Electronic Supplementary Materials for

NiCo$_2$O$_4$-Based Hybrid Nanocomposites for High-Performance Pseudocapacitor Electrodes

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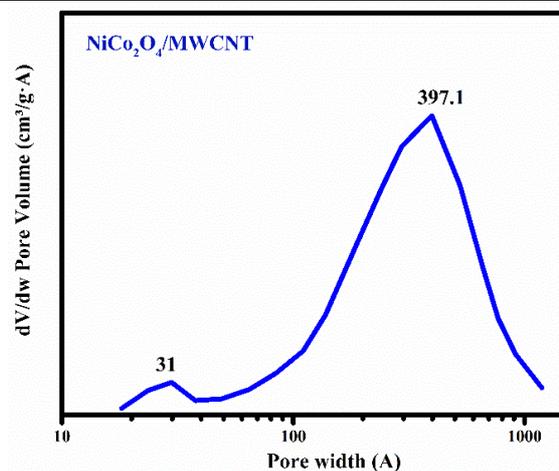
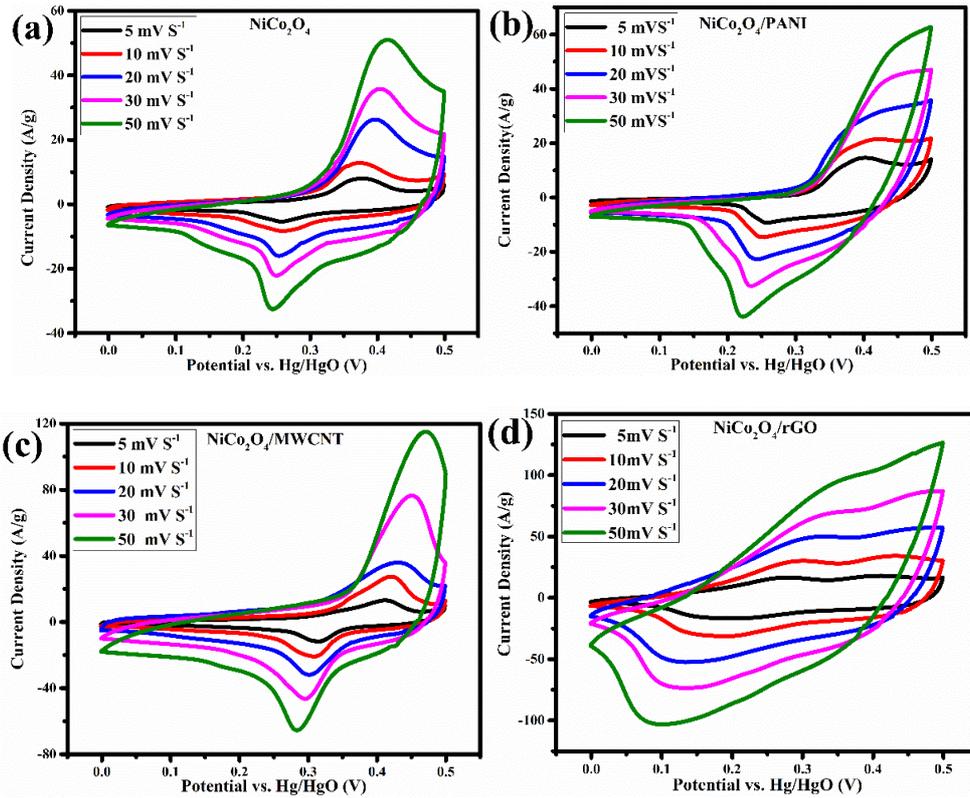**Figure S1**. BJH pore size distributions of NiCo$_2$O$_4$/MWCNT

Figure S2: Evaluation of the electrochemical performance of the hybrid nanocomposites in a three-electrode configuration: CV of (a) $NiCo_2O_4$ cores, (b) $NiCo_2O_4$/PANI, (c) $NiCo_2O_4$/MWCNT and (d) $NiCo_2O_4$/r-GO nanocomposites at scan rates of 5 mVs^{-1} – 50 mVs^{-1} in an aqueous 3 M KOH electrolyte solution.

Determination of specific capacitances

Specific capacitance can be calculated from CV plots at different scan rates by the following relationship:

$$C = \frac{Q}{|(V_2 - V_1)|} \tag{S1}$$

where C is the capacitance (F), V2 the upper voltage (V), V1 the lower voltage (V), and Q the electric charge (C), which can be calculated by integrating the area enclosed in the rectangular CV plot. Moreover, Q can be calculated by integrating the area enclosed in the rectangular CV plot by:

$$Q = \frac{1}{2}\int_{t_1}^{t_2} i(t)dt = \frac{1}{2 \cdot v}\int_{V_1}^{V_2} i(V)dV \tag{S2}$$

assuming:

$$dt = \frac{dV}{v} \tag{S3}$$

where i is the current intensity (A), v is the scan rate (V/s), and t is the time (s). The factor ½ is intriduced to calculate the charge in either the forward or backward scan, and it must be present in the relationship because the enclosed area accounts for both scans. Finally, the capacitance can be calculated as:

$$C = \frac{\int_{V_1}^{V_2} i(V)dV}{2 \cdot v |(V_2 - V_1)|} \tag{S4}$$

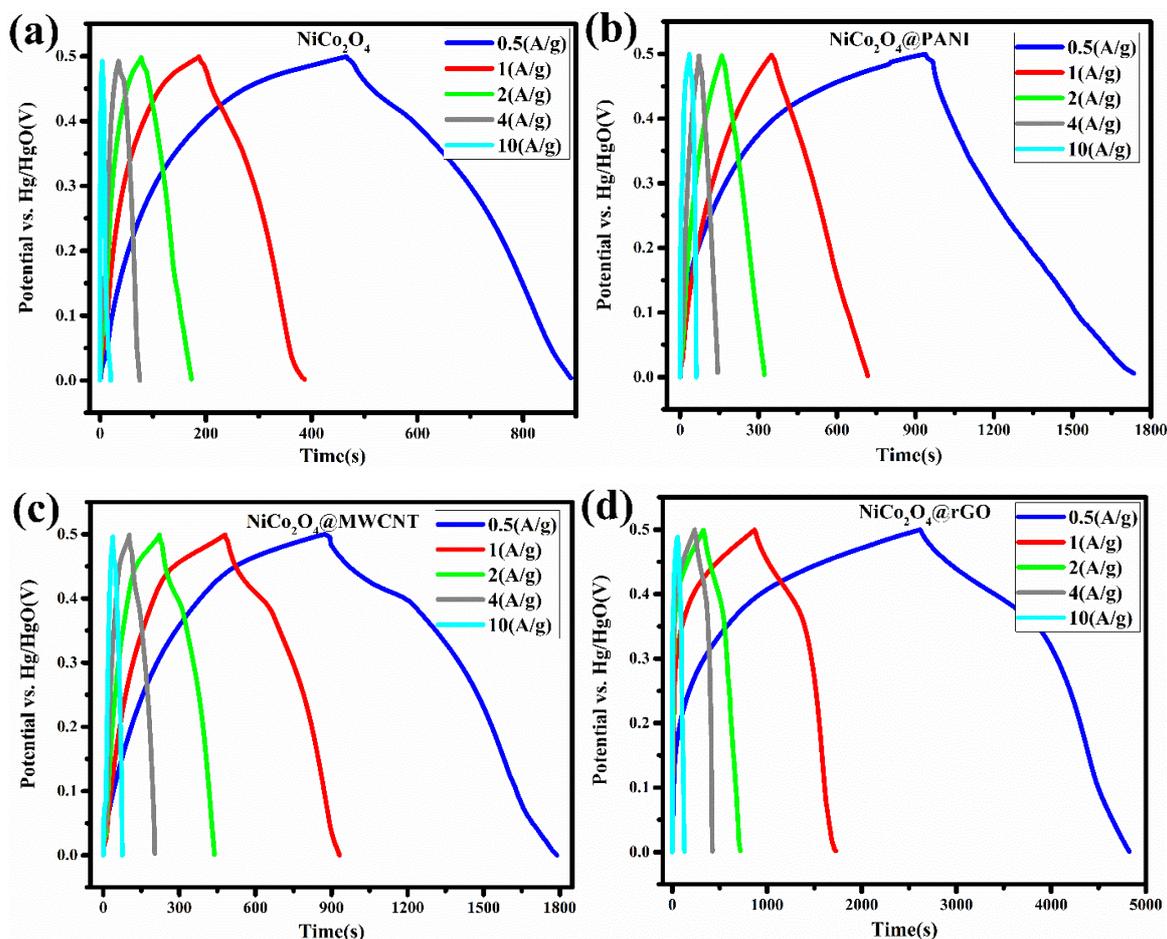To obtain the specific capacitances (C_{sp}), the following equation was used:

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$$C_{sp} = \frac{c}{m}$$
(S5)

41   where m is the mass (g) of loaded material on electrode[1].

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44   **Figure S3**: Galvanostatic charge/discharge plots at of (a) NiCo₂O₄ nanocores, (b) NiCo₂O₄/PANI, (c)
45   NiCo₂O₄/MWCNTs, and (d) NiCo₂O₄/r-GO nanostructured-based electrodes st various current
46   densities.

47   **Table S1**. Comparison of the electrochemical performance of NiCo₂O₄/MWCNTs and NiCo₂O₄-rGO
48   nanocomposites here developed with others previously obtained following different synthetic
49   procedures.

Electrode Material	Synthesis method Electrode	Specific capacitance	electrolyte	Stability	Ref.
CNT@NiCo₂O₄	Chemical co-deposition & calcination	1038F/g (0.5A/g)	6 M KOH	100%	[2]
NiCo₂O₄/CNT	Electrochemical deposition	694F/g (1A/g)	6 M KOH	79.6%	[3]
NiCo₂O₄–GO	Electrodeposition	1078F/g (1mA)	3 M KOH	60%	[4]
RGO-NiCo₂O₄	Hydrothermal	676F/g (5mV s⁻¹)	6 M KOH	----	[5]
NiCo₂O₄@RGO	Hydrothermal	737F/g (1A/g)	2 M KOH	94%	[6]

NiCo₂O₄@GO	Microwave	925F/g (1.5A/g)	2M KOH	94%	[7]
NiCo₂O₄–RGO	Self-assembled	835F/g (1A/g)	6 MKOH	>100%	[8]
NiCo₂O₄@rGO	Dipping and Drying	1125F/g (5 mA cm⁻²)	6 MKOH	90%	[9]
NiCo₂O₄-rGO	Solvothermal	870F/g (2A/g)	2 M KOH	90%	[10]
rGO-NiCo2O4	Solution mixing	385.3C/g (1A/g)	3 M KOH	76%	[11]
NiCo₂O₄/RGO (NCG)	Reflux method	1186.3F/g (0.5 A/ g)	3 M KOH	97% of	[12]
NiCo₂O₄-rGO	Spray precursor	783F/g (1A/g)	2 M KOH	87.6%	[13]
NiCo₂O₄-rGO	Hydrothermal	1185F/g (2A/g)	2 M KOH	98%	[14]
NiCo₂O₄/rGO/ CF	Hydrothermal	931.7F/g (1A/g),	3 M KOH	83.8%	[15]
NiCo₂O₄/MWC NT	Solution Mixing	900F/g (1A/g)	3 M KOH	92%	This work
NiCo₂O₄/r-GO	Chornoamperometry	1760F/g (1A/g)	3 M KOH	91%	This work

S2. Obtaining of capacitances from equivalent circuits

To calculate the capacitances of the resulting equivalent circuits, the following equation was used:

$$C = \frac{(Q_0 \times R)^{\frac{1}{n}}}{R} \tag{S6}$$

where R (Ω) is the resistivity, and Q_0 (s) and n are related to the CPE as a fundamental circuit element (see Table S1). To construct Bode and phase impedance plots, the impedance must be previously calculated by means of:

$$|Z| = \sqrt{Z'^2 + Z''^2} \tag{S7}$$

where Z' and Z'' are the real and imaginary parts of impedance, respectively. It is possible to calculate the capacitance based on the relationship between the impedance $|Z|$ and the frequency by:
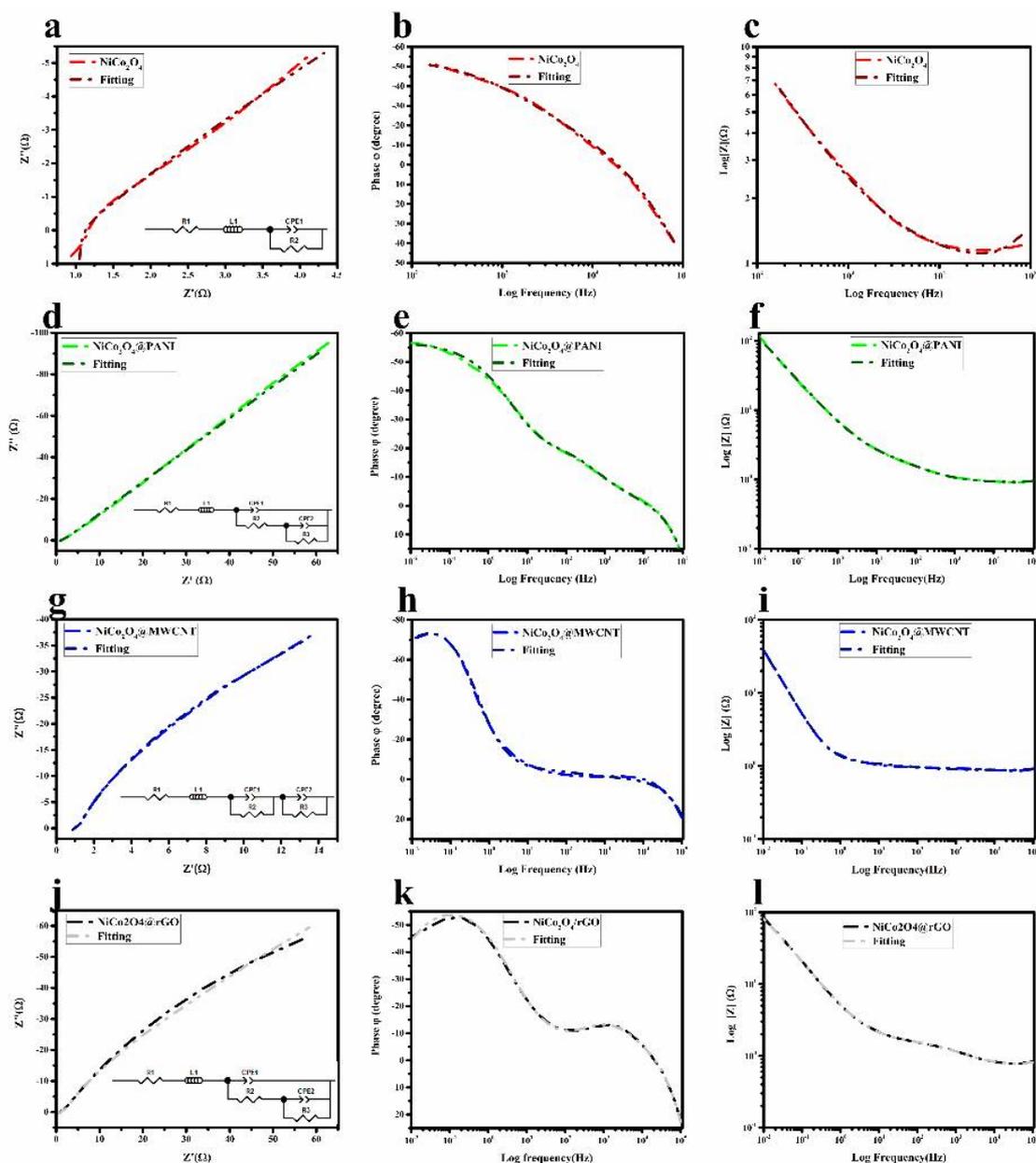
$$C = 1/2\pi f |Z| \tag{S8}$$

Table S2: Capacitances and fitting parameters for equivalent circuits of NiCo₂O₄, NiCo₂O₄/PANI, NiCo₂O₄/MWCNTs, and NiCo₂O₄/r-GO nanoelectrodes.

	NiCo₂O₄	**NiCo₂O₄@PANI**	**NiCo₂O₄@MWCNT**	**NiCo₂O₄@r-GO**
R₁(Ω)	1.1	0.9	0.87	0.73
CPE₁ [Q₀](s)	0.0015	0.0168	0.2340	0.0042
CPE₁ [n]	0.669	0.621	0.524	0.660
R₂(Ω)	1.8	1.8	1.2	1.5
C₁ (μF)	84	1995	120746	312
CPE₂[Q₀](s)	----	0.030	0.305	0.063
CPE₂[n]	----	0.639	0.904	0.684
R₃ (Ω)	----	60	15	60

C_2 (μF)	----	41832	358311	116143
C_{total} (μF)	84	43827	90312	118863

Figure S4: Nyquist, Phase and Bode plots with corresponding fitted plots for a-c) NiCo$_2$O$_4$ cores, d-f) NiCo$_2$O$_4$/PANI, g-i) NiCo$_2$O$_4$/MWCNTs, and j-l) NiCo$_2$O$_4$/r-GO nanocomposite-based electrodes based on equivalent circuits.

References

1. Xiong, C.; Li, T.; Zhao, T.; Shang, Y.; Dang, A.; Ji, X.; Li, H.; Wang, J. Electrochimica Acta Two – Step Approach of Fabrication of Three – Dimensional Reduced Graphene Oxide – Carbon Nanotubes – Nickel Foams Hybrid as a Binder – Free Supercapacitor Electrode. *Electrochim. Acta* **2016**, *217*, 9–15.

2. Cai, F.; Kang, Y.; Chen, H.; Li, Q. Hierarchical CNT@NiCo2O4 Core–shell Hybrid Nanostructure for High-Performance Supercapacitors. *J. Mater. Chem. A* **2014**, *2*, 11509–11515.

3. Liu, W. W.; Lu, C.; Liang, K.; Tay, B. K. A Three Dimensional Vertically Aligned Multiwall Carbon Nanotube/NiCo2O4core/Shell Structure for Novel High-Performance Supercapacitors. *J. Mater. Chem. A* **2014**, *2*, 5100–5107.

4. Mitchell, E.; Jimenez, A.; Gupta, R. K.; Gupta, B. K.; Ramasamy, K.; Shahabuddin, M.; Mishra, S. R. Ultrathin Porous Hierarchically Textured NiCo2O4-Graphene Oxide Flexible Nanosheets for High-Performance Supercapacitors. *New J. Chem.* **2015**, *39*, 2181–2187.

5. Shen, J.; Li, X.; Huang, W.; Li, N.; Ye, M. One-Pot Polyelectrolyte Assisted Hydrothermal Synthesis of NiFe2O4-Reduced Graphene Oxide Nanocomposites with Improved Electrochemical and Photocatalytic Properties. *J. Mater. Res.* **2014**, *29*, 2211–2219.

6. He, G.; Wang, L.; Chen, H.; Sun, X.; Wang, X. Preparation and Performance of NiCo2O4nanowires-Loaded Graphene as Supercapacitor Material. *Mater. Lett.* **2013**, *98*, 164–167.

7. Carriazo, D.; Patiño, J.; Gutiérrez, M. C.; Ferrer, M. L.; Del Monte, F. Microwave-Assisted Synthesis of NiCo2O4-Graphene Oxide Nanocomposites Suitable as Electrodes for Supercapacitors. *RSC Adv.* **2013**, *3*, 13690–13695.

8. Wang, H. W.; Hu, Z. A.; Chang, Y. Q.; Chen, Y. L.; Wu, H. Y.; Zhang, Z. Y.; Yang, Y. Y. Design and Synthesis of NiCo2O4-Reduced Graphene Oxide Composites for High Performance Supercapacitors. *J. Mater. Chem.* **2011**, *21*, 10504–10511.

9. Zhang, C.; Geng, X.; Tang, S.; Deng, M.; Du, Y. NiCo2O4@rGO Hybrid Nanostructures on Ni Foam as High-Performance High-Performance Supercapacitor Electrodes. *J. Mater. Chem. A* **2017**, *49*, 1–9.

10. Umeshbabu, E.; Rajeshkhanna, G.; Justin, P.; Ranga Rao, G. Synthesis of Mesoporous NiCo2O4-RGO by a Solvothermal Method for Charge Storage Applications. *RSC Adv.* **2015**, *5*, 66657–66666.

11. Mondal, A.; Maiti, S.; Mahanty, S.; Baran Panda, A. Large-Scale Synthesis of Porous NiCo2O4and RGO-NiCo2O4hollow-Spheres with Superior Electrochemical Performance as a Faradaic Electrode. *J. Mater. Chem. A* **2017**, *5*, 16854–16864.

12. Ma, L.; Shen, X.; Ji, Z.; Cai, X.; Zhu, G.; Chen, K. Porous NiCo2O4nanosheets/Reduced Graphene Oxide Composite: Facile Synthesis and Excellent Capacitive Performance for Supercapacitors. *J. Colloid Interface Sci.* **2015**, *440*, 211–218.

13. Luo, Y.; Zhang, H.; Guo, D.; Ma, J.; Li, Q.; Chen, L.; Wang, T. Porous NiCo2O4-Reduced Graphene Oxide (RGO) Composite with Superior Capacitance Retention for Supercapacitors. *Electrochim. Acta* **2014**, *132*, 332–337.

14. Al-Rubaye, S.; Rajagopalan, R.; Dou, S. X.; Cheng, Z. Facile Synthesis of a Reduced Graphene Oxide Wrapped Porous NiCo2O4composite with Superior Performance as an Electrode Material for Supercapacitors. *J. Mater. Chem. A* **2017**, *5*, 18989–18997.

15. Jiang, H.; Yang, K.; Ye, P.; Huang, Q.; Wang, L.; Li, S. Optimized NiCo2O4/RGO Hybrid Nanostructures on Carbon Fiber as an Electrode for Asymmetric Supercapacitors. *RSC Adv.* **2018**, *8*, 37550–37556.