Supporting Information

Co_3O_4 Nanoparticles Embedded in Mesoporous Carbon for Supercapacitor Applications

Sirine Zallouz[1,2], Bénédicte Réty[1,2,3], Loïc Vidal[1,2], Jean-Marc Le Meins[1,2], Camélia Matei Ghimbeu[1,2,3,]*

[1] Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse (IS2M) UMR 7361, F-68100 Mulhouse, France

[2] Université de Strasbourg, F-67081 Strasbourg, France

[3] Réseau sur le stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, 80039 Amiens Cedex, France

*Corresponding author.

E-mail address: camelia.ghimbeu@uha.fr (C. Matei Ghimbeu).

Tel: + 33 (0) 3 89 60 87 43

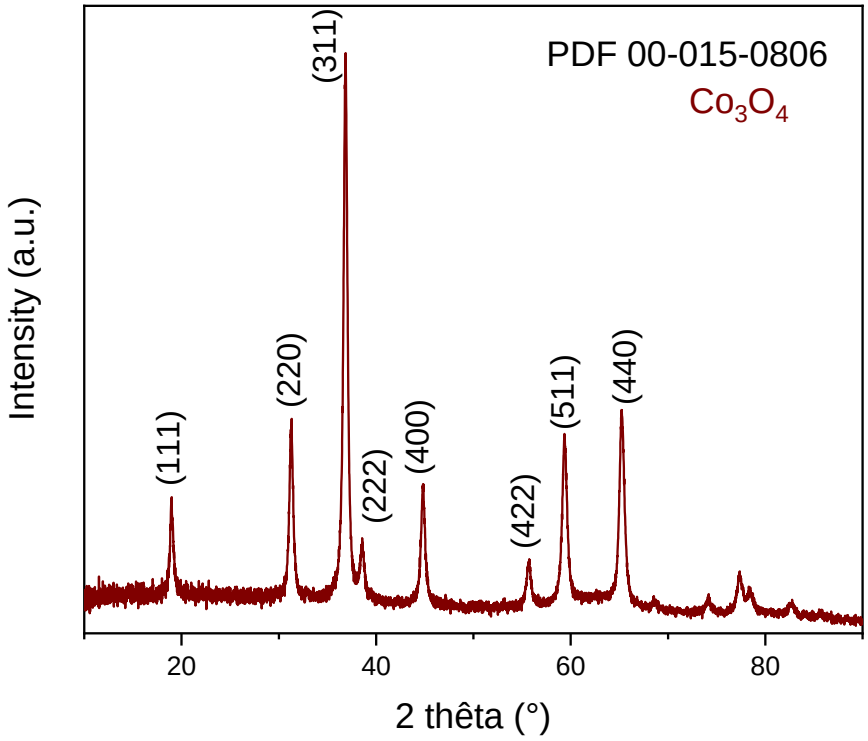

Figure S1: XRD patterns of TGA residue under air of C/Co-650 composite.

Table S1: Calculations of number of unit cells per particle before and after oxidation for a pyrolysis temperature of 750 °C.

Sample	Particles size by TEM (Å)	Lattice parameter (Å)	Number of unit cells per particle
C/Co-750	2.3	3.54470	6.488
C/Co_3O_4-750	4.3	8.08370	5.319

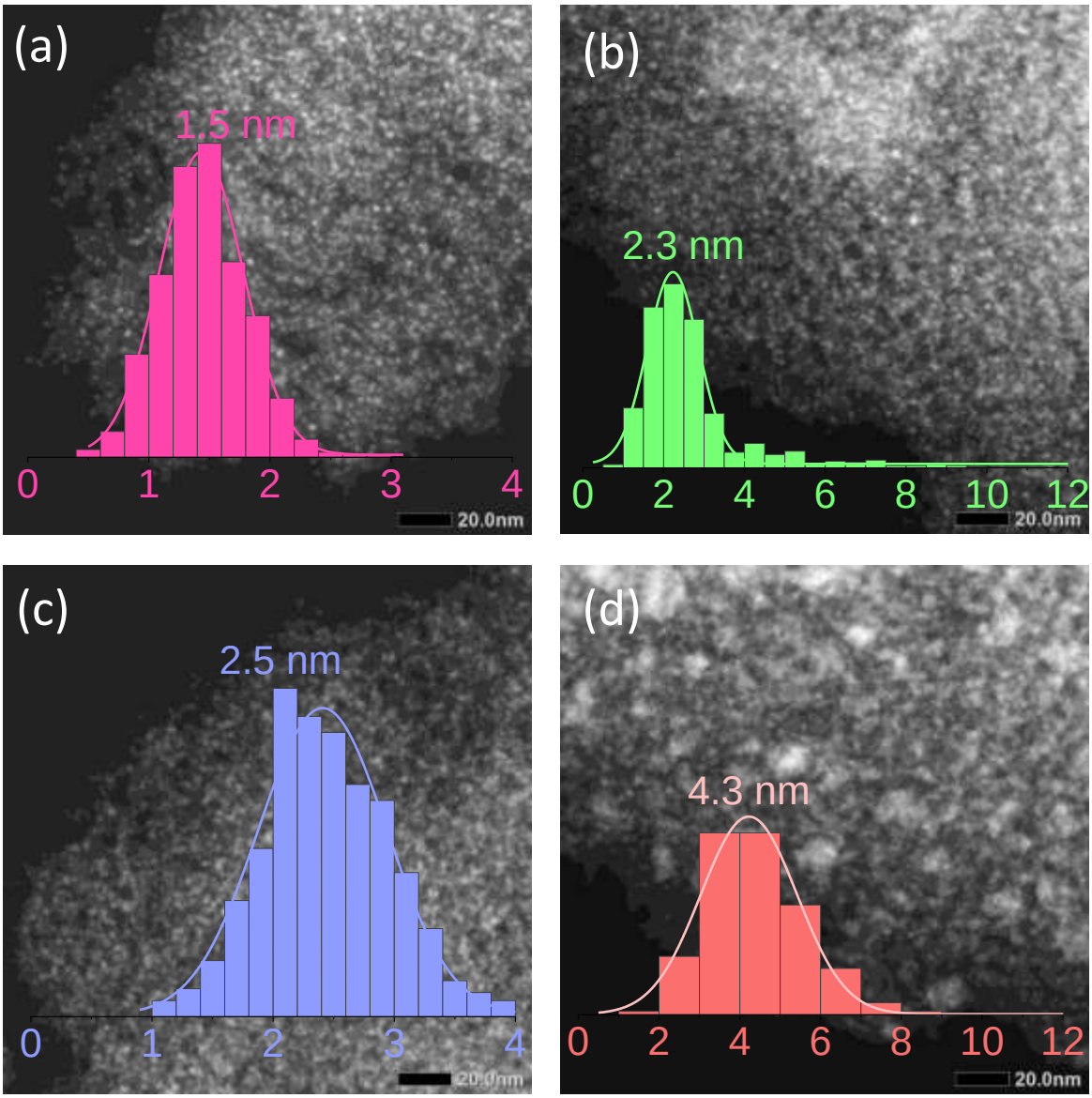

Figure S2: STEM images of Carbon/Cobalt based composites pyrolyzed at (a) 650 °C, (b) 750 °C, respectively, and the corresponding C/Co_3O_4 composites oxidized at (c) 215 °C and (d) 230 °C.

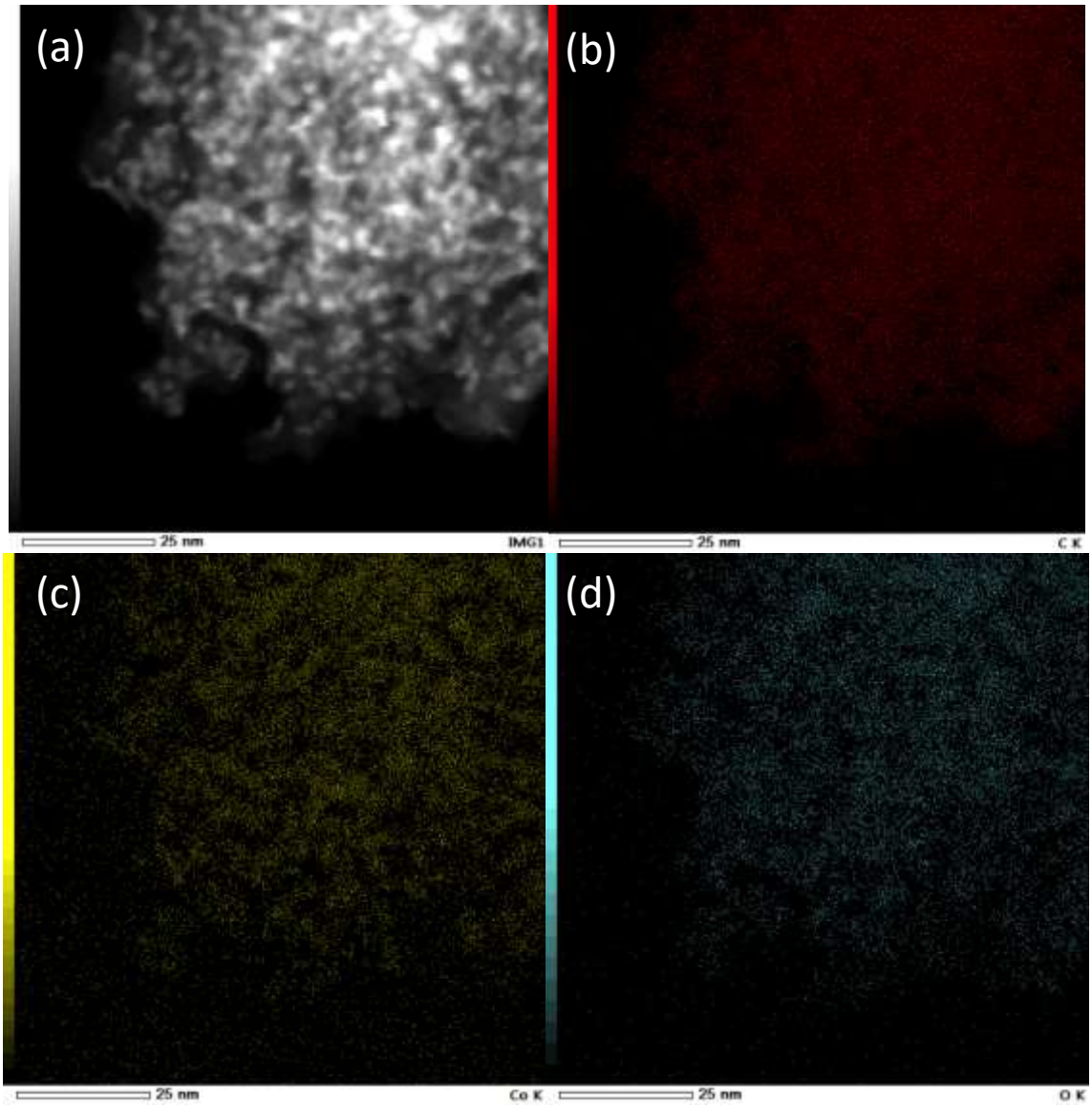

Figure S3: STEM image of (a) of C/Co_3O_4 -700 composite along with the EDX mapping showing the chemical contribution of (b) carbon (c) cobalt and (d) oxygen.

Table S2: Chemical composition derived from EDX and XPS for C/Co_3O_4-600 , C/Co_3O_4-700, C/Co_3O_4-800.

	EDX			XPS		
Material	C *wt.*%	O *wt.* %	Co *wt.* %	C *wt.* %	O *wt.*%	Co *wt.* %
C/Co_3O_4-600	52.1	9.4	38.5	70.1	18.5	11.4
C/Co_3O_4-700	70.5	6.9	22.7	63.0	18.5	18.9
C/Co_3O_4-800	78.5	7.0	15.0	60.2	16.6	23.1

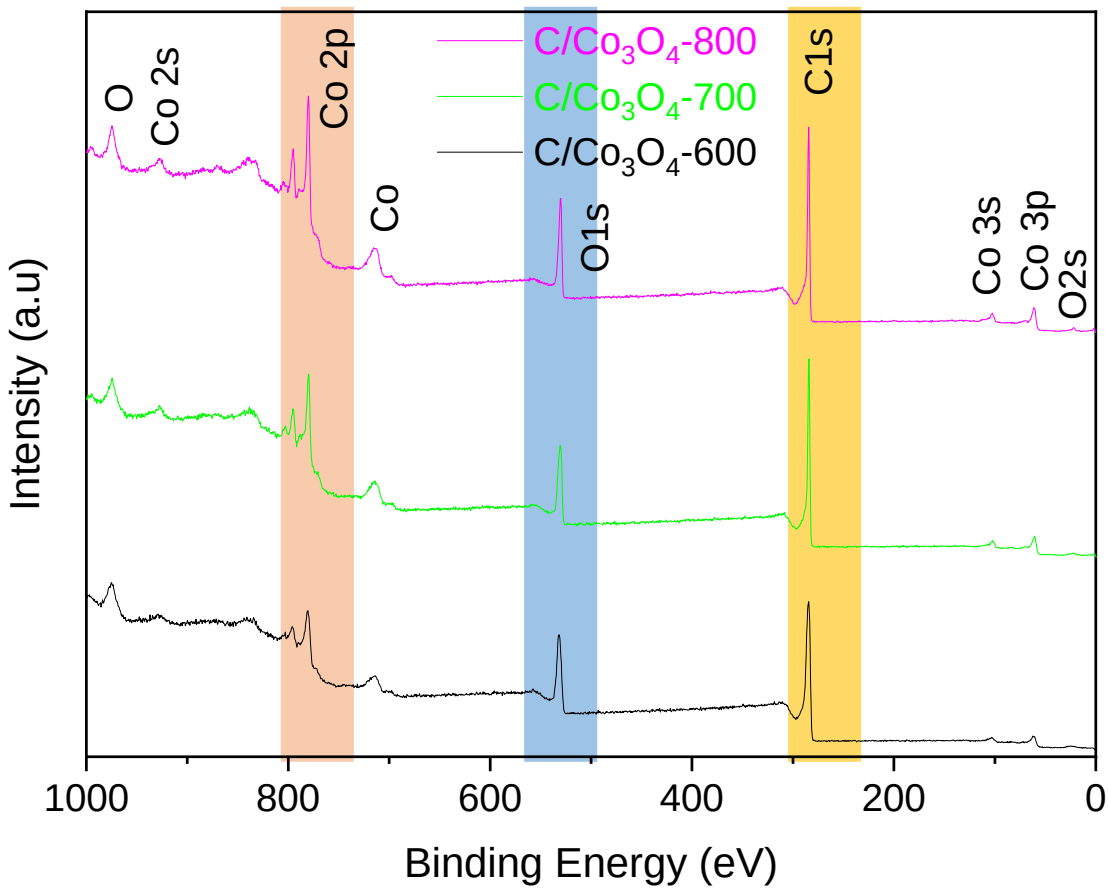

Figure S4: XPS survey spectra of C/Co_3O_4 composites pyrolyzed and oxidized at different temperatures.

Table S3: Chemical composition derived from XPS of C/Co_3O_4-600, C/Co_3O_4-700, C/Co_3O_4-800 composites materials.

Material	C (at %)	O (at %)	Co (at %)	C sp^2 (at %)	O-C (at %)	O-Co (at %)	C sp^2/ O-C (at %)
C/Co_3O_4-600	81.18	16.13	2.68	69.43	4.70	2.09	14.8
C/Co_3O_4-700	78.29	16.94	4.77	59.39	3.79	3.32	15.6
C/Co_3O_4-800	77.79	16.11	6.09	60.83	2.96	4.46	20.0

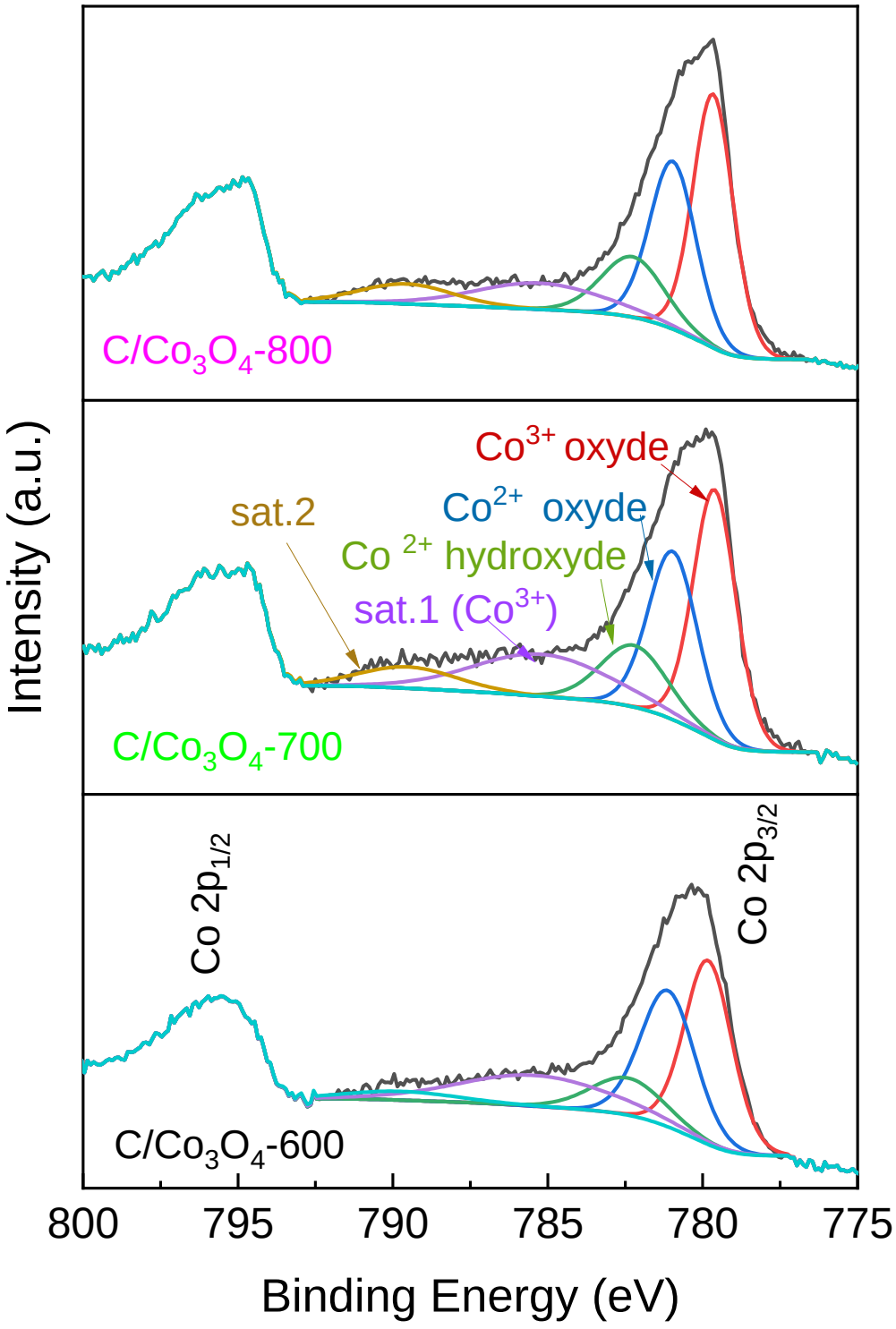

Figure S5: XPS High resolution deconvoluted spectra of Co *2p* peaks in C/Co_3O_4-600, C/Co_3O_4-700 and C/Co_3O_4-800 composites.

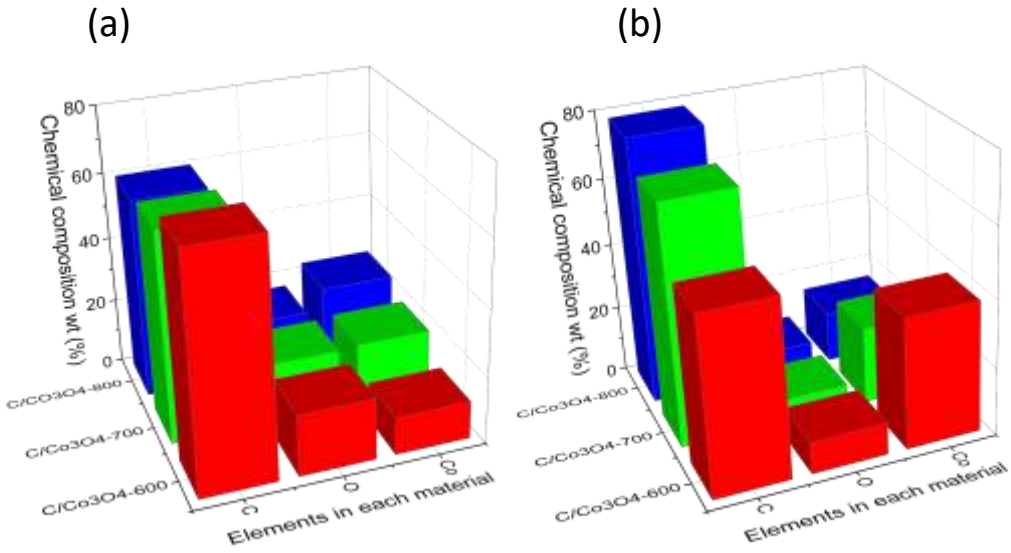

Figure S6: Chemical composition wt. (%) by (a) XPS and (b) EDX of C, O and Co for C/Co_3O_4-600 , C/Co_3O_4-700, C/Co_3O_4-800

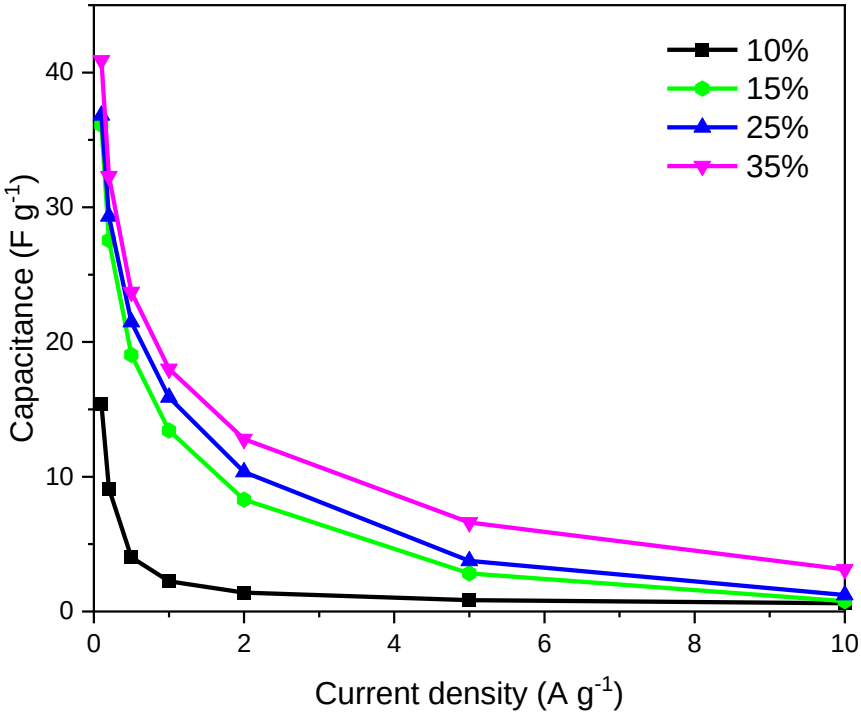

Figure S7: Capacitance vs current density of C-Co_3O_4-600 with different amounts of carbon black.

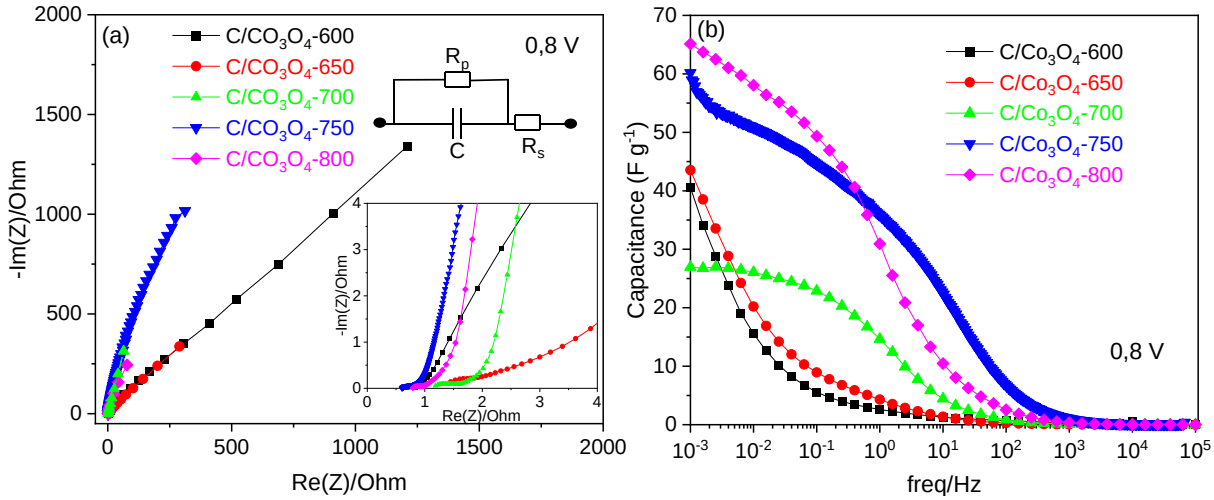

Figure S8: Electrochemical impedance spectroscopy recorded at 0.8 V for symmetric cells, Nyquist Plot at 0.8 V (inset: equivalent circuit diagram) (a), specific capacitance vs. frequency of C/Co_3O_4 –T symmetric capacitors at 0.8 V (b)

The conductivity (σ) was calculated using the following formula.

$$\sigma = \frac{\mathrm{L}}{\mathrm{R} * \mathrm{A}}$$

Where: L is the thickness of the self-standing electrode (cm), R is the resistance given by EIS (Ω) and A is the surface of the self-standing electrode (cm^2). The result is given in mS cm^{-1}. It is important to highlight that the resistance R measured by EIS has been done in several places and several values were collected. The average has been used here. Hence the values may slightly differ from one spot in the material to another.

Table S4: Comparison of different carbon/Co_3O_4 materials performance in two-electrode configuration for supercapacitors

Material	Mass loading	Type of device	Negative electrode material	Electrolyte	Specific capacitance	Maximum energy and power density	Capacitance retention	Ref
Co_3O_4/ Graphene aerogel	-	Asymmetric	Graphene aerogel	LiOH-PVA gel	193.1 F g^{-1} at 1 A g^{-1}	68.1 Wh kg^{-1}, 982.9 W kg^{-1}	81.5%, 5000 cycles	[1]
Co_3O_4/ reduced graphene oxide	-	Asymmetric	Activated carbon	6 M KOH	114.1 F g^{-1} at 0.375 A g^{-1}	35 Wh $kg^{-1,}$ 100 W kg^{-1}	95%, 1000 cycles	[2]
Co_3O_4/ 3D porous carbon	1.99 mg cm-2	Asymmetric	Activated carbon	3 M KOH	60.7 F g^{-1} at 1 A g^{-1}	21.1 Wh kg^{-1}, 790 W kg^{-1}	83%, 2000 cycles	[3]
Co_3O_4/ Graphene	3 mg cm^{-2}	Asymmetric	Porous carbon	6 M KOH	130 F g^{-1} at 0.455 A g^{-1}	40 Wh kg^{-1}, 340 W kg^{-1}	98%, 2000 cycles	[4]
Co_3O_4/ carbon nanofibers	-	Symmetric	-	6 M KOH	299 F g^{-1} at 1 A g^{-1}	-	74%, 2000 cycles	[5]
Co_3O_4/ Bio-inspired Carbon	-	Symmetric	-	PVA-KOH gel	28.38 F g^{-1} at 0.1 A g^{-1}	17 Wh kg^{-1}, 184 W kg^{-1}	87%, 10000 cycles	[6]
Co_3O_4/ Graphene	50 µg cm^{-2}	Symmetric	-	PVA-KOH gel	300 F g^{-1} at 5 A g^{-1}	27 Wh kg^{-1}, 2000 W kg^{-1}	86%, 20000 cycles	[7]
Co_3O_4/ reduced grapheme oxide	0.8 mg cm^{-2}	Symmetric	-	2 M KOH	458 F g^{-1} at 0.5 A g^{-1}	47.2 Wh kg^{-1}, 200.6 W kg^{-1}	95.6%, 1000 cycles	[8]
Co_3O_4/ Carbon	19 - 25 mg cm^{-2}	Symmetric	-	2 M KOH	54 F g^{-1} at 0.1 A g^{-1}	1.66 Wh kg^{-1}, 1223 W kg^{-1}	82%, 10000 cycles	This work

References:

(1) Yan, H.; Bai, J.; Liao, M.; He, Y.; Liu, Q.; Liu, J.; Zhang, H.; Li, Z.; Wang, J. One-Step Synthesis of Co3O4/Graphene Aerogels and Their All-Solid-State Asymmetric Supercapacitor. *European Journal of Inorganic Chemistry* **2017**, *2017*, 1143–1152.

(2) Xie, L.-J.; Wu, J.-F.; Chen, C.-M.; Zhang, C.-M.; Wan, L.; Wang, J.-L.; Kong, Q.-Q.; Lv, C.-X.; Li, K.-X.; Sun, G.-H. A Novel Asymmetric Supercapacitor with an Activated Carbon Cathode and a Reduced Graphene Oxide–Cobalt Oxide Nanocomposite Anode. *Journal of Power Sources* **2013**, *242*, 148–156.

(3) Li, S.; Yang, K.; Ye, P.; Ma, K.; Zhang, Z.; Huang, Q. Three-Dimensional Porous Carbon/Co3O4 Composites Derived from Graphene/Co-MOF for High Performance Supercapacitor Electrodes. *Applied Surface Science* **2020**, *503*, 144090.

(4) Xie, L.; Su, F.; Xie, L.; Li, X.; Liu, Z.; Kong, Q.; Guo, X.; Zhang, Y.; Wan, L.; Li, K.; Lv, C.; Chen, C. Self-Assembled 3D Graphene-Based Aerogel with Co_3O_4 Nanoparticles as High-Performance Asymmetric Supercapacitor Electrode. *ChemSusChem* **2015**, *8*, 2917–2926.

(5) Abouali, S.; Akbari Garakani, M.; Zhang, B.; Xu, Z.-L.; Kamali Heidari, E.; Huang, J.; Huang, J.; Kim, J.-K. Electrospun Carbon Nanofibers with in Situ Encapsulated Co_3O_4 Nanoparticles as Electrodes for High-Performance Supercapacitors. *ACS Appl. Mater. Interfaces* **2015**, *7*, 13503–13511.

(6) Samdani, K. J.; Kim, S. H.; Park, J. H.; Hong, S. H.; Lee, K. T. Morphology-Controlled Synthesis of Co3O4 Composites with Bio-Inspired Carbons as High-Performance Supercapacitor Electrode Materials. *Journal of Industrial and Engineering Chemistry* **2019**, *74*, 96–102.

(7) Liao, Q.; Li, N.; Jin, S.; Yang, G.; Wang, C. All-Solid-State Symmetric Supercapacitor Based on Co_3O_4 Nanoparticles on Vertically Aligned Graphene. *ACS Nano* **2015**, *9*, 5310–5317.

(8) Xiang, C.; Li, M.; Zhi, M.; Manivannan, A.; Wu, N. A Reduced Graphene Oxide/Co3O4 Composite for Supercapacitor Electrode. *Journal of Power Sources* **2013**, *226*, 65–70.