Electronic Supplementary Information

Direct 3D Printing of Graphene Oxide Hydrogel for Fabrication of High Areal Specific Capacitance Micro-supercapacitor

Xiawei Yun,[#a] Bingchuan Lu,[#b,c,d] Zhiyuan Xiong,[a] Bo Jia,[b,c,d] Bo Tang,[a] Henan Mao,[a] Ting Zhang,*[b,c,d] Xiaogong Wang*[a]

[a] Department of Chemical Engineering, Laboratory of Advanced Materials (MOE), Tsinghua University, Beijing 100084, P. R. China

[b] Biomanufacturing Center, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, P. R. China

[c] Biomanufacturing and Rapid Forming Technology Key Laboratory of Beijing, Beijing 100084, P. R. China

[d] Biomanufacturing and Engineering Living Systems, Innovation International Talents Base (111 Base), Beijing 10084, P. R. China

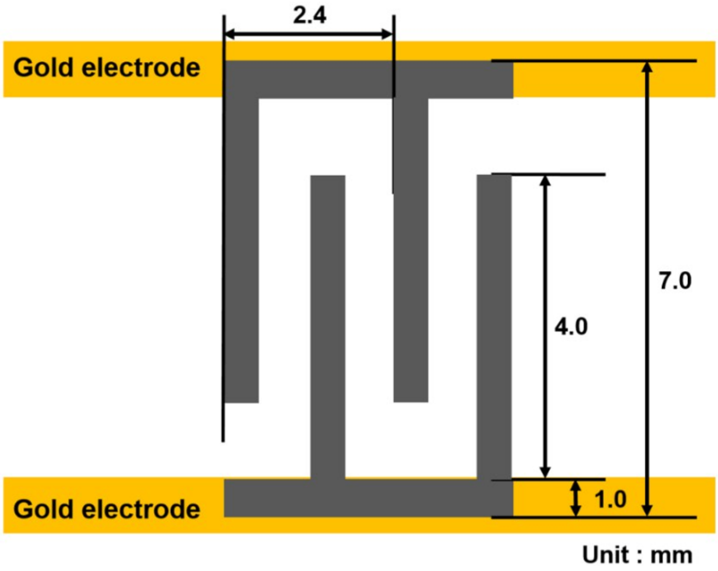

Fig. S1. Dimensional drawing of a single layer of the printed 3D structure (top-view).

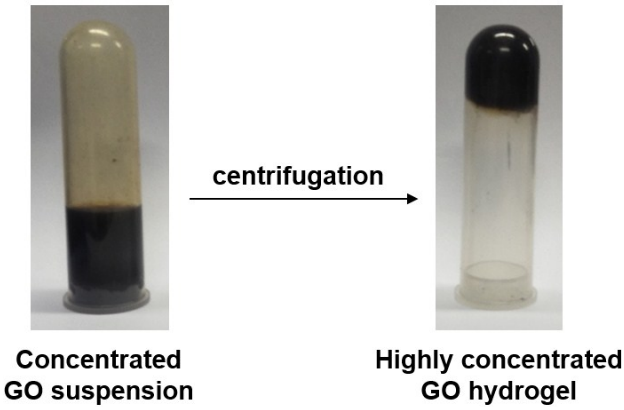

Fig. S2. Test tube inversion experiment of the highly concentrated GO suspension (17.5 mg mL^{-1}).

Table S1. Concentration, volume fraction (Φ_V) and parameters obtained from the fitting of the experimental data with the Herschel-Bulkley model.

Concentration	Φ_V	τ_0	n	K	R^2
17.5 mg mL^{-1}	0.0133	19.79	0.460	7.96	0.9997
21.5 mg mL^{-1}	0.0164	31.56	0.458	11.69	0.9991
25.5 mg mL^{-1}	0.0194	43.35	0.450	19.16	0.9997
31.5 mg mL^{-1}	0.0240	60.92	0.433	35.25	0.9998
40.0 mg mL^{-1}	0.0306	91.50	0.421	39.75	0.9989
50.0 mg mL^{-1}	0.0383	126.00	0.400	58.46	0.9992

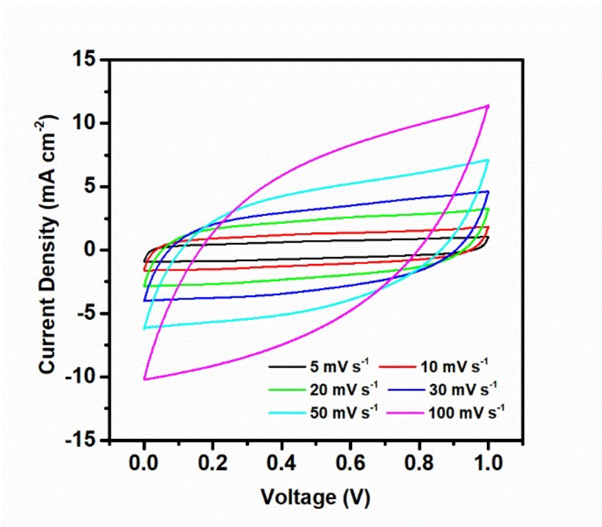

Fig. S3. CV curves at scan rates of 5, 10, 20, 30, 50 and 100 mV s^{-1}.

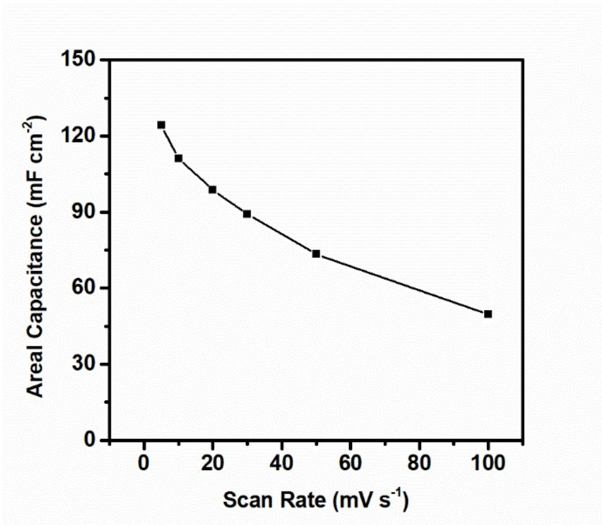

Fig. S4. Areal specific capacitances calculated from CV curves as a function of the scan rate.

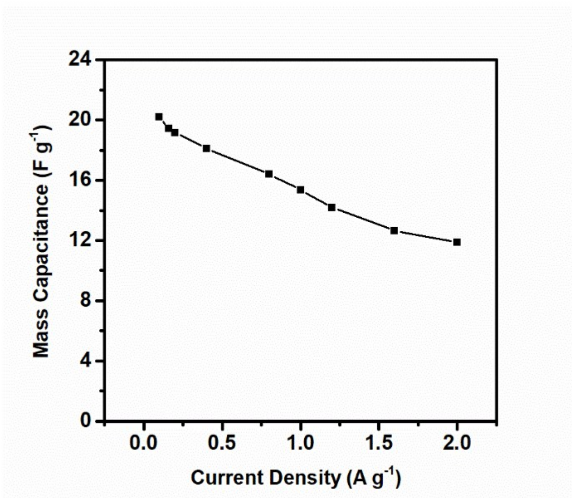

Fig. S5. Mass specific capacitances from GCD curves as a function of the current density.

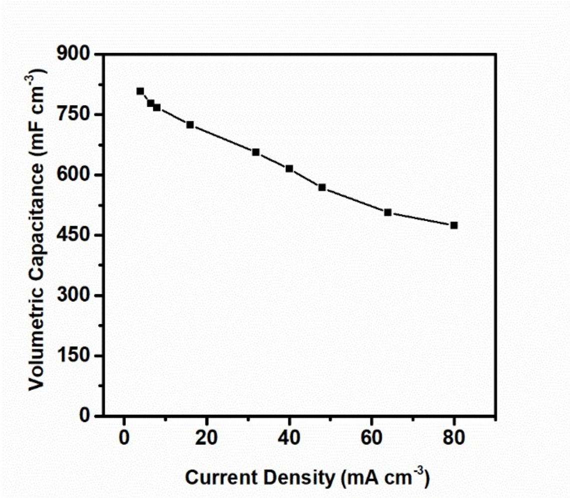

Fig. S6. Volumetric specific capacitances calculated from GCD curves as a function of the current density.

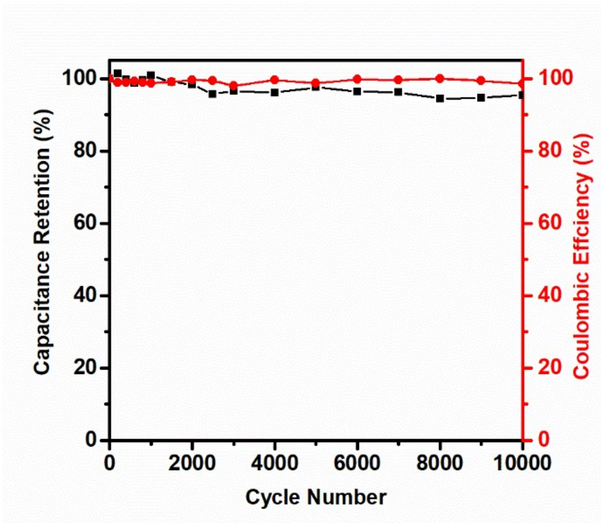

Fig. S7. Cycling performance and coulombic efficiency of the 3DHG-MSC at the current density of 8 mA cm^{-2} for 10000 cycles.

Table S2. Comparison of the electrochemical performances of various graphene MSCs

System	Electrolyte	Capacitance
3DHG[a] (This work)	H_3PO_4/PVA	111.1 mF cm^{-2} (10 mV s^{-1}) 101.0 mF cm^{-2} (0.5 mA cm^{-2})
3D printed graphene MSCs with interdigitated architecture (Ref. S1)	H_2SO_4/PVA	74.31 mF cm^{-2} (5 mV s^{-1}) (8 layers) 7.37 F g^{-1} (0.1 A g^{-1})
3D printed graphene SCs with sandwich	3M KOH aqueous	0.96 F cm^{-3} (2.6 A cm^{-3})

structure (Ref. S2)	electrolyte	
Printed planar MSCs (Ref. S3)	H_2SO_4/PVA	19.8 mF cm^{-2} (4 layers) 18.2 F cm^{-3} (3 A cm^{-3})
LPG[b] (Ref. S4)	H_2SO_4/PVA	36.4 mF cm^{-2} (10 mV s^{-1}) 37.9 mF cm^{-2} (0.6 mA cm^{-2})
LEG[c] (Ref. S5)	H_3PO_4/PVA	13.0 mF cm^{-2} (10 mV s^{-1}) 15.4 mF cm^{-2} (0.1 mA cm^{-2})
LIG[d] (Ref. S6)	H_3PO_4/PVA	0.8 mF cm^{-2} (10 mV s^{-1})

[a] 3DHG is the electrode with interdigitated architecture obtained by 3D printing of the highly concentrated GO hydrogel

[b] LPG is the electrode obtained by laser carving the porous graphene film

[c] LEG is laser-carved graphene, followed by electrochemical activation

[d] LIG is laser-induced graphene

Notes and references

S1 W. Li, Y. Li, M. Su, B. An, J. Liu, D. Su, L. Li, F. Li and Y. Song, *J. Mater. Chem. A*, 2017, **5**, 16281-16288.

S2 C. Zhu, T. Liu, F. Qian, T. Y. Han, E. B. Duoss, J. D. Kuntz, C. M. Spadaccini, M. A. Worsley and Y. Li, *Nano Lett*, 2016, **16**, 3448-3456.

S3 G. Sun, J. An, C. K. Chua, H. Pang, J. Zhang and P. Chen, *Electrochem. Commun.*, 2015, **51**, 33-36.

S4 X. W. Yun, Z. Y. Xiong, L. Tu, L. Bai and X. G. Wang, *Carbon*, 2017, **125**, 308-317

S5 M. Wu, Y. Li, B. Yao, J. Chen, C. Li and G. Shi, *J. Mater. Chem. A*, 2016, **4**, 16213-16218.

S6 J. B. In, B. Hsia, J.-H. Yoo, S. Hyun, C. Carraro, R. Maboudian and C. P. Grigoropoulos, *Carbon*, 2015, **83**, 144-151.