Supplementary Data

Gram-Scale Synthesis of rGO Wrapped Porous α-Fe_2O_3 as an Advanced Anode Material for Na-ion Batteries with Superior Cyclic Stability

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Characterization of the α-Fe_2O_3@rGO core@shell nanocubes

The phase purity of the α-Fe_2O_3@rGO core@shell nanocubes was analyzed using a high-power powder X-ray diffractometer (Rigaku, Japan) in a 2θ range of 10-70^o with a scan rate of 2^o min^{-1}. Thermogravimetric analysis (TGA) of the samples was accomplished in an air atmosphere using a Q50 TGA analyzer (TA Instruments) at a temperature of 30-700°C with a heating rate 10°C min^{-1}. Raman spectroscopy of the samples was demonstrated using a Renishaw inVia spectrometer with a He:Ne laser (λ = 633 nm) in the wavelength range of 200-2,000 cm^{-1}. The N_2 adsorption/desorption isotherms of the α-Fe_2O_3@rGO core@shell nanocubes samples were determined at a temperature of 77 K (Belsorp-MAX, SBEL, Japan Inc.), and the specific surface area (SSA) was estimated using the BET method. The morphology of the α-Fe_2O_3@rGO core@shell nanocubes was examined by a field emission scanning electron microscopy (FE-SEM, Sigma 300, JEOL) and the transmission electron microscopy (TEM, Tecnai F20, FEI). The elemental composition was analyzed using energy dispersive analysis (EDS) coupled with FE-SEM and TEM instruments. The XPS analysis of the samples was performed using a K_α X-ray photoelectron spectrometer (Thermo Scientific Inc.) for the elemental composition and electronic/chemical state of the elements.

Electrochemical study of the α-Fe_2O_3@rGO core@shell nanocubes

The electrochemical performance of the α-Fe_2O_3@rGO core@shell nanocubes was studied using CR2032 coin-type cells. For the making of the working electrode, 80.0 wt.% of α-Fe_2O_3@rGO core@shell nanocubes were mixed with 20.0 wt.% of SWCNT (MEIJO eDIPS) in 5.0 mL of ethanol and sonicated for about 10 min. Afterward, a vacuum filter (PVDF, hydrophilic filter paper, 1.2 cm × 1.2 cm) was carried out and dried the electrodes at 80°C under a vacuum oven for overnight to evaporate the solvent molecules. The mass loading was about 1.0 mg cm^{-2} for all the electrodes. For the fabrication of Na-ion half cells, metallic Na-

foil (Na-cubes, Sigma-Aldrich) was employed as a counter electrode and 0.6 M sodium hexafluorophosphate ($NaPF_6$) in 1:1 wt.% ethylene carbonate (EC): propylene carbonate (PC) with 0.02 wt.% of fluoroethylene carbonate (FEC) was used as an electrolyte (50.0 μL). Here, a Whatman® glass microfiber filter (Grade GF/A) was employed as a separator. The fabrication of Na-ion half cells was carried out under an argon-filled glove box with below 0.1 ppm levels of oxygen and moisture. After the fabrication of cells, for a better interaction of electrolyte with a working electrode, cells were kept under aging for about 2 h. The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves, as well as cyclic stability studies, were carried out in a potential window of 0.005-3.0 V vs. Na/Na^+ using a multichannel battery tester (WMPG1000S, WonA Tech). The electrode kinetics were performed using electrochemical impedance spectroscopy (EIS) in the frequency range of 0.01 Hz to 100 kHz on Bio-Logic Science Instruments (SP-200) electrochemical workstation. The galvanostatic intermittent titration technique (GITT) analysis of the samples was carried out at a pulse time of 10 min with a rest time of 60 min at a 0.1 C rate.

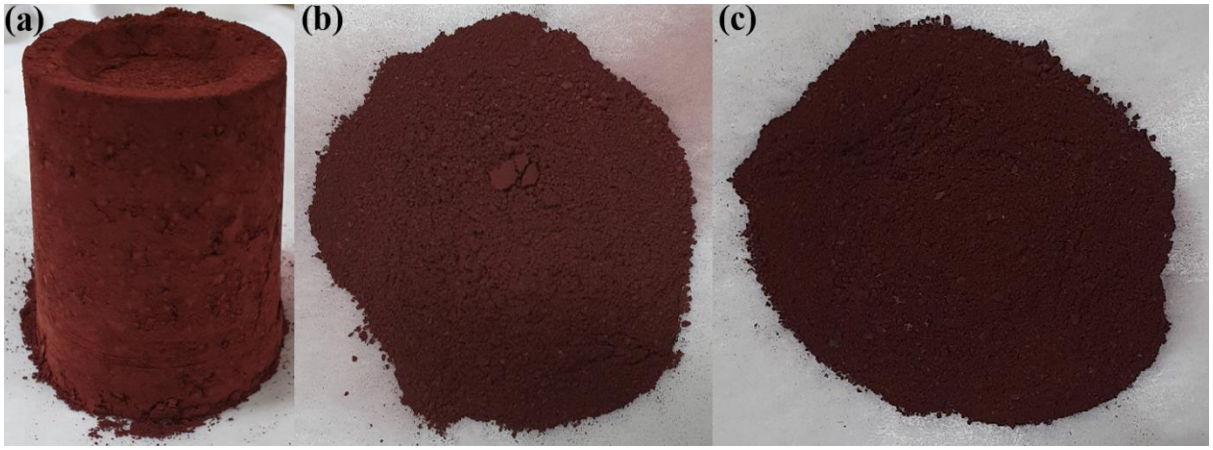


Figure. S1 Digital images of (a) α-Fe_2O_3, (b) α-Fe_2O_3@rGO-10 wt.%, and (c) α-Fe_2O_3@rGO-20 wt.% powder samples.

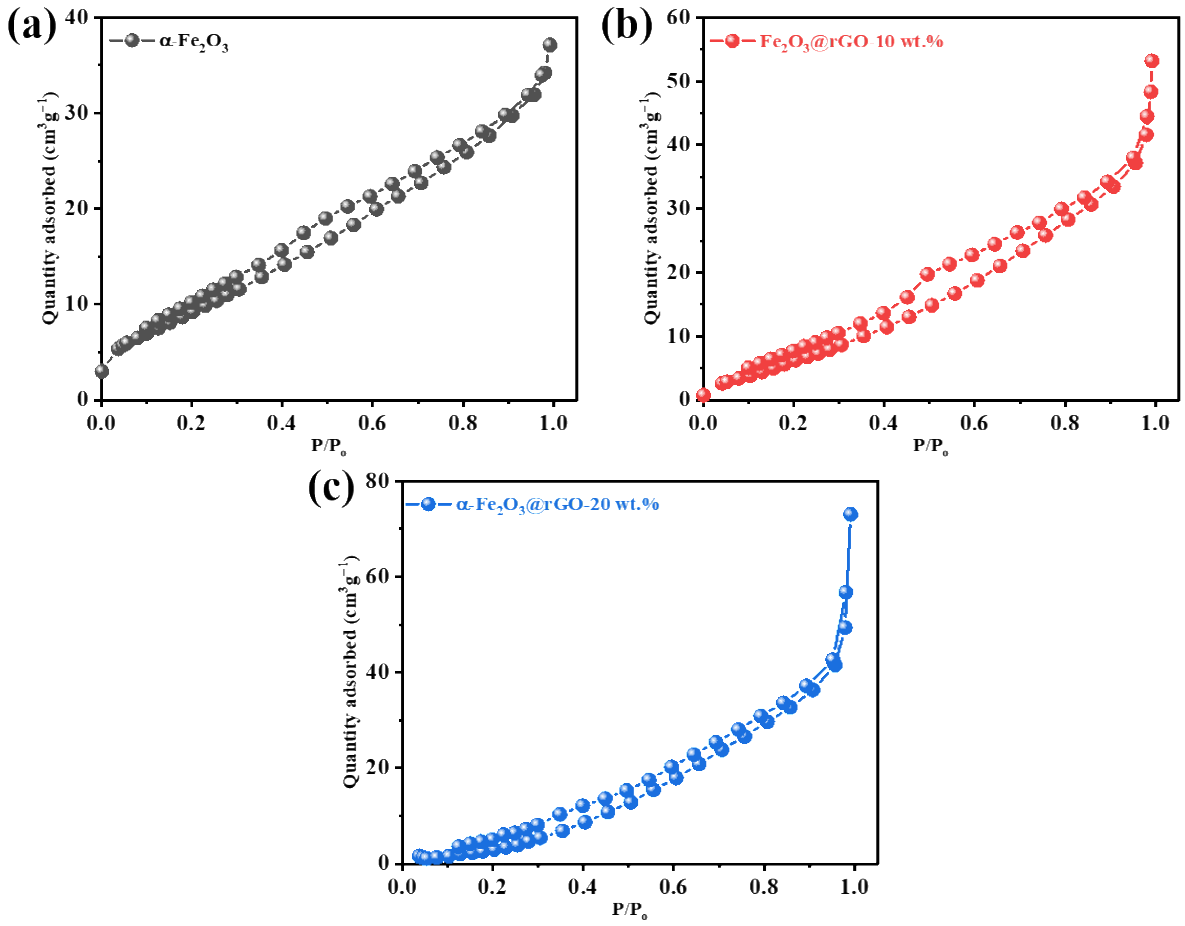


Figure. S2 BET surface area plots of (a) α-Fe_2O_3, and (b & c) α-Fe_2O_3@rGO core@shell nanocubes.

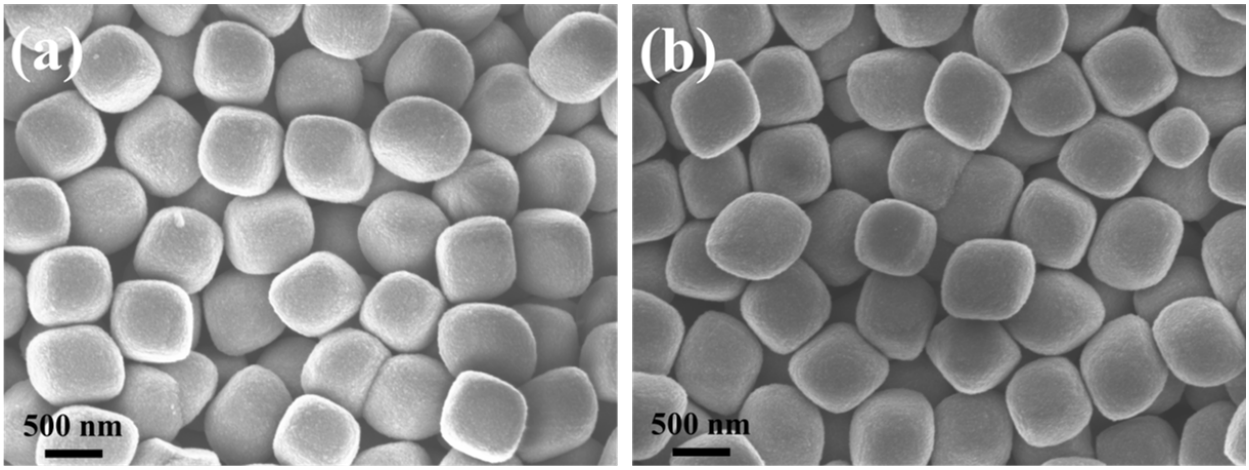


Figure. S3 FE-SEM images (a) α-Fe_2O_3, and (b) PEI-α-Fe_2O_3 nanocubes.

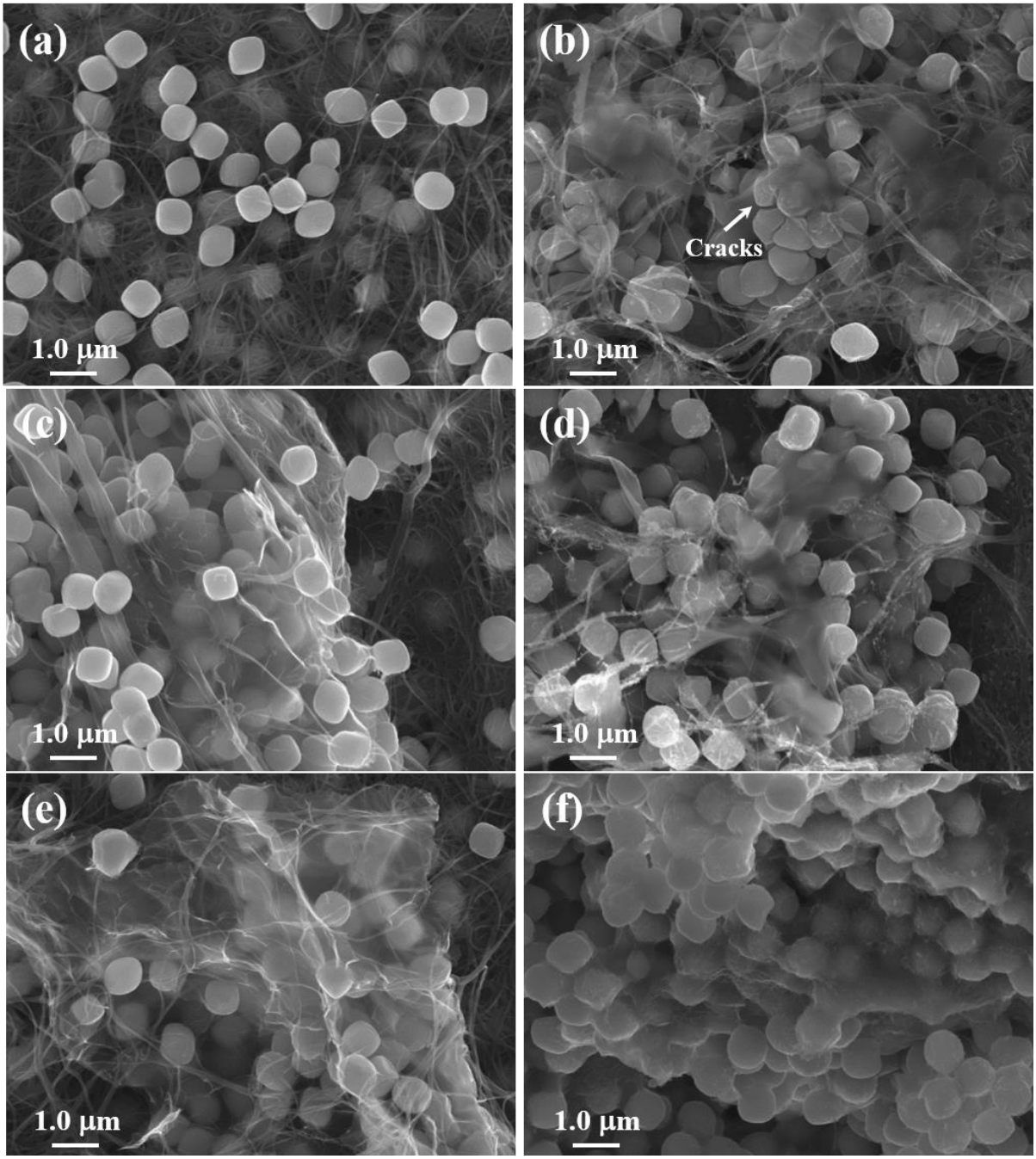
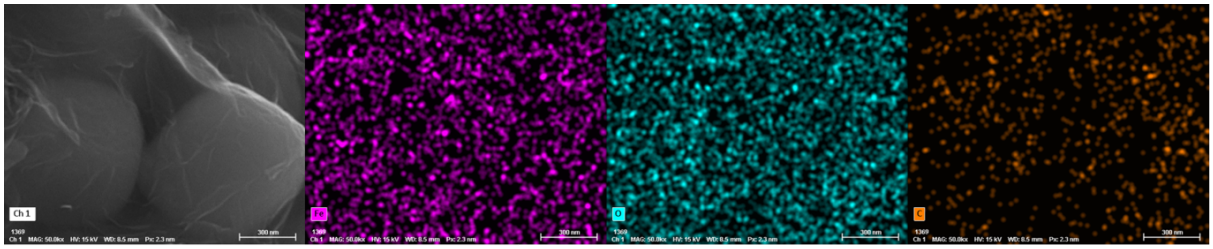
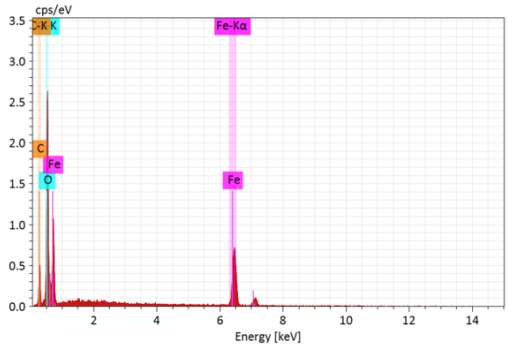


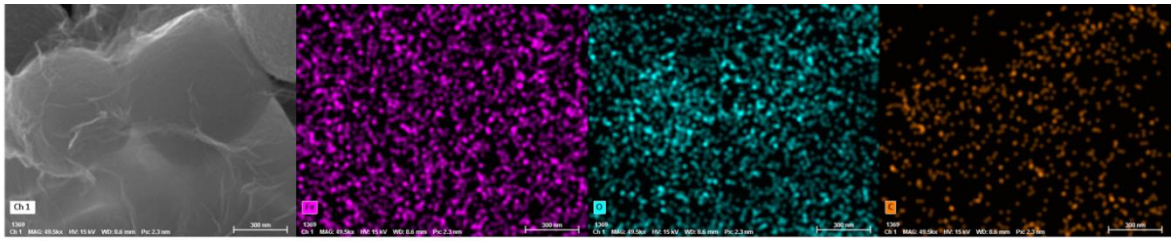
Figure. S4 FE-SEM images of (a) α-Fe_2O_3/SWCNT, (c) α-Fe_2O_3@rGO-10 wt.%/SWCNT, (e) α-Fe_2O_3@rGO-20 wt.%/SWCNT samples before, and (b) α-Fe_2O_3/SWCNT, (d) α-Fe_2O_3@rGO-10 wt.%/SWCNT and (f) α-Fe_2O_3@rGO-20 wt.%/SWCNT samples after 20 cycles at 0.1 C-rate.

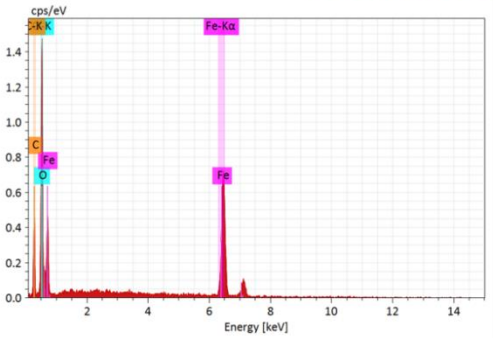




Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	Abs. Error [%] (3 sigma)
Fe	26	32.61	54.58	22.80	3.62
O	8	13.64	22.83	33.30	7.98
C	6	13.50	22.59	43.89	9.17
		59.75	**100.00**	**100.00**	

Figure. S5 SEM-EDS color mapping, and EDS spectra of α-Fe_2O_3@rGO-10 wt.% core@shell nanocubes.





Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	Abs. Error [%] (3 sigma)
Fe	26	31.87	48.09	19.25	3.65
O	8	17.74	17.71	32.96	8.62
C	6	22.67	34.20	47.49	11.89
		66.28	**100.00**	**100.00**	

Figure. S6 SEM-EDS color mapping, and EDS spectra of α-Fe_2O_3@rGO-20 wt.% core@shell nanocubes.

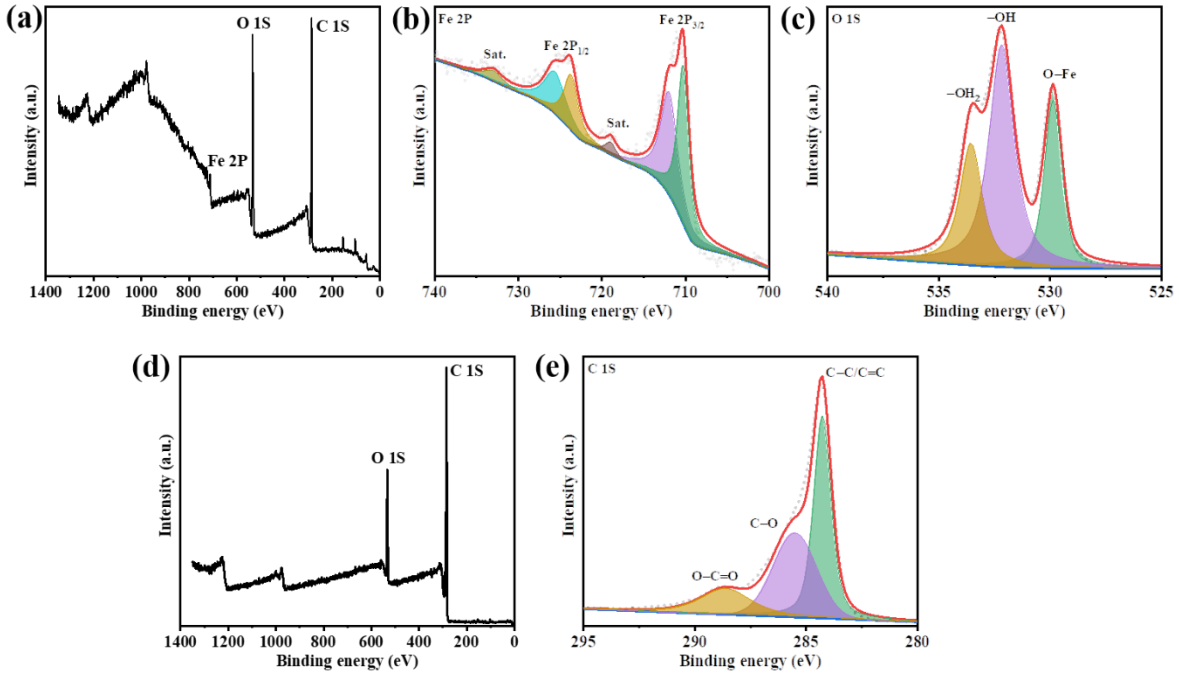


Figure. S7 (a & d) XPS survey spectrums of α-Fe_2O_3 and rGO, and (b & c) high-resolution XPS spectra of Fe2p, and O1s of α-Fe_2O_3, and (e) high-resolution XPS spectra of C1s of rGO.

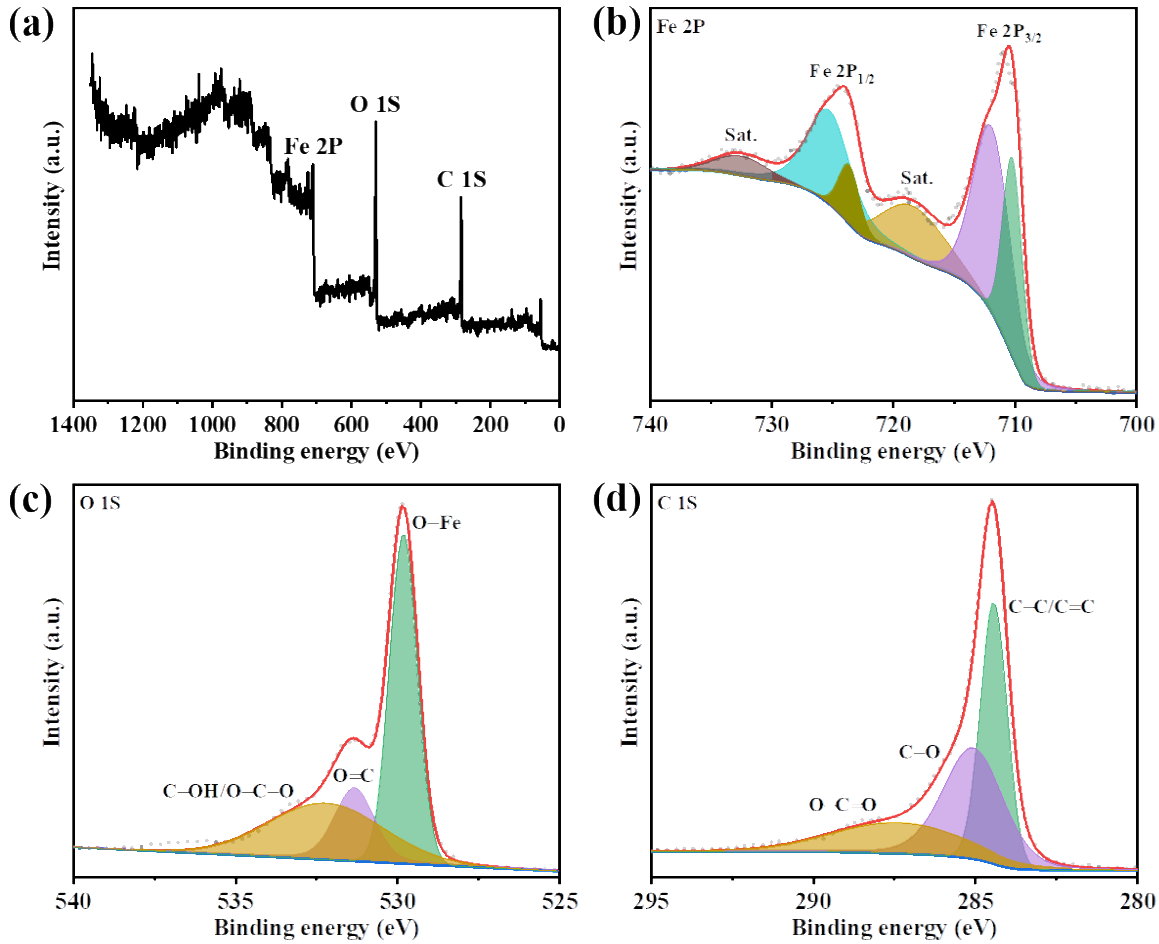


Figure. S8 (a) XPS survey spectrum, and (b-d) high-resolution XPS spectra of Fe2p, O1s, and C1s of α-Fe_2O_3@rGO-20 wt.% core@shell nanocubes.

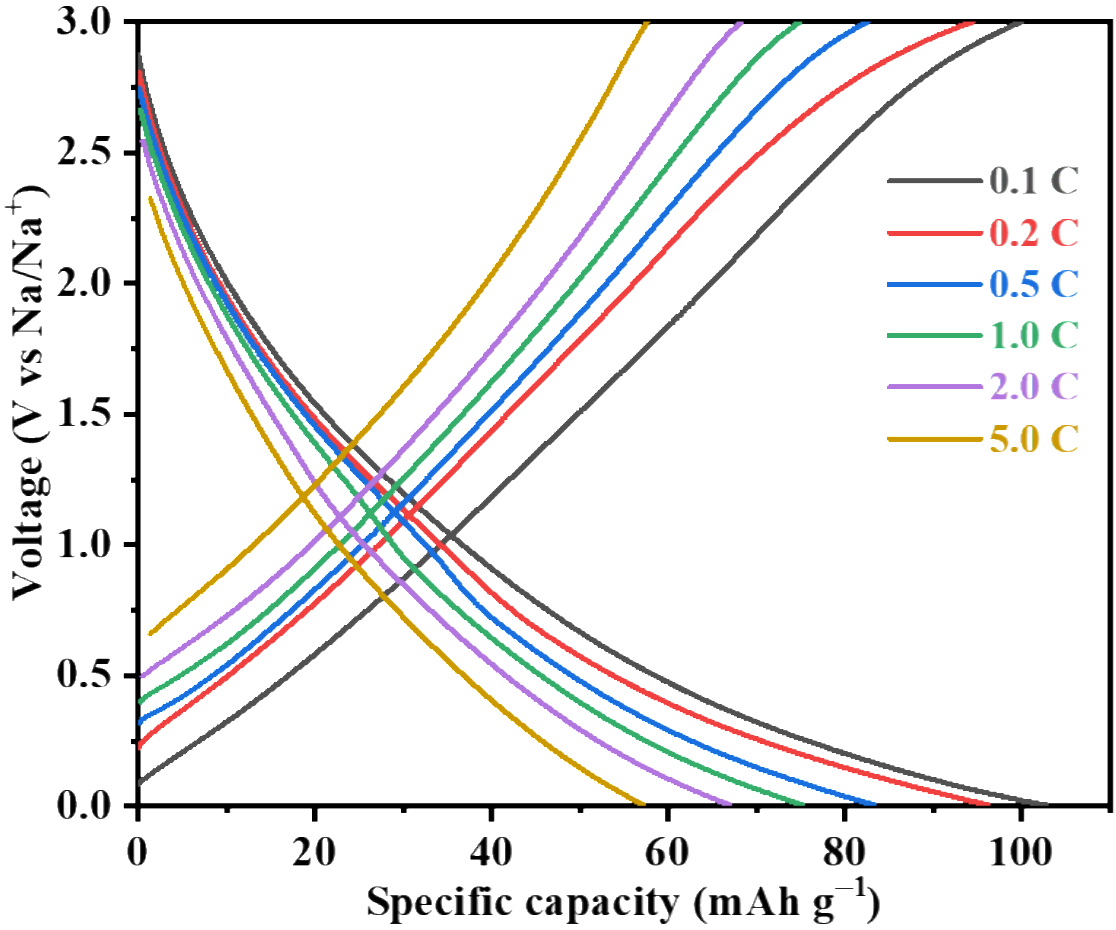


Figure. S9 GCD plot of SWCNTs electrode at various C-rates with an electrode mass of 1.0 mg cm^{-2}.

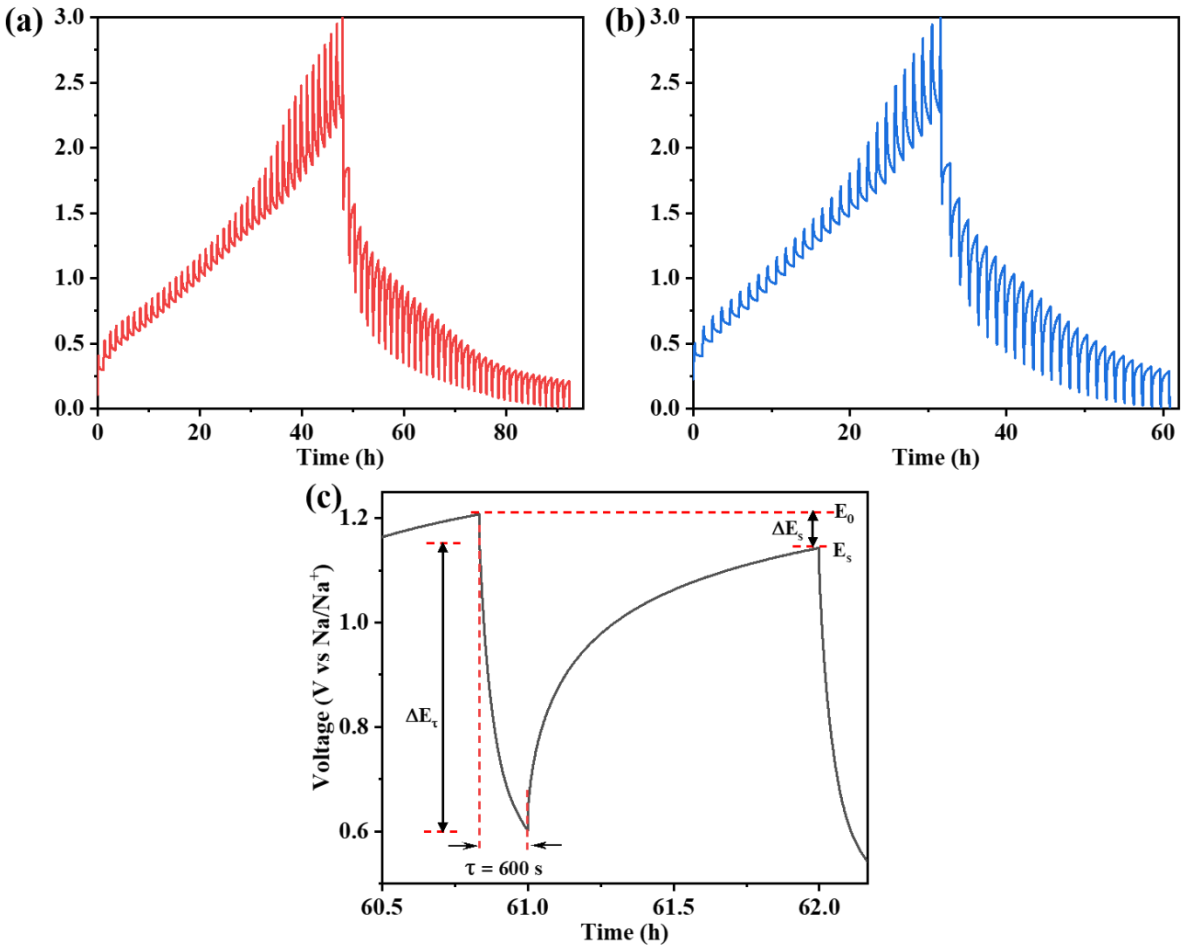


Figure. S10 GITT plots of (a) α-Fe_2O_3, and (b) α-Fe_2O_3@rGO-20 wt.% samples, and (c) single titration curve of α-Fe_2O_3@rGO-10 wt.% sample during the discharge.

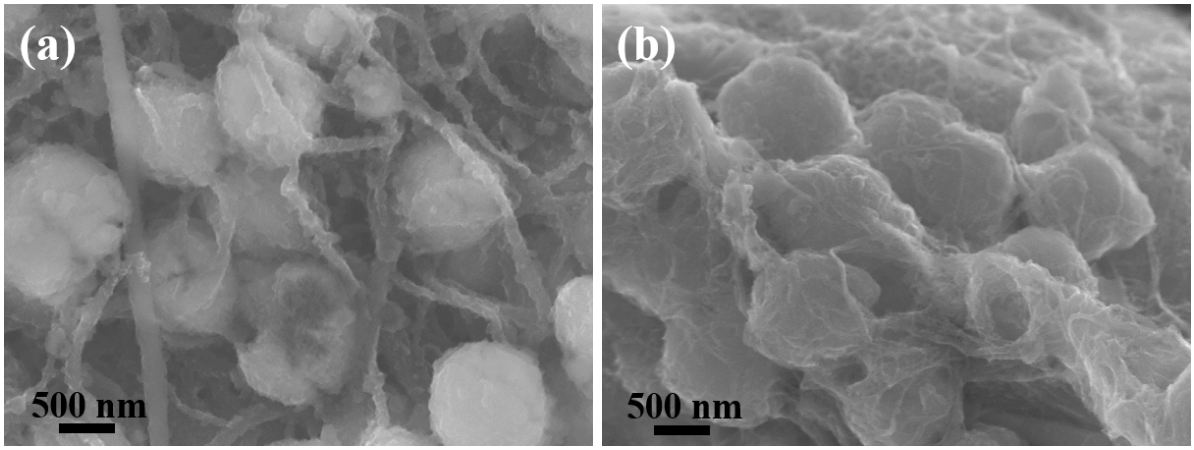


Figure. S11 FE-SEM images of (a) α-Fe_2O_3@rGO-10 wt.%, and (b) α-Fe_2O_3@rGO-20 wt.% core@shell nanocubes after the 650^{th} cycle.

Table T1. Comparison of electrochemical performance of α-Fe_2O_3@rGO core@shell nanocubes with the reported Fe_2O_3/rGO materials (DEC = Diethyl Carbonate, Diglyme = Diethylene Glycol Dimethyl Ether, DMC = Dimethyl Carbonate, EC = Ethylene Carbonate, FEC = Fluoroethylene Carbonate, PC = Propylene Carbonate).

S.No	Electrode material	Electrolyte	Specific capacity (vs. Na, mAh g^{-1})	Rate capability (mAh g^{-1})	Cyclic stability	Reference
1	α-Fe_2O_3/rGO nanocomposite	1.0 M $NaClO_4$ in 1:1 EC:DEC	~ 700.0 at 0.1 C	~ 77.0 at 2.0 C	~ 310.0 at 0.1 C after 150 cycles	[12]
2	α-Fe_2O_3@rGO nanorods	1.0 M $NaPF_6$ in 1:1:0.05 EC:DEC:FEC	~ 450.0 at 0.1 C	~ 92.0 at 1.6 C	~ 332.0 at 0.2 C after 300 cycles	[13]
3	α-Fe_2O_3@C/rGO nanocomposite	1.0 M $NaClO_4$ in PC with 2 vol.% FEC	~ 720.0 at 0.05 C	-	~ 300.0 at 0.05 C after 50 cycles	[19]
4	N, S co-doped modified rGO/Fe_2O_3	1.0 M $NaClO_4$ in 1:1 EC:DMC	~ 670.0 at 0.1 C	~ 200.2 at 2.0 C	~ 440.0 at 0.1 C after 110 cycles	[20]
5	Fe_2O_3/rGO nanocomposite	1.0 M $NaClO_4$ in 1:1 EC:PC	~ 251.9 at 0.1 C	~ 32.8 at 2.0 C	~ 289.0 at 0.05 C after 50 cycles	[21]
6	Fe_2O_3/rGO nanocomposite	1.0 M $NaPF_6$ in 1:1 EC:DEC with 5 % FEC	~ 500.0 at 0.1 C	~ 200.0 at 2.0 C	~ 500.0 at 0.05 C after 100 cycles	[22]
7	Amorphous Fe_2O_3/rGO nanocomposite	1.0 M $NaSO_3CF_3$ in Diglyme	~ 561.0 at 0.1 C	~ 194.0 at 2.0 C	~ 350.0 at 0.1 C after 50 cycles	[23]

8	Fe_2O_3/N-graphene nanocomposite	1.0 M $NaClO_4$ in 1:1 EC:DEC	~ 285.0 at 0.1 C	~ 132.0 at 1.0 C	~ 306.0 at 0.05 C after 50 cycles	[24]
9	Fe_2O_3/N-graphene nanocomposite	1.0 M $NaSO_3CF_3$ in Diglyme	~ 638.4 at 0.1 C	~ 297.4 at 2.0 C	~ 412.8 at 0.5 C after 100 cycles	[45]
10	Mn-doped α-Fe_2O_3/rGO nanocomposite	1.0 M $NaClO_4$ in PC with 2 wt.% FEC	~ 150.0 at 0.1 C	~ 56.0 at 2.0 C	-	[46]
11	Fe_2O_3@N-C nanocomposite	1.0 M $NaClO_4$ in PC with 5 vol.% FEC	~ 412.6 at 0.1 C	~ 206.5 at 2.0 C	~ 473.7 at 0.1 C after 100 cycles	[47]
12	Fe_2O_3@N-C nanocomposite	1.0 M $NaClO_4$ in 1:1 EC:PC	~ 248.0 at 0.1 C	~ 100.0 at 2.5 C	~ 260.0 at 0.1 C after 150 cycles	[48]
13	M-Fe_2O_3@N-C nanocomposite	1.0 M $NaClO_4$ in 1:1 EC:PC with 10 vol.% FEC	~ 292.3 at 0.1 C	~ 166.0 at 2.0 C	~ 270.0 at 0.1 C after 100 cycles	[49]
14	α-Fe_2O_3@rGO-10 wt.% core@shell nanocubes	0.6 M $NaPF_6$ in 1:1 EC:PC with 5 wt. % FEC	~ 970.2 at 0.1 C	~ 77.8 at 5.0 C	~ 586.9 at 0.1 C after 100 cycles & ~ 98.2 at 0.1 C after 650 cycles	Present work