## **Supporting Information for**

Free-standing three-dimensional graphene/manganese oxide hybrid as binder-free electrode material for energy storage applications

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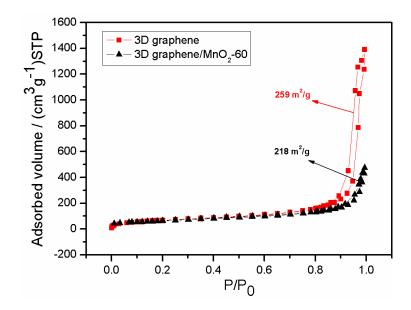


Figure S1. Nitrogen adsorption/desorption isotherms of 3D graphene and 3D graphene/MnO<sub>2</sub>-60 samples.

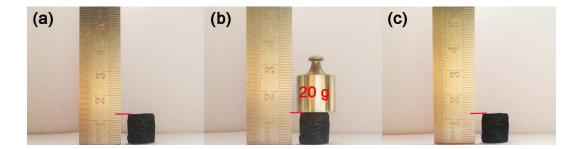


Figure S2. Digital photographs of a freestanding 3D graphene/ $MnO_2$ -60: (a) initial status, (b) supporting weight, and (c) releasing weight. The sample of 3D graphene/ $MnO_2$ -60 can endure a weight of 20 g without any damage and deformation, exhibiting the desirable strength property.

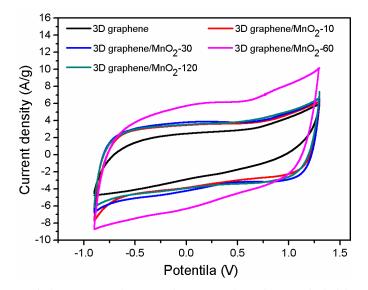


Figure S3. CVs of the 3D graphene and 3D graphene/MnO<sub>2</sub> hybrids prepared with different reaction times at scans rates of 50 mv/s. Among the four different 3D graphene/MnO<sub>2</sub> hybrids, the 3D graphene/MnO<sub>2</sub>-60 sample displays the largest area of CV profile. It also can be seen that there is no obvious difference of the CVs between the 3D graphene/MnO<sub>2</sub>-30 and the 3D graphene/MnO<sub>2</sub>-120, indicating that the over-high MnO<sub>2</sub> loading would lead to the decrease of the specific capacitance. The results show that the 3D graphene/MnO<sub>2</sub>-60 delivers high specific capacitance.

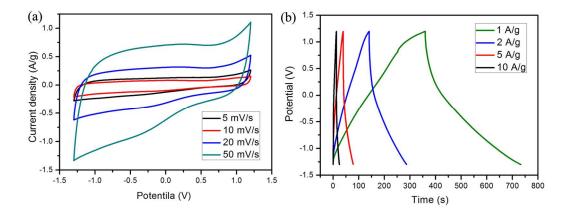


Figure S4. (a) CVs of the 3D graphene at scan rates of 5, 10, 20, and 50 mV/s. (b) Galvanostatic charging/discharging curves of the 3D graphene at different current densities. It can be seen that 3D graphene electrode shows relatively rectangular CV curves, indicating a nearly ideal supercapacitor behavior. Also, the 3D graphene

electrode presents approximate symmetric charge/discharge curves and good capacitive behavior with a rapid I-V response. At same time, it is achieving high-capacitance performance with the specific capacitance up to 150 F/g at 1 A/g.

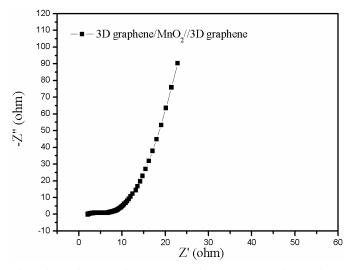


Figure S5. Nyquist plot of as-made asymmetric supercapacitor. The series resistance of the asymmetric supercapacitor is ~2.7  $\Omega$ , indicating a low internal resistance for the whole device.

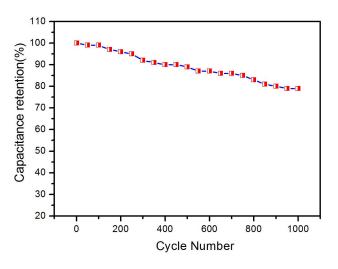


Figure S6. Cycling performance of as-made asymmetric supercapacitor testing at a current density of 10A/g. After 1000 charging/discharging cycles, the capacitance retention rates remained over 80%. The decay is mainly due to the relatively poor stability of  $MnO_2$  in ionic liquid electrolyte.