Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Coupled Flower-like Bi_2S_3 and Graphene Aerogels for Superior Sodium Storage Performance

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EXPERIMENT SECTION:

1. Materials synthesis: Graphene oxide aqueous solution was prepared by oxidization graphite powder according to a modified Hummers method.[1] For Bi_2S_3/GAs composites: first, 0.54 g $Bi(NO_3)_3{\cdot}5H_2O$, 0.52 g ethylenediaminetetraacetic acid disodium salt dehydrate(EDTA-2Na·$2H_2O$) and 70 mL GO(1 mg mL^{-1}) were mixed by ultrasonic treatment for 1 h and stirred for another 30 min; Next, 0.41 g L-cysteine was added to suspension and stirring for 30 min. Subsequently, the as-prepared suspension was hydrothermally treated at 180 °C for 24 h in 100 mL autoclave; and the obtained Bi_2S_3/GAs was washed with water and ethanol several times, and finally freeze-dried for 3 days. The Bi_2S_3 were obtained using the same condition, but without GO.

2. Materials characterization: XRD patterns was determined by PANalytical X'Pert PRO (Cu Kα radiation). The morphology of the products was characterized by Field-emission scanning electron microscope (Hitachi Limited SU-8010) and the nanostructure was characterized by transmission electron microscopy (Tecnai G2F30, FEI, US). X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo

Fisher Scientific K-Alpha(Fisher Scientific Ltd, Nepean, ON). Thermogravimetric analysis (TGA) was performed in air with 10 ℃ min^{-1}.

3. Electrochemical measurements: The working electrode slurry was prepared by mixing active materials, Super-P, carboxymethyl cellulose in a weight ratio of 7:2:1, and deionized water as solvent. The slurry was pressed onto a cleaned copper foil by a doctor-balding method and dried in a vacuum oven at 80 °C overnight. The thickness of the prepared electrode film is 100 μm and the loading of active material is 0.2~0.5 mg cm^{-2}.The performance of the SIBs was tested using standard 2032 type coin cells in an argon-filled glovebox. The separator was Glass fiber (GF/D) from Whatman, sodium foils was used as counter and reference electrodes, and the electrolyte was 1.0 M $NaCF_3SO_3$ in DIGLYME. The cells were galvanostatically charged and discharged over a cutoff voltage window of 0.01–3.00 V at room temperature on a battery test system (Shenzhen Neware Electronic Co., China). Cyclic voltammetry behavior was studied by CHI 650d electrochemical workstation at a scan rate of 0.2 mV s^{-1}. Electrical impedance spectroscopy (EIS) measurements were carried out on Princeton Applied Research PARSTAT 2273 advanced electrochemical system with 5 mV amplitude over the frequency range between 100 KHz and 10 mHz.

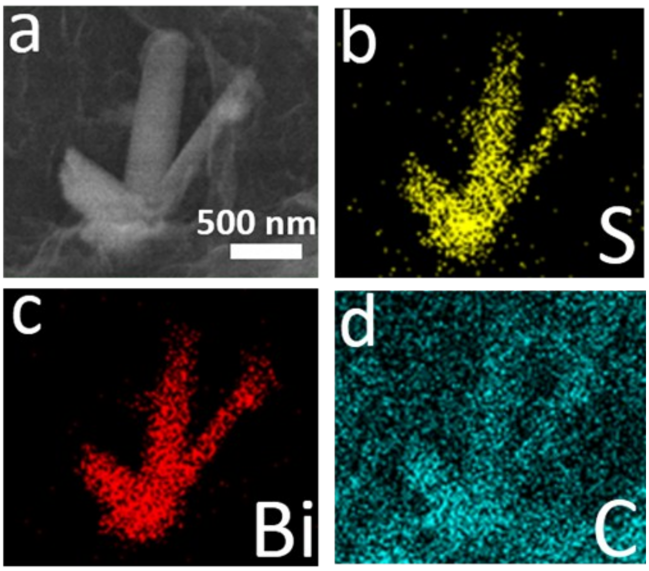

Fig S1. EDX mappings of Bi, S, and C in the selected area of Bi_2S_3/GAs.

Table 1. Comparison of sodium storage performance of Bi_2S_3/GAs with other reported carbon containing materials.

Sample	Cycle stability Capacity/Current/Cycles mAh g^{-1}/A g^{-1}/n	Rate capability Capacity/Current mAh g^{-1}/A g^{-1}	Cut-off voltage V	References
Bi_2S_3/GAs	397/ 0.1/50	336/2	0.01~3	This work
Bi_2S_3/PPy	381/0.3/100	335/1.2		2
SnS/rGO	386/0.1/100	240/0.4	0.01~2	3
Co_3S_4/PANI	252.5/0.2/100	189.3/2	0.05~2	4
MoS_2/carbon paper	286/0.08/100	205/1	0.01~3	5
Co_3S_4/graphene	329/0.5/50	307/2	0.005~3	6
MnS/RGO	308/0.1/125	118/0.8	0.01~2.6	7
NiS/rGO	160/0.2/10		0.005~3	8
SnO_2/NG	238/0.04/100	170/0.6	0.01~3	9
MWNT/Fe_2O_3/C	272/0.16/100	251/1	0.05~3	10
SnO_2/Graphene aerogels	322/0.02/100	220/0.64	0.01~3	11
$Li_4Ti_5O_{12}$/graphene	195/0.035/115	58/2.1	0.05~3	12
SnO_2/Graphene Dual Aerogel	270/0.2/20	184/1	0.01~2.5	13

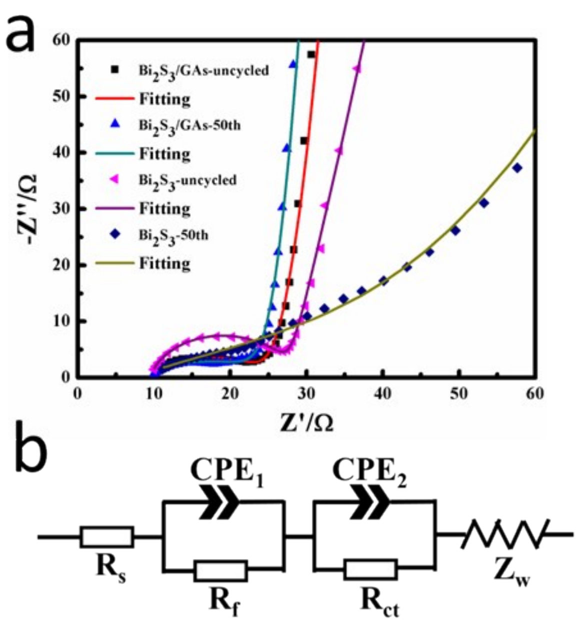

Fig S2. (a) EIS analysis of Bi_2S_3/GAs and Bi_2S_3 before and after cycling. (b) Equivalent circuits used for fitting the experimental EIS data.

Table S2 Fitting result of EIS spectra with the equivalent circuit proposed.

Samples	Before cycles		After 50 cycles	
	$R_s(\Omega)$	$R_{ct}(\Omega)$	$R_s(\Omega)$	$R_{ct}(\Omega)$
Bi_2S_3/GAs	8.59	15.84	8.37	16.3
Bi_2S_3	9.42	27.09	6.78	194

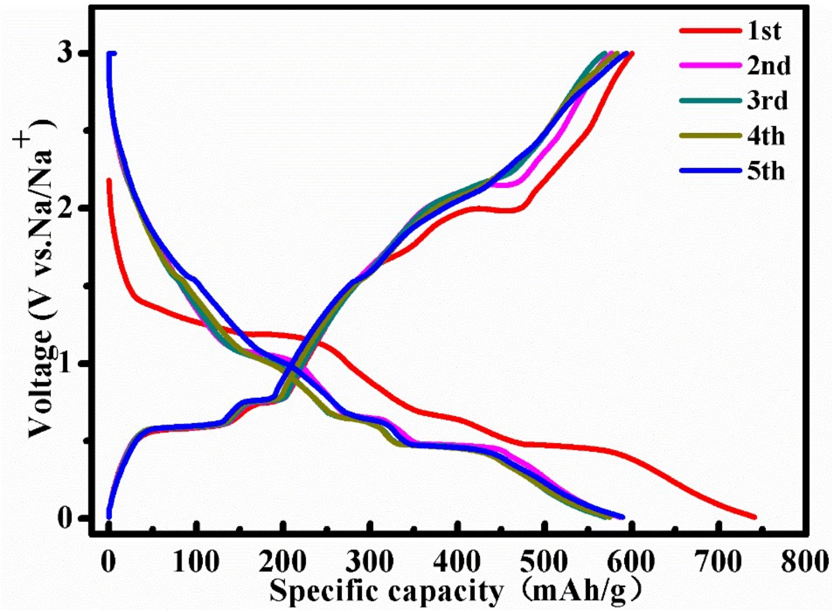

Fig S3. The first five discharge/charge profiles of Bi_2S_3 between 0.01 V and 3.0 V at a current density of 100 mA g^{-1}.

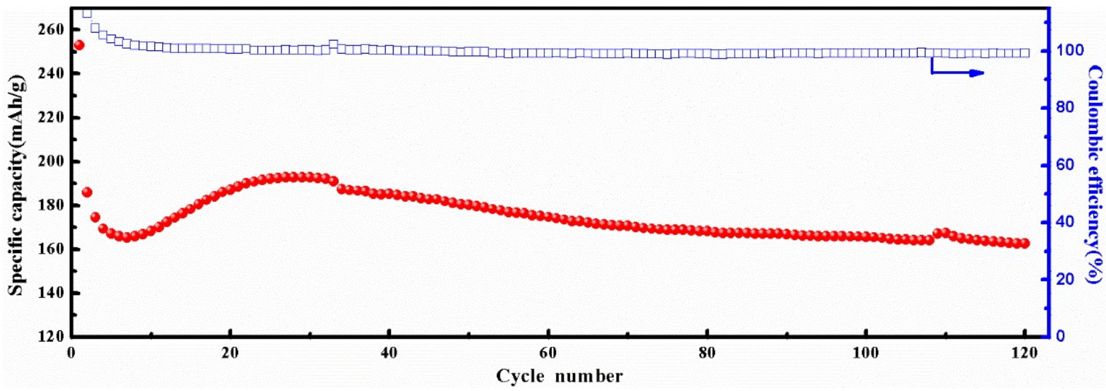

Fig S4. The cycle performance of individual graphene aerogels at 1A g^{-1}.

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