Supporting Information for

Freestanding 3D Graphene/Cobalt Sulfide Composites for Supercapacitors and Hydrogen Evolution Reaction

Yang Wang, Jing Tang, Biao Kong, Dingsi Jia, Yuhang Wang, Tiance An, Jun Li, Lijuan Zhang, and Gengfeng Zheng**

Laboratory of Advanced Materials, Department of Chemistry, Fudan University, Shanghai, 200433, China

* Address correspondence to: gfzheng@fudan.edu.cn, zhanglijuan@fudan.edu.cn .

Preparation of the CoS_x elelctrode

The CoS_x electrodes without 3DG were fabricated by mixing the as-prepared CoS_x powder, acetylene black and polytetrafluoroethylene (PTFE) binder in a weight ratio of 80:10:10. At first, CoS_x powder and acetylene black were blended together in an agate mortar until homogeneous black powder was achieved. Then PTFE was added to the mixture with a few drops of isopropanol. The synthesized paste was vaccum dried at 60 °C overnight and then pressed at 20 MPa onto a piece sponge which just serves as a scaffold or onto Ni foams for control test.

Supporting Figures

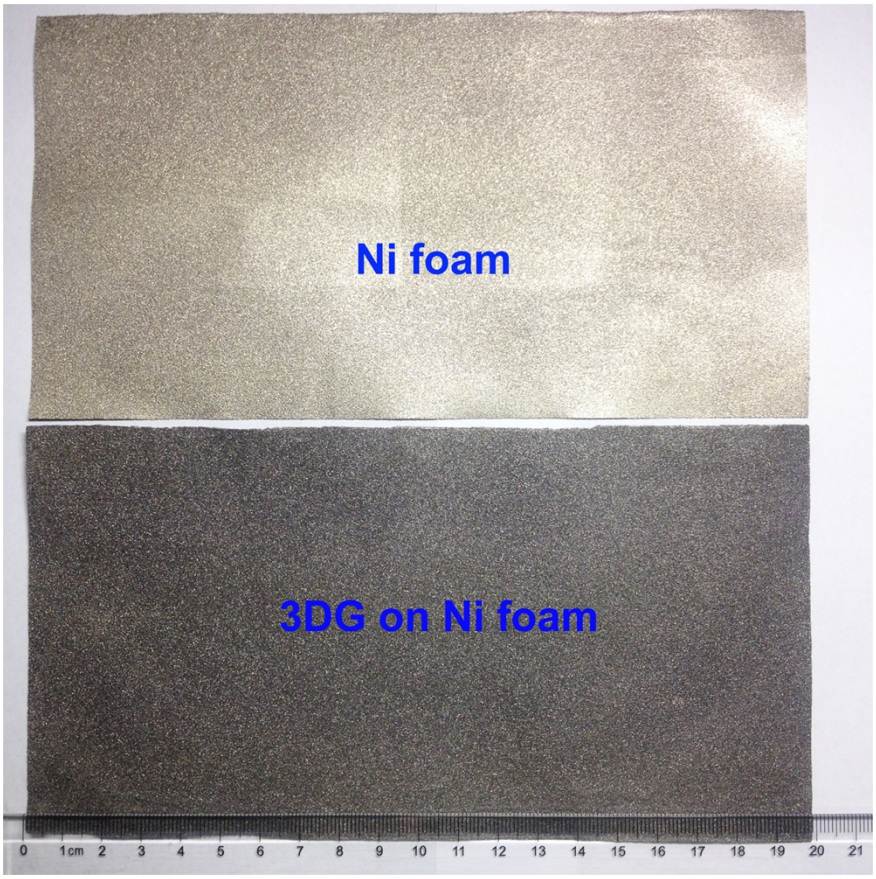

Figure S1. Photographs of (top) a Ni foam growth substrate, and (bottom) a 3-dimensional graphene (3DG) thin film grown on Ni foams.

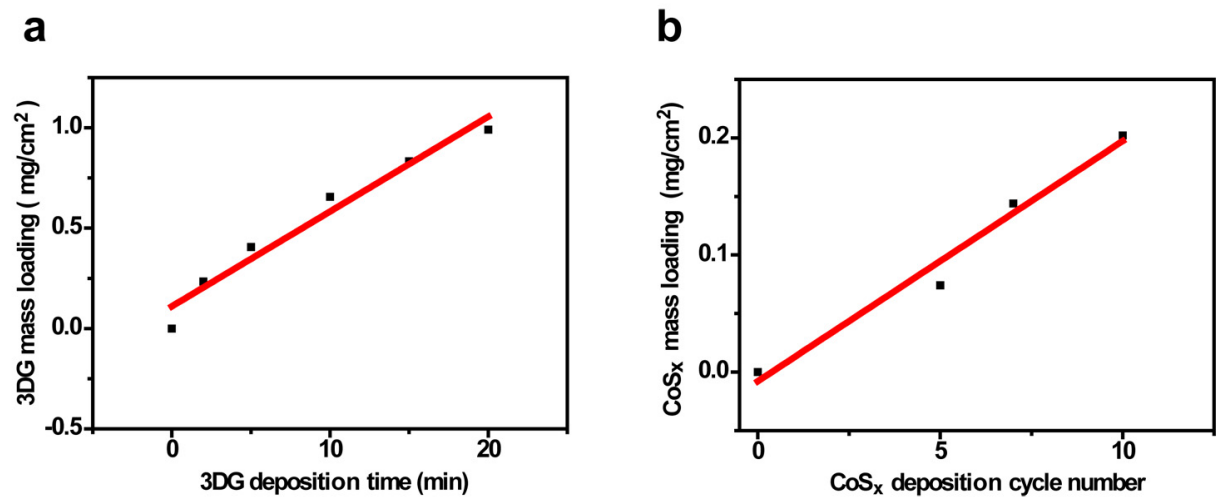

Figure S2. (a) The increase of mass loading of 3DG thin film with the deposition time. (b) The increase of mass loading of CoS_x nanoflakes with the electrodeposition cycle number.

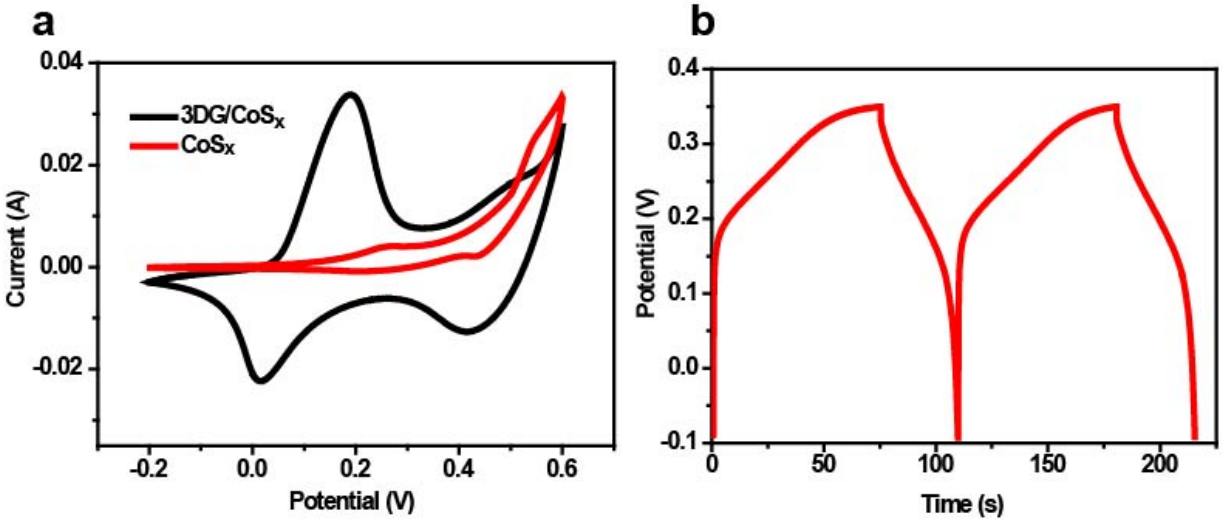

Figure S3. (a) CV curves of 3DG/CoS_x (black) and pure CoS_x (red) at a scan rate of 20 mv/s. (b) Galvanostatic charge-discharge curves of CoS_x electrode at a current density of 1 A/g.

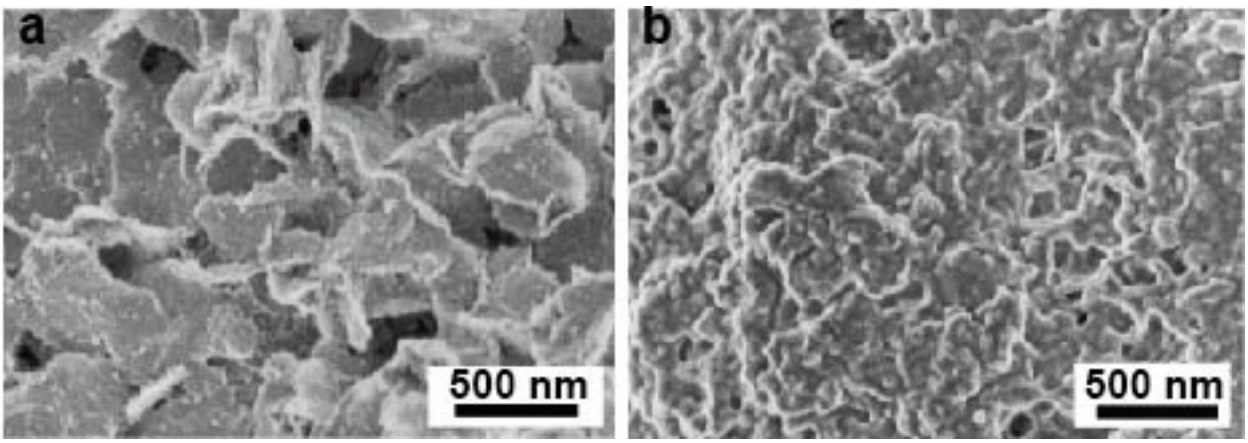

Figure S4. The images of 3DG/CoS_x after 5000 cycles at 2A/g in 1.0 M KOH electrolytes (a) and after controlled potential electrolysis for 24h in 1.0 M PBS (b).

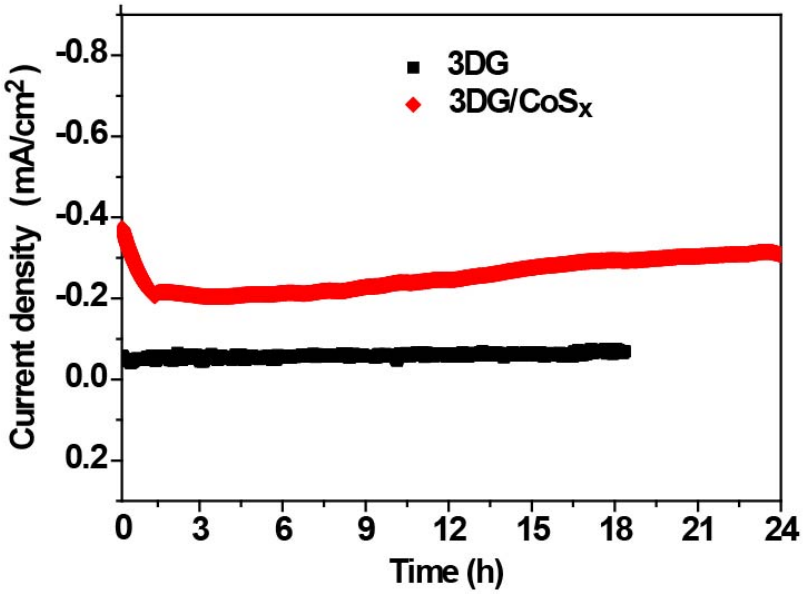

Figure S5. Current versus time during the long-term controlled potential electrolysis of 3DG/CoS_x (red) and 3DG (black).

Table S1. Electrochemical performance of the 3DG/CoSx as supercapacitor electrode materials, compared with other cobalt sulfide electrode materials.

Materials	***Specific capacitance***	***Cycling Stability***	***Reference***
3DG/CoS_x	443 F/g at 1 A/g	86% after 5000cycles at 2A/g	This work
CoS spheres	354 F/g at 0.5 A/g	75% after 300 cycles at 0.5 A/g	S1
Cobalt sulfide nanotubes	285 F/g at 0.5 A/g	86.5% after 1000 cycles at 0.5 A/g	S2
CoS_2 ellipsoids	224 F/g at 10 A/g	66% after 1000 cycles at 5.0 A/g	S3
Flower-like CoS	277 F/g at 50 mA/cm2	_	S4
ZIF-67 derived CoS nanocages	1475 F/g at 1A/ g	70.3% after 3000cycles at 10 A/g	S5
CoS_x/Ni foams	1471 F/ g at 4 A/ g	~100% after 1000cycles at 8A/g	S6
β-$CoS_{1.097}$/graphene	1535 F/g at 2 A/g	98% after 4000cycles at 20 A/g	S7
Co_3S_4/N-Graphene	2427 F/g at 2 mV/s	98% after 800cycles at 30 mV/s	S8
Co_3S_4 nanospheres/N-Graphene	675.9 F/g at 0.5 A/g	99% after 1000 cycles at 0 .5 A/g	S9

References:

S1. P. Justin and G. Ranga Rao, *Int. J. Hydrogen Energ.*, 2010, **35**, 9709-9715.

S2. H. Wan, X. Ji, J. Jiang, J. Yu, L. Miao, L. Zhang, S. Bie, H. Chen and Y. Ruan, *J. Power Sources*, 2013, **24**, 396- 402.

S3. L. Zhang, H.B. Wu and X.W. (David) Lou, *Chem. Commun*., 2012, **48**, 6912-6914.

S4. W. Dong, X. Wang, B. Li, L. Wang, B. Chen, C. Li, X. Li, X. Li, T. Zhang and Z. Shi, *Dalton Trans.*, 2011, **40**, 243-248.

S5. Z. Jiang, W. Lu, Z. Li, K. H. Ho, X. Li, X. Jiao, and D. Chen, *J. Mater. Chem. A*, 2014, **2,** 8603-8606.

S6. J. -Y. Lin and S. -W. Chou, *RSC Adv*., 2013, **3**, 2043-2048.

S7. B. Qu, Y. Chen, M. Zhan g, L. Hu, D. Lei, B. Lu, Q. Li, Y. Wang , L. Chen and T. Wang, *Nanoscale*, 2012, **4**, 7810 - 7816.

S8. A. N. Grace, R. Ramachandran, M. Vinoba, S.Y. Choi, D.H. Chu, Y. Yoon, S. C. Nam and S. K. Jeong, *Electroanal*., 2014, **26**, 199 - 208.

S9 Q. Wang, L. Jiao, H. Du, Y. Si, Y. Wang and H. Yuan, *J. Mater. Chem*., 2012, **22**, 21387-21391.