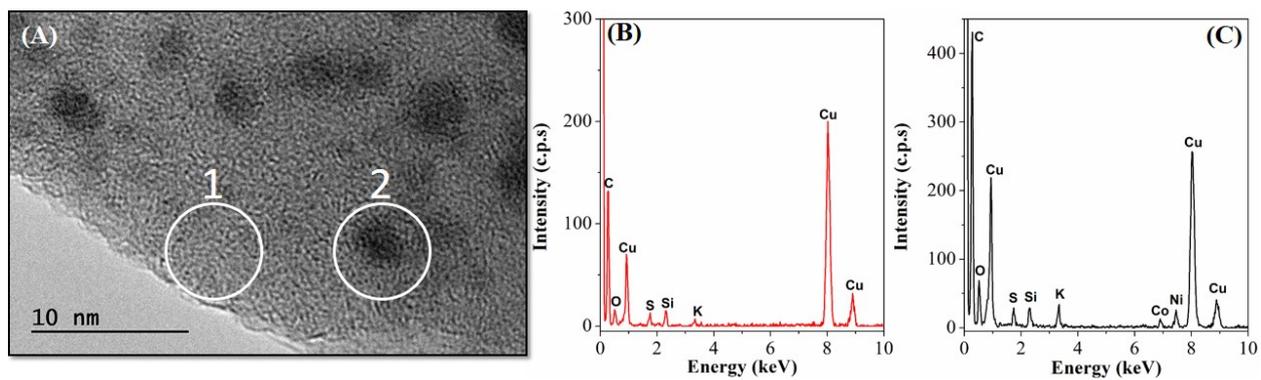


Fig. S5. TEM image of a sheet of NiCo@rGO (A) and the EDS spectrum of an area without (B) and with (C) a NiCo mixed oxide NP.

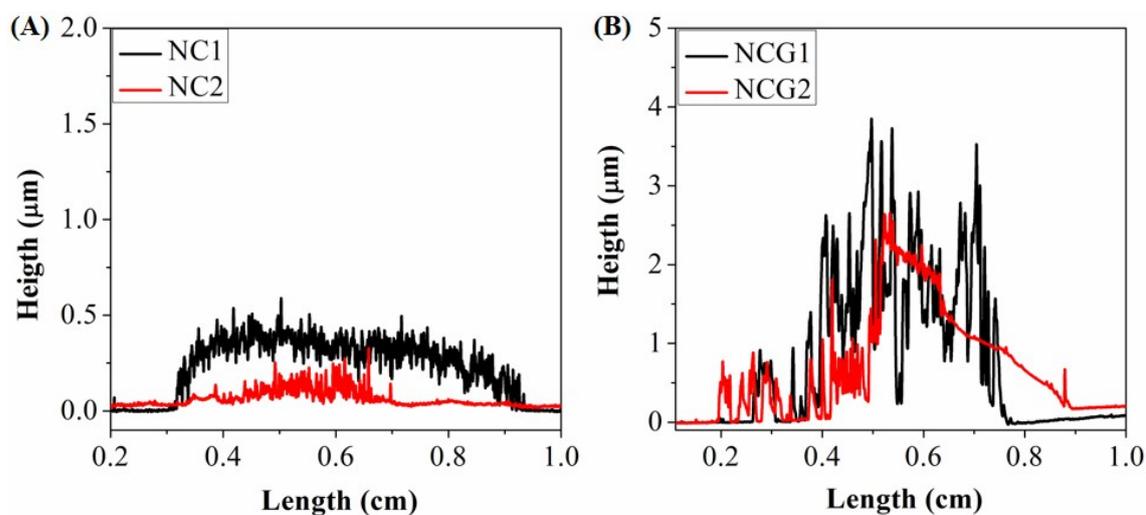


Fig. S6. Dektak profile of an FTO glass with a α -NiCo(OH)₂ (NC1 and NC2) (A) and NiCo@rGO (NCG1 and NCG2) nanocomposite film deposited in a selected area defined by Scotch tape after heat treatment at 240 °C (B). The deposition was carried out by spin coating at 1500 and 2500 rpm respectively.

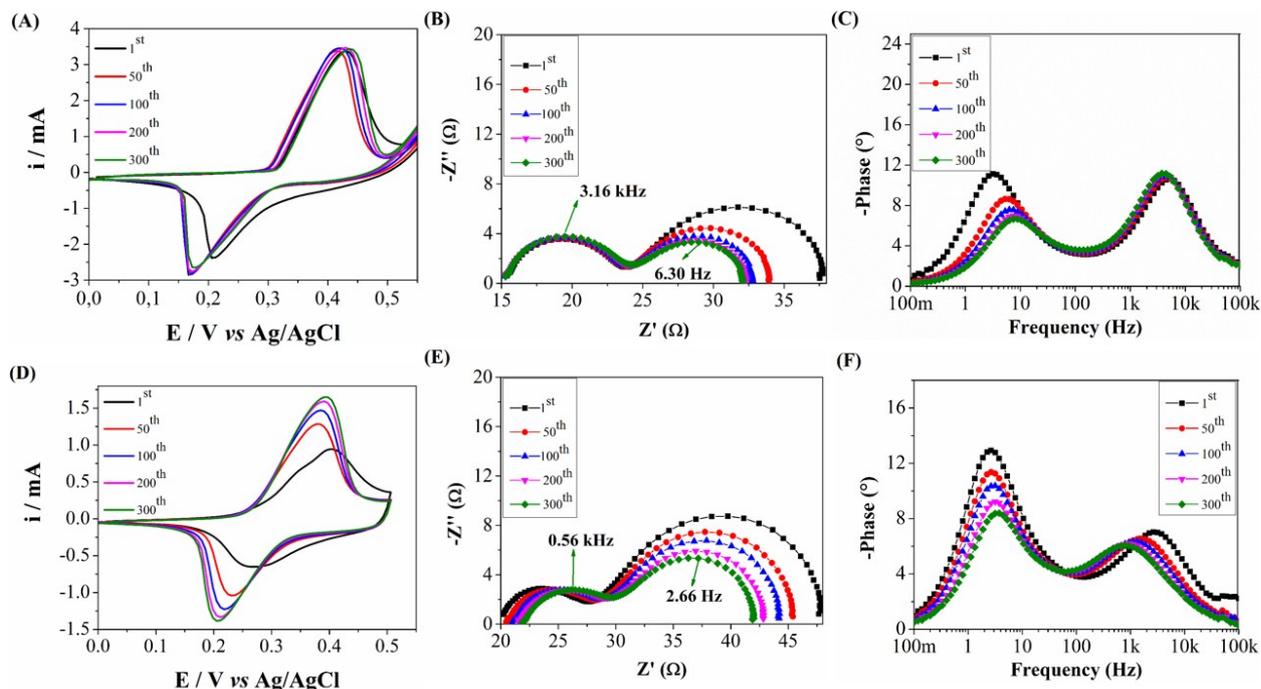


Fig. S7. Cyclic voltammograms (A, D), Nyquist (B, E) and Bode phase (C, F) plots of EIS data registered for α -Ni(OH)₂ (A, B, C) and α -NiCo(OH)₂ (D, E, F), along 300 CV cycles intercalated by EIS measurements at DC potential of 0.6 V superimposing an AC perturbation ($\Delta E=10$ mV) in the 0.01 to 100,000,000 Hz range (1500 rpm).

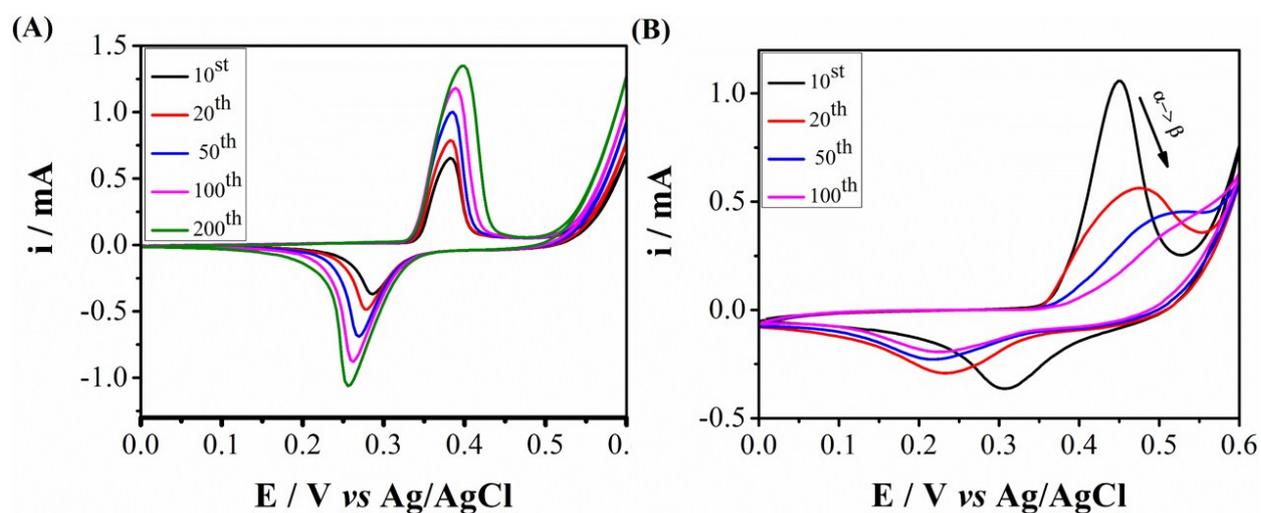


Fig. S8. Cyclic voltammograms of a glassy carbon electrode spin coated (4000 rpm) with (A) as prepared α -Ni(OH)₂ sol and (B) after washing with water.

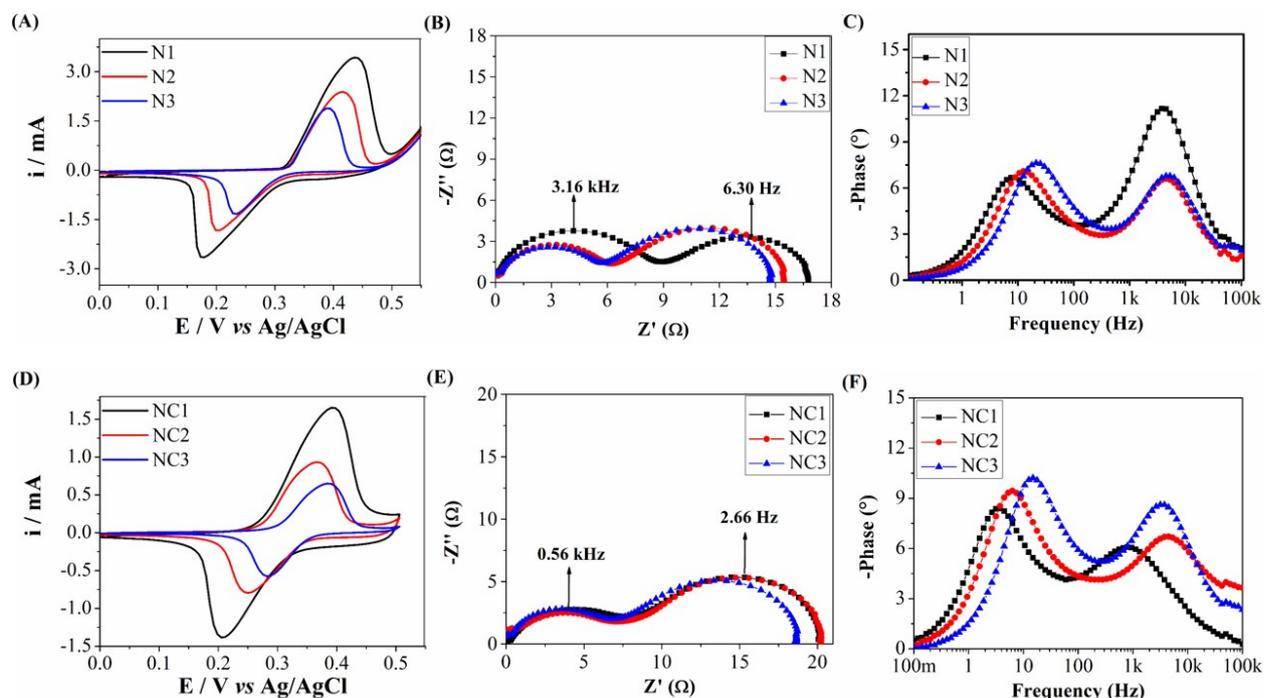


Fig. S9. Cyclic voltammograms at $v = 50 \text{ mV}\cdot\text{s}^{-1}$ (A, D), Nyquist (B, E) and Bode (C, F) plots of EIS data registered for $\alpha\text{-Ni(OH)}_2$ (A, B, C) and $\alpha\text{-NiCo(OH)}_2$ (D, E, F) as a function of thickness, after 300 CV cycles, in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH solution. The EIS measurements were carried out at DC potential of 0.6 V superimposing an AC perturbation ($\Delta E=10 \text{ mV}$) in the frequency range from 0.01 to $100,000 \text{ Hz}$ (R_s value was subtracted from Z').

The nanocomposite was deposited on FTO electrodes by spin-coating and the thickness controlled by the rotation rate. The thickness of films after heat treatment at $240 \text{ }^\circ\text{C}$ was measured using a Dektak Stylus Profiler. As expected, the pure NiCo films are more homogeneous than that of the NiCo@rGO composite, particularly when a larger amount of material is deposited forming about $0.3\text{-}0.4 \text{ }\mu\text{m}$ thick films (Fig. S9B). Thinner films showed to be more heterogeneous, probably because of formation of islands a tendency more clearly seen in the nanocomposite. In this case, the films are much more heterogeneous due to the presence of rGO nanosheets that seems to stack generating islands whose height can be as large as $2.5\text{-}3.5 \text{ }\mu\text{m}$ (NCG1). Thin films are produced at 4000 rpm (NCG4) as confirmed by the possibility of clearly imaging the FTO substrate (Fig. S9A).

Thin films of NiCo@rGO composite with some few sheets of rGO covered with NiCo nanoparticles superimposed to each other are formed at 4000 rpm (NCG 3) as revealed by the SEM images in which the FTO nanocrystals are clearly seen (Fig. S10). Clearly the film is not completely homogeneous but there are darker areas with larger thickness. This tendency of stacking becomes more pronounced as the surface concentration increases, as shown in Figures S9A-B discussed above (referee 1), leading to the formation of islands with larger electronic conductivity whereas the spaces in between them favoring the ionic diffusion. Both should be acting synergically to enhance the electron transfer rate in the composite material and the NiCo(OH)₂/NiCoOOH redox process.

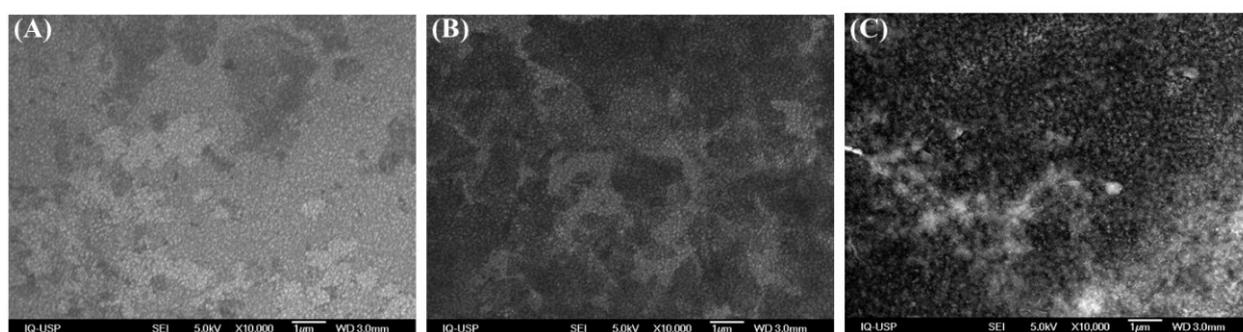


Fig. S10. SEM images of FTO electrodes with NiCo@rGO films deposited by spin coating at (A) 4000 rpm (NCG3), (B) 2500 rpm (NCG2) and (C) 1500 rpm (NCG1), after heat treatment at 240 °C for 30 min.

Tables

Table S1: Average thickness and mass of nanocomposite material deposited on the FTO electrodes measured by Dektak Stylus Profiler and by weighing the FTO before and after deposition of nanomaterial and heat treatment at 240 °C.

Electrode	Thickness (μm)	Mass (mg)
NC1	0.3 \pm 0.1	3.4 \pm 0.3
NC2	0.1 \pm 0.07	1.2 \pm 0.2
NC3	-	0.7 \pm 0.2
NCG1	3 \pm 2	3.2 \pm 0.3
NCG2	2 \pm 1.5	1.3 \pm 0.2
NCG3	-	0.9 \pm 0.2

Table S2. Electrochemical parameters determined from the CVs of all modified electrodes in 1.0 mol·L⁻¹ KOH solution as supporting electrolyte.

Sample	Cycle	Peak Potencial (mV)		
		E _{ap}	E _{cp}	ΔE _p
N1	300 th	388	233	155
N2	300 th	415	203	212
N3	300 th	436	179	257
NG1	300 th	404	255	149
NG2	300 th	408	251	157
NG3	300 th	448	222	226
NC1	300 th	386	285	101
NC2	300 th	368	249	119
NC3	300 th	392	209	183
NCG1	300 th	390	256	134
NCG2	300 th	399	255	144
NCG3	300 th	417	255	162