Supplementary Information

Multi-Porous Co₃O₄ Nanoflakes @ Sponge-Like Few-Layer Partially Reduced Graphene Oxide Hybrid: Towards Highly Stable Asymmetric Supercapacitor[†]

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Materials	Electrolytes	C _V (F cm⁻³)	Rate	Stability	Ref.
			Capability Retention	Retention	
$NiCo_2O_4$ - MnO_2 /graphene foam	6 M KOH	_(c)	~27%	94.3% 5000 #	1
$Co_3S_4/CoMo_2S_4$ ultrathin nanosheets on rGO	3 М КОН	~276 @ 2 mA cm ⁻² for <i>l</i> =105 μm	~45%	97% 2000 #	2
Ni–Co binary hydroxide/rGO	6 M KOH	~15 @ 2 mA cm ⁻² for <i>l</i> =200 μm	~47%	80% 10 000 #	3
3D ultrathin Ni(OH) ₂	2 M KOH	~30 @ 2 mA cm ⁻² for <i>l</i> =1600 μm	~54%	75% 3000 #	4
3D Co ₃ O ₄ -rGO	6 М КОН	_	~76%	92.92% 2000 #	5
Nanohoneycomb-Like CoMoO₄−3D Graphene	2 М КОН	~100 @ 2.55 mA cm ⁻² for <i>l</i> =100-120 μm	≥40%	87.42% 10 000 #	6
NiCo ₂ O ₄ nanosheets on Ni wire	3 М КОН	10.3 @ 1 mA cm ⁻²	~60%	81.2% 1000 #	7
RuO ₂ /Co ₃ O ₄ on graphitized carbon paper	30 wt% KOH	≤226 @ 1 mA cm ⁻² for <i>l</i> ≥20 μm	~78%	96% 5000 #	8
Co_3O_4 -C nanofiber	6 M KOH	≤83 @ 1.2 mA cm ⁻² for <i>l</i> =80 μm	~72%	No decay 2000 #	9
Layered α -Co(OH) ₂ nanocones	2 M KOH	≤10.5 @ 2 mA cm ⁻² for <i>l</i> =2000 μm	~28%	95% 2000 #	10
Ni(OH)₂ on 3D ultrathin- graphite foam	6 M KOH	93.5 for <i>l</i> =37 μm	~68%	63.2% 10 000 #	11
3D graphene/MnO ₂ Composite	0.5 M Na₂SO₄	≥71 for <i>l</i> ≤200 µm	≥38%	81% 5000 #	12
Co_3O_4 /rGO/CNTs hybrid	6 M KOH	<i>l</i> =50 μm	~76%	~96% 3000 #	13
Co₃O₄ nanoflakes @ sponge- like rGO	1 M KOH	178 @ 2.6 mA cm ⁻² for <i>l</i> =45 μm ^(a)	≥80%	No decay 20 000 # ^(b)	Current work

Table S1 The volumetric capacitance value, rate capability retention and stability retention of our hybrid electrode against previous reports on the similar 3D structures.

^(a) The quantity *I* is the thickness of the prepared layers. ^(b) The symbol # stands for GCD cycles. ^(c) Underline symbol (_) stands for not available information in the mentioned reference. [¹ M. Akbari Garakani, et al., J. Mater. Chem. A, 2017, DOI: 10.1039/C6TA08929A; ²X. Yang, et al., J. Mater. Chem. A, 2016, 4, 18857-18867; ³M. Jana, et al., J. Mater. Chem. A, 2016, 4, 2188-2197; ⁴X. Xiong, et al., Nano Energy, 2015, 11, 154-161; ⁵L. Xie, et al., ChemSusChem, 2015, 8, 2917-2926; ⁶X. Yu, et al., Advanced Materials, 2014, 26, 1044-1051; ⁷Q. Wang, et al., Nano Energy, 2014, 8, 44-51; ⁸R. B. Rakhi, et al., ACS Appl. Mater. Interfaces, 2014, 6, 4196-4206; ⁹F. Zhang, et al., Adv. Funct. Mater., 2013, 23, 2909-3915; ¹⁰L. Wang, et al., Adv. Funct. Mater., 2013, 23, 2758-2764; ¹¹J. Ji, et al., ACS Nano, 2013, 7, 6237-6243; ¹²Y. He, et al., ACS Nano, 2013, 7, 174-182; ¹³C. Yuan, et al., Adv. Funct. Mater., 2012, 22, 2560-2566].



Fig. S1. AFM image and the corresponding height profile of the synthesized graphene oxide (GO) sheets on SiO_2 substrate. The GO nanosheets were synthesized exactly based on our previous report [N. Naseri, et al., ACS Sustainable Chem. Eng., 2016, 4, 3151-3159]. It demonstrates that the average thickness of GO sheets is approximately 2 nm (about 2-3 layers).



Fig. S2. Low and high magnification FESEM images of the as prepared mixed GO nanosheets with PMMA nanoparticles: low PMMA:GO=5 (top images) and high PMMA:GO=40 (bottom images) ratios. We believe that the agglomeration of PMMA nanoparticles and also the lower amount of GO nanosheets (relative to PMMA) is the reason of the inhomogeneity of the prepared mixed powder for high PMMA:GO ratio. Inset shows the SEM image of the pristine PMMA nanoparticles with diameter of 300±20 nm.



Fig. S3. Thermogravimetric analysis (TGA) curve of the PMMA particles with ramping rate of 5 $^{\circ}$ C min⁻¹ in N₂ ambient. It shows that the PMMA material was degraded completely by increasing the temperature higher than 450 $^{\circ}$ C. Hence, the annealed and functionalized sponge-like reduced graphene oxide (SrGO) did not contain carbon elements from PMMA template.



Fig. S4. Top view FESEM images of the SrGO framework prepared with low and high PMMA:GO ratios after functionalization process. The frameworks have prepared by higher PMMA:GO ratio contained more agglomerated regions. From the insets, it is obvious that the homogeneity of the SrGO layer diminished by increasing the concentration of PMMA nanoparticles relative to the GO nanosheets.



Fig. S5. N₂ adsorption/desorption isotherms of the activated carbon (AC), GO, SrGO (low PMMA concentration), and SrGO (high PMMA concentration). The specific BET surface area of 212±3, 94±2, 196±3, and 332±5 m² g⁻¹ were calculated for AC, GO, SrGO (low PMMA concentration), and SrGO (high PMMA concentration), respectively.



Fig. S6. (a) FESEM image from the cross-section of the SrGO framework loaded on graphite substrate. The thickness of the uniformly loaded layer is about 45±5 μ m. SEM images from the cross-section of pristine SrGO (b), Co-L@SrGO (c), Co-M@SrGO (d), and Co-H@SrGO (e). L (=Low), M (=Medium) and H (=high) stand for 0.5 C cm⁻², 2 C cm⁻² and 4 C cm⁻², respectively. Insets show the high resolution FESEM images of the grown nanostructures within the micrometric pores of the SrGO.



Fig. S7. (a) The mass of the grown Co_3O_4 material within the SrGO versus of the electrodeposited charge density, namely Q; For sake of simplicity, the masses of 0.26, 0.93 and 1.98 mg are selected with Co-L(=Low)@SrGO, Co-M(=Medium)@SrGO and Co-H(=high)@SrGO, which also stand for 0.5 C cm⁻², 2 C cm⁻² and 4 C cm⁻² electrodeposited charge densities, respectively. (b) XRD patterns of $Co_3O_4@SrGO$ hybrid. It is obvious that the GO peaks were shifted to right due to the intercalation of Co ions. On the other hand, the SrGO host was reduced indicating graphitization of SrGO during the anchoring of Co_3O_4 ; it is completely consistent with Raman data. Moreover, Co-H@SrGO sample contains both Co_3O_4 and $Co(OH)_2$ crystal phases.



Fig. S8. (a) Back-scattered (BS) FESEM image from the cross-section of Co-M@SrGO sample. It shows the reflected and BS electrons from the heavy elements. The bright regions indicate the presence of Co atoms (as a heavy elements) relative to carbon and oxygen, and show they are uniformly loaded within the SrGO. (b) Energy dispersed X-ray spectroscopy (EDS) elemental mapping analysis of Co-M@SrGO. Elemental mapping result shows a homogeneous distribution of Co atoms, which indicates the good dispersion of Co_3O_4 on the pore surface of entire SrGO.



Fig. S9. FESEM image from the top view of the Co_3O_4 @ SrGO by direct electrodeposition process (Q=2 C cm⁻²). It shows formation of a thick layer on top of the SrGO framework which blocked the surface and resulted in low electrochemical performances. The inset shows a typical photograph of the sample which was prepared by direct electrodeposition process. In this process, the cobalt ions consume resulted in a lower concentration of these ions in the deeper regions of the SrGO. On the other hand, cobalt ions do not have enough time to diffuse into the thick SrGO layer (45±5 µm) in comparison with the rate of applied electrodeposition charge density. Therefore, the outer regions (surface of the electrode) play role as an active interfaces for deposition of cobalt ions. Hence, in here, we suggest the sequential-electrodeposition method to keep the cobalt ions' concentration constant during the growth process.



Fig. S10. Cross-sectional EDS of the normalized atomic percentage (relative to carbon element) for the pristine SrGO, Co-L@SrGO, Co-M@SrGO, and Co-H@SrGO samples (for cross-sectional region). It shows the presence of Co, O, and C elements in the sample. Moreover, the O:C (is about 11% for the pristine SrGO) and Co:C (is increased from ~11 to ~27% for low and high loading of cobalt oxide) are roughly proportional to the Q.



Fig. S11. XRD pattern of CoCl₂.6H₂O precursor (top pattern) and the standard PDF #29-0466 (bottom pattern).



Fig. S12. CV curves of the pristine SrGO (a), Co-L@SrGO (b), Co-M@SrGO (c), and Co-H@SrGO (d) at different scan rates from 10 to 100 mV s⁻¹.



Fig. S13. (a) Specific capacitance (red line) and Coulombic efficiency (blue line) versus the different discharge current densities for the Co-M@SrGO as an optimum electrode. It illustrates acceptable Coulombic efficiency of about 91-95% for all GCD current densities as well as good rate capability which is important for electrode materials utilized in high power density SC applications. (b) The CV curves of the Co-M@SrGO and Co-M@rGO. It shows that Co-M@SrGO performance is about 5-6 times higher than the performance of Co-M@rGO.



Fig. S14. EIS of the pristine SrGO (a), Co-L@SrGO (b), Co-M@SrGO (c), and Co-H@SrGO (d) measured at different bias potentials. It is obvious that the capacitive mechanism is dominant at higher applied bias. At minus potential (-100 mV), the dominant mechanism is mass transfer through the porous structures especially for high loading mass.

Table S2. Equivalent circuit parameters of the pristine SrGO and cobalt oxide @ SrGO electrodes. The maximum chisquare of the fitting for all sample is less than 0.006. The amount of C_{μ} is proportional to the electrodeposited cobalt oxide mass into the SrGO. It can be related to the formation of the depletion layer in semiconductor (graphene oxide/cobalt oxide) and electrolyte interfaces.

Elements	Pristine SrGO	Co-L@SrGO	Co-M@SrGO	Co-H@SrGO
<i>R</i> _s (Ω)	1.43	1.64	1.65	1.55
<i>R</i> _{ct,1} (Ω)	0.13	0.132	0.109	0.086
$R_{_{ct},2}$ (Ω)	0.96	2.79	0.764	1.43
C_{μ} (mF)	0.64	6.01	10.34	11.97
$Q_{_1}$ (mF)	0.0076	0.0530	0.1805	0.1919
n_1	0.86	0.81	0.79	0.65
$Q_{ m 2}$ (mF)	0.0083	0.0325	0.3740	0.4621
n_{2}	0.93	1.00	0.88	0.88



Fig. S15. Evolution of the real part capacitance of the pristine SrGO, Co-L@SrGO, Co-M@SrGO, and Co-H@SrGO electrodes versus frequency at 0.15 V bias potential. It shows that the capacitance of the Co-M@SrGO is higher than other prepared electrodes in all frequencies. Inset shows the evolution of the real capacitance of the optimum sample, i. e. Co-M@SrGO, versus the frequency at different bias potentials. It is obvious that in low frequency range the real capacitance is higher at 0.15 V bias potential and also at higher frequencies, the real capacitance at higher bias potential, i. e. 0.40 V, is higher than other potentials due to the shift of faradaic reactions.



Fig. S16. (a) CV curves of the activated carbon (AC) sample at different scan rates, and (b) the calculated specific capacitance vs. the scan rate. The working potential window of the AC is from -1 to 0 V.



Fig. S17. (a) CV curves of the AC (red line) and the Co-M@SrGO (black line) at 50 mV s⁻¹.



Fig. S18. The GCD curves in different potential windows from 0.7 V to 1.5 V at constant current density of 2 A g⁻¹.



Fig. S19. The ohmic (iR) drop versus different discharge current densities of the Co-M@SrGO//AC system. It shows a small iR drop of 30 mV at 2 A g^{-1} which corresponds to ohmic resistance of 15 m Ω .