Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Large scale synthesis of porous $NiCo_2O_4$ and rGO-$NiCo_2O_4$ hollow-spheres with superior electrochemical performance as faradaic electrode

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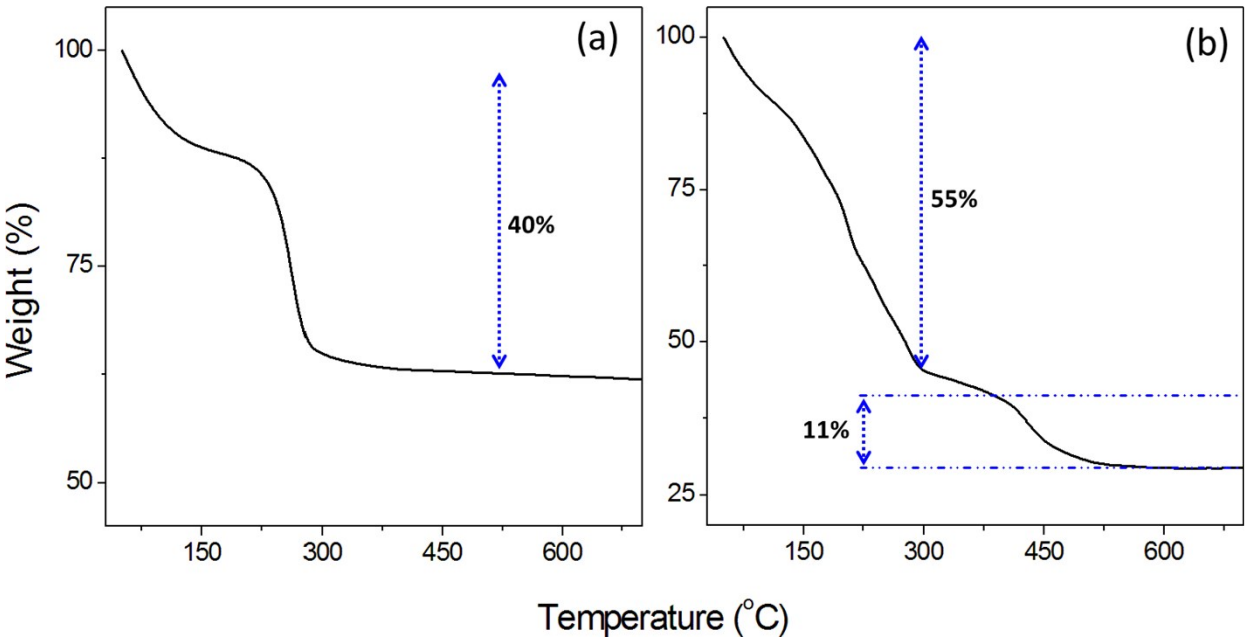

Fig.S1 Thermogravimetric analysis (TGA) curve of (a) pristine and (b) GO incorporated spray dried $NiCo_2O_4$ precursor.

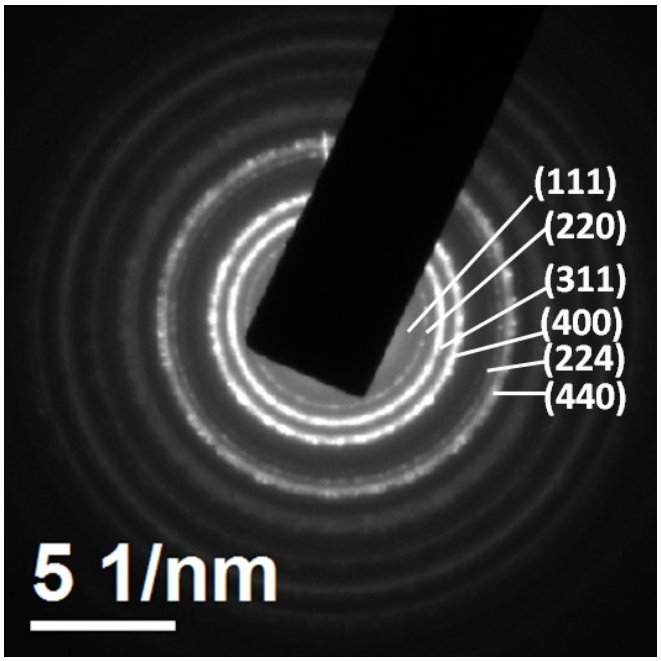

Fig.S2 SAED pattern of synthesized $NiCo_2O_4$ hollow spheres.

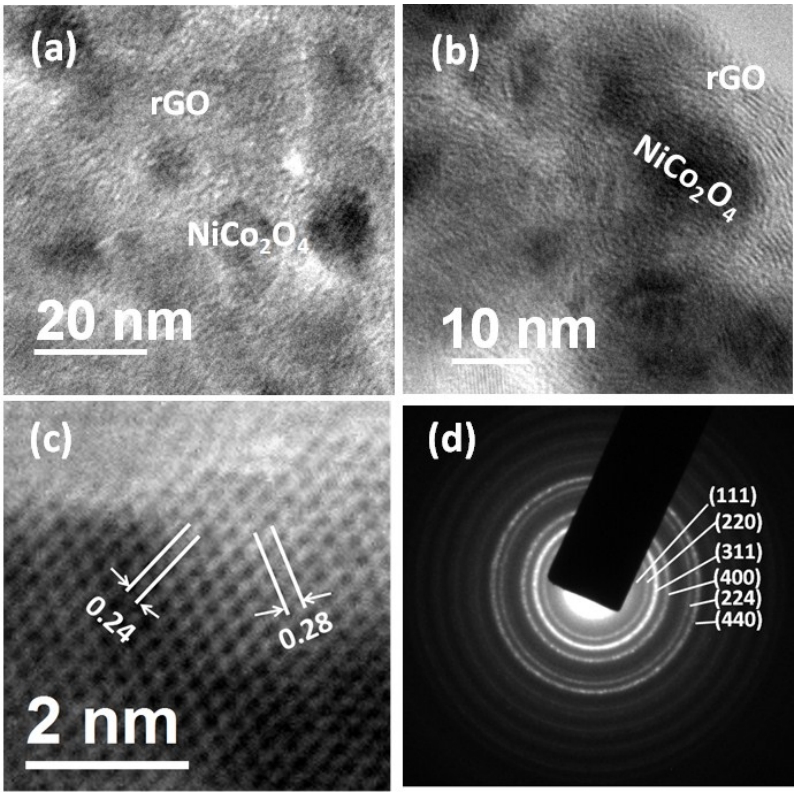

Fig.S3. (a-b) TEM, (c) HR-TEM images and (d) SAED pattern of synthesized rGO- $NiCo_2O_4$ nanocomposite hollow spheres

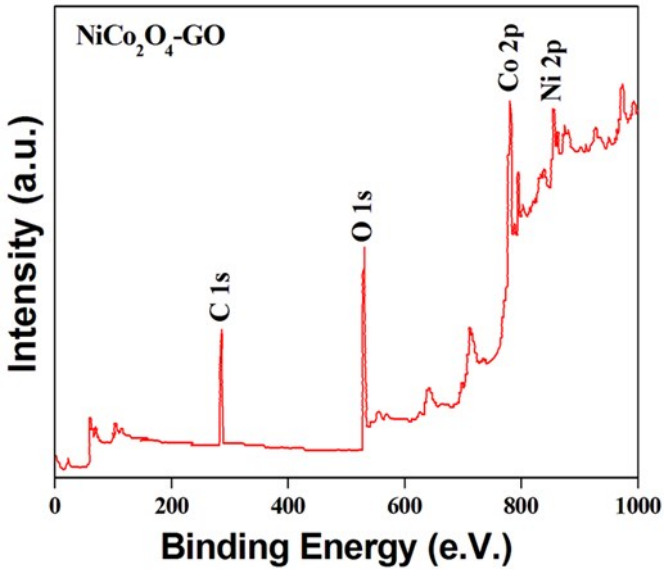

Fig.S4 XPS survey spectrum of the rGO- $NiCo_2O_4$ nano-composite hollow sphere.

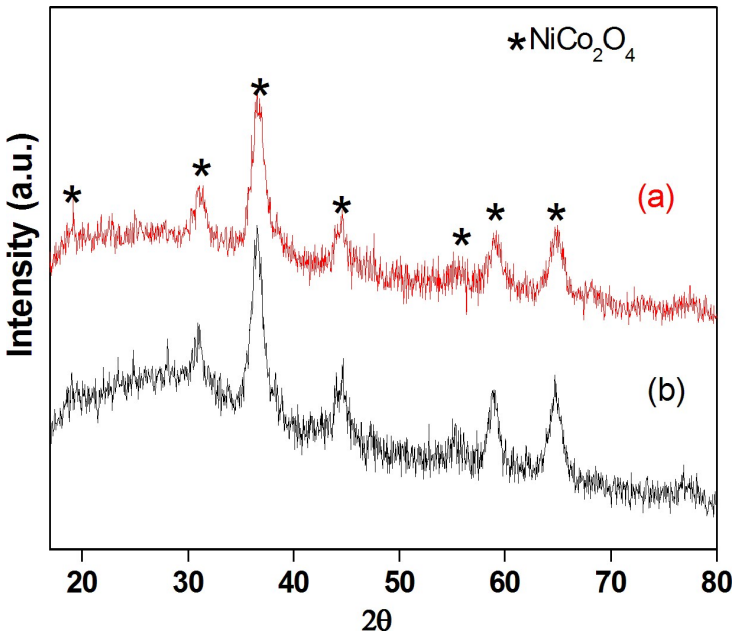

Fig.S5 XRD of the samples obtained after calcination of rGO containing spray fried precursor (a) under air at 350°C for 4h and (b) under air at 350°C for 4h followed by under N_2 for 4h at 350°C.

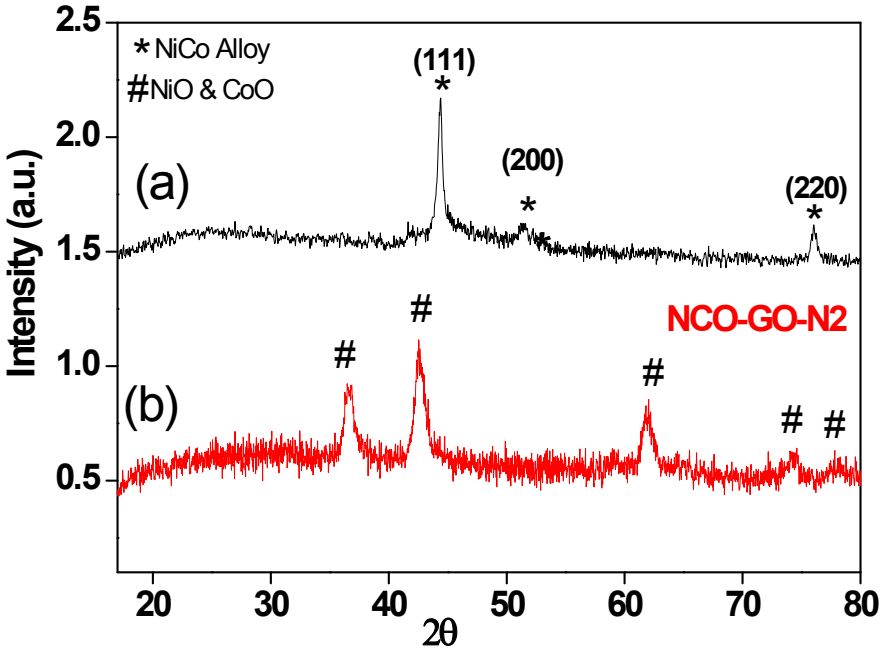

Fig.S6 XRD of the samples obtained after calcination of spray dried $NiCo_2O_4$ precursor (a) under H_2 at 350°C for 4h and (b) under N_2 at 350°C for 4h.

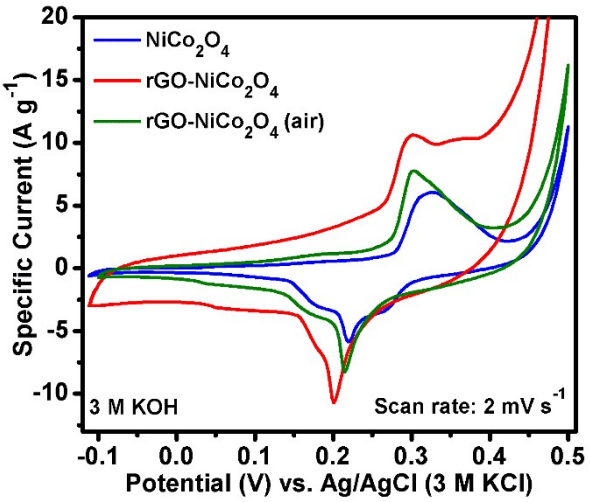

Fig.S7 CV plots of pristine $NiCo_2O_4$, rGO-$NiCo_2O_4$ and rGO-$NiCo_2O_4$ (air) at a scan rate of 2 mV s^{-1} in 3 M KOH

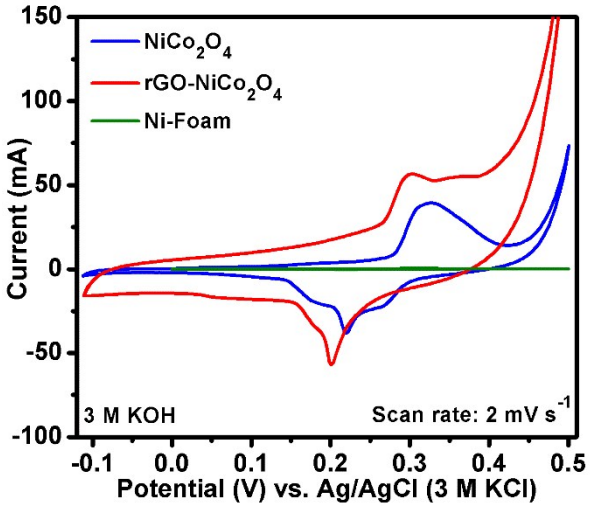

Fig.S8 CV plots of pristine $NiCo_2O_4$, rGO-$NiCo_2O_4$ and bare Ni-foam at a scan rate of 2 mV s^{-1} in 3 M KOH

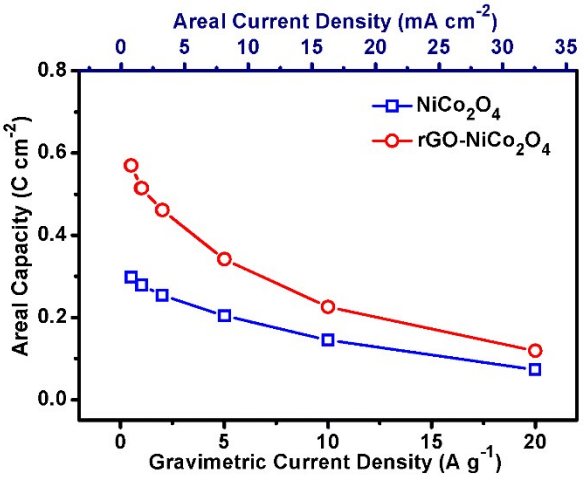

Fig.S9 Areal capacity vs. current density plot for $NiCo_2O_4$ and rGO-$NiCo_2O_4$ in three-electrode configuration.

Areal capacity vs. Current density (gravimetric and areal) plot has been given here. The calculated areal capacity values of the synthesized rGO-$NiCo_2O_4$ are found to be 0.57, 0.51, 0.46, 0.34, 0.23 and 0.12 C cm^{-2} at current densities of 1, 2, 5, 10 and 20 A g^{-1} respectively. The corresponding areal capacity values for pristine $NiCo_2O_4$ are 0.30, 0.28, 0.25, 0.20, 0.15 and 0.073 C cm^{-2}.

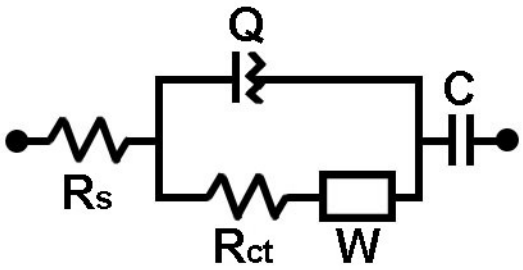

Fig.S10 Equivalent circuit model for fitting the impedance spectra of pristine $NiCo_2O_4$, rGO-$NiCo_2O_4$ at as assembled state.

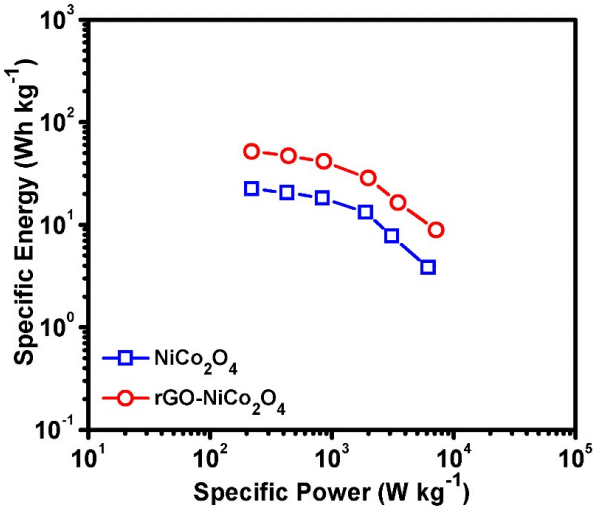

Fig. S11 Ragone plot for pristine $NiCo_2O_4$ and rGO-$NiCo_2O_4$.

Table S1 A comparison of performance of different $NiCo_2O_4$ nanostructures including hollow-spheres.

Electrode system	Type of device	Potential window	Electrolyte	Current Density	Capacitance/ Capacity	Cycling	Ref.
$NiCo_2O_4$ hollow spherical nano-architecture							
Pt//$NiCo_2O_4$ hollow spheres	3 electrode (Ag/AgCl)	CV (-0.1 to 0.55 V) GCD (0.0 to 0.45 V)	6.0 M KOH	2 A g^{-1}	1204.4 F g^{-1}	10000	s1
Pt//CNS/ $NiCo_2O_4$ core-shell sub-microspheres	3 electrode (SCE)	CV (0.0 to 0.5 V) GCD (0.0 to 0.5 V)	6.0 M KOH	1 A g^{-1}	1420 F g^{-1}	3000	s2
Pt//$NiCo_2O_4$ hollow microspheres	3 electrode (Hg/HgO)	CV (0.0 to 0.55 V) GCD (0.0 to 0.5 V)	2.0 M KOH	2 A g^{-1}	764 F g^{-1}	1500	s3
Pt//$NiCo_2O_4$ hollow spheres	3 electrode (SCE)	CV (-0.2 to 0.6 V) GCD (0.0 to 0.4 V)	6.0 M KOH	1 A g^{-1}	718 F g^{-1}	2000	s4
Pt//Hollow $NiCo_2O_4$ submicro-spheres	3 electrode (Hg/HgO)	CV (0.0 to 0.55 V) GCD (0.0 to 0.5 V)	2.0 M KOH	1 A g^{-1}	987 F g^{-1}	5000	s5
Pt//Hollow urchin-like $NiCo_2O_4$ microspheres/ graphite sheet	3 electrode (Hg/HgO)	CV (-0.1 to 0.6 V) GCD (0.0 to 0.5 V)	6.0 M KOH	1 A g^{-1}	~950 F g^{-1}	1600	s6
Pt//Uniform $NiCo_2O_4$ Hollow Spheres	3 electrode (SCE)	CV (0.0 to 0.6 V) GCD (0.0 to 0.5 V)	6.0 M KOH	1 A g^{-1}	1141 F g^{-1}	4000	s7
Pt//Mesoporous $NiCo_2O_4$ hollow spheres	3 electrode (Hg/HgO)	CV (0.0 to 0.55 V) GCD (0.0 to 0.5 V)	2.0 M KOH	2 A g^{-1}	106.3 mAh g^{-1}	1000	s8
Result of Present work							
Pt//rGO- $NiCo_2O_4$ hollow sphere	**3 electrode (Ag/AgCl)**	**CV (-0.1 to 0.5 V) GCD (0.0 to 0.45 V)**	**3.0 M KOH**	**0.5 A g^{-1}**	**427 C g^{-1} (971 F g^{-1})**	**5000**	**This Work**
$NiCo_2O_4$ /Graphene/rGO composite							
Pt//$NiCo_2O_4$/graphene	3 electrode (Ag/AgCl)	CV (-0.2 to 0.8 V)	1.0 M KOH	5 mV s^{-1}	886 F g^{-1}	2000	s9
Pt//$NiCo_2O_4$/3D graphene	3 electrode (SCE)	CV (-0.1 to 0.5 V) GCD (-0.05 to 0.4 V)	2.0 M KOH	1 A g^{-1}	2300 F g^{-1}	4000	s10
Pt//$NiCo_2O_4$-Nanosheet/rGO	3 electrode (Hg/HgO)	CV (0.0 to 0.5 V) GCD (0.0 to 0.45 V)	6.0 M KOH	1 A g^{-1}	1217.4 F g^{-1}	1000	s11
Pt//$NiCo_2O_4$-Nanowire/rGO	3 electrode (Hg/HgO)	CV (0.0 to 0.5 V) GCD (0.0 to 0.45 V)	6.0 M KOH	1 A g^{-1}	1137.8 F g^{-1}	1000	s11
Pt//$NiCo_2O_4$-rGO	3 electrode (Hg/HgO)	CV (0.0 to 0.55 V) GCD (0.0 to 0.55 V)	2 M KOH	2 A g^{-1}	870 F g^{-1}	5000	s12
Pt//$NiCo_2O_4$ Nanoparticle/graphene	3 electrode (SCE)	CV (-0.1 to 0.5 V) GCD (-0.05 to 0.4 V)	2.0 M KOH	1 A g^{-1}	1238 F g^{-1}	1000	s13
Pt//Mesoporous NCO/GO	3 electrode (Ag/AgCl)	CV (-0.15 to 0.35 V) GCD (-0.15 to 0.35 V)	6.0 M KOH	1 A g^{-1}	1211 F g^{-1}	2000	s14
Pt//Mesoporous NCO/RGO	3 electrode (SCE)	CV (0.0 to 0.65 V)	1 M KOH	5 mV s^{-1}	662 C g^{-1}	2000	s15
Pt//$NiCo_2O_4$ nanobelt/graphene	3 electrode (Hg/HgO)	CV (0.0 to 0.55 V) GCD (0.0 to 0.55 V)	6.0 M KOH	1 A g^{-1}	1073 F g^{-1}	3000	s16
Pt//$NiCo_2O_4$-RGO	3 electrode (Hg/HgO)	CV (0.0 to 0.55 V) GCD (0.1 to 0.5 V)	6.0 M KOH	1 A g^{-1}	835 F g^{-1}	4000	s17

Table S2 Impedance parameters obtained after fitting EIS data.

Sample	**R_s (Ohm)**	**R_{ct} (Ohm)**	**Q (CPE) (mF)**	**Diffusion admittance, Y_0 (mMho) [W]**	**C (mF)**
$NiCo_2O_4$	0.93	0.83	0.74	95.1	232
rGO-$NiCo_2O_4$	0.95	0.35	0.75	400	90

Table S3 A comparison of energy density and power density (full cell study) of $NiCo_2O_4$ nanostructures obtained by different synthetic protocol

Material	Method of Synthesis	Energy Density (Wh kg^{-1})	Power Density (W kg^{-1})	Ref.
$NiCo_2O_4$ hollow spherical nano-architecture				
$NiCo_2O_4$ hollow spheres	Solvothermally in a 50 ml Teflon liner at 180 °C for 24 h. Followed by heat treatment at 450 °C (air).	--	--	s1
CNS/ $NiCo_2O_4$ core-shell sub-microspheres	Hydrothermally in a Teflon liner at 180 °C for 12 h. Followed by heat treatment at 350 °C (air). CNS was added initially to obtain the morphology. (CNS act as template)	--	--	s2
$NiCo_2O_4$ hollow microspheres	Solvothermally in a Teflon liner at 120 °C for 10 h. Followed by heat treatment at 300 °C (air).	--	--	s3
$NiCo_2O_4$ hollow spheres	Reflux method in a flask at 90 °C for 4 h. Followed by heat treatment at 400 °C (air). Carbon sphere was added initially to obtain the morphology. (carbon sphere act as template)	34.8/11.6	464/5220	s4
Hollow $NiCo_2O_4$ submicro-spheres	Reflux method in a RB at 180 °C for 3 h in an oil bath. Followed by heat treatment at 300 °C (air).	27.2/10.9	102/8160	s5
Hollow urchin-like $NiCo_2O_4$ microspheres/graphite sheet	Co-precipitation method at 35 °C for 12 h. Followed by heat treatment at 250 °C (air).	36/16.5	852/11900	s6
Uniform $NiCo_2O_4$ Hollow Spheres	Solvothermally in a Teflon liner at 180 °C for 6 h. Followed by heat treatment at 350 °C (air).	--	--	s7
Mesoporous $NiCo_2O_4$ hollow spheres	Solvothermally in a Teflon liner at 100 °C for 24 h. Followed by heat treatment at 300 °C (air)	--	--	s8
rGO-$NiCo_2O_4$ hollow sphere	**Spray drying method using a spray dryer. Followed by heat treatment at 350 °C (air then N_2)**	**72.4/20.8**	**745/27800**	**This Work**
$NiCo_2O_4$ /Graphene/rGO composite				
$NiCo_2O_4$/graphene	Dry synthesis technique (solid state mixing). Followed by heat treatment at 300 °C (air).	--	--	s9
$NiCo_2O_4$/3D graphene	Hydrothermally in a 100 ml Teflon liner at 180 °C for 12 h. Followed by heat treatment at 300 °C (air).	73.8/26.7	800/8000	s10
$NiCo_2O_4$-Nanosheet/rGO	Reflux method in a 250 ml RB at 90 °C for 6 h in an oil bath. Followed by heat treatment at 330 °C (air).	--	--	s11
$NiCo_2O_4$-Nanowire/rGO	Reflux method in a 250 ml RB at 90 °C for 8 h in an oil bath. Followed by heat treatment at 300 °C (air).	--	--	s11
$NiCo_2O_4$-rGO	Hydrothermally in a Teflon liner at 180 °C for 12 h. Followed by heat treatment at 350 °C (air).	--	--	s12
$NiCo_2O_4$ Nanoparticle/graphene	Hydrothermally in a 100 ml Teflon liner at 180 °C for 12 h. Followed by heat treatment at 800 °C (N_2) and then at 350 °C (air).	--	--	s13
Mesoporous NCO/GO	Chemical co-precipitation route. Followed by heat treatment at 250 °C (air).	51.4/4.2	990/50000	s14
Mesoporous NCO/RGO	Self-combustion method. No further heat treatment.	--	--	s15
$NiCo_2O_4$ nanobelt/graphene	Hydrothermally in a 50 ml Teflon liner at 100 °C for 12 h. Followed by heat treatment at 250 °C (air).	--	--	s16
$NiCo_2O_4$-RGO	Hetero-assembly of oppositely charged nano-sheets at the molecular layer was used to design and synthesize RGO-based precursor. Followed by heat treatment at 200 °C (air).	--	--	s17

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