Supporting Information

Free-Standing Three-Dimensional Graphene/MnO_2 Composite Networks as Ultra-Light and Flexible Supercapacitor Electrodes

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Calculation of specific capacitance, areal capacitance and specific power and energy densities

1. The specific capacitance and the areal capacitance of the electrode with respect to three-electrode configuration can be calculated according to the following equations:

$$Q = \frac{1}{v}\int I_{(V)}\, dV \qquad (1)$$

where Q is the charge obtained from the CV curves based on graphene/MnO_2 composite（defined as G+MnO_2） and 3D graphene networks (defined as G), respectively. v (mV/s) is the potential scan rates, and $I_{(V)}$ is the applied current.

$$C_{S1} = \frac{Q_{(G+MnO_2)} - Q_{(G)}}{m_1 \cdot \Delta V} \ \&\ C_{A1} = \frac{Q_{(G+MnO_2)} - Q_{(G)}}{s \cdot \Delta V} \qquad (2)$$

$$C_{S2} = \frac{Q_{(G+MnO_2)}}{m_2 \cdot \Delta V} \qquad (3)$$

where C_{S1}(F/g) is the specific capacitance of MnO_2, C_{A1} (F/cm^2) is the areal capacitance of MnO_2, C_{S2} (F/g) is the specific capacitance of the entire electrode marked by the words “calculated for the entire electrode” in paper, ΔV (V) is the sweep potential window, s(cm^2) is the area of the electrode and m_1(g) is the mass of active materials in single electrode, m_2(g) is the entire mass of the single electrode. And, $Q_{(G+MnO_2)}$ and $Q_{(G)}$ are the charge obtained from equation(1), respectively. In addition, $Q_{(G)}$ is much smaller than $Q_{(G+MnO_2)}$ in our work.

2. The average specific capacitance (*C*, F/g), power density (*P*, kW/kg), and energy density(*E*,Wh/kg) with respect to two-electrode full cell from the charge/discharge curves can be calculated based on equations.

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (4)$$

$$P = \frac{E}{t} = \frac{1}{2} \cdot I \cdot \Delta V \quad (5)$$

$$E = \frac{1}{2} \cdot C \cdot (\Delta V)^2 \quad (6)$$

where *m*(g) is the total mass of the active material from the electrodes, ΔV (V) is the sweep potential window, *I*(A) is the applied current, and Δt (s) is the discharge time.

Supporting Figures and Tables

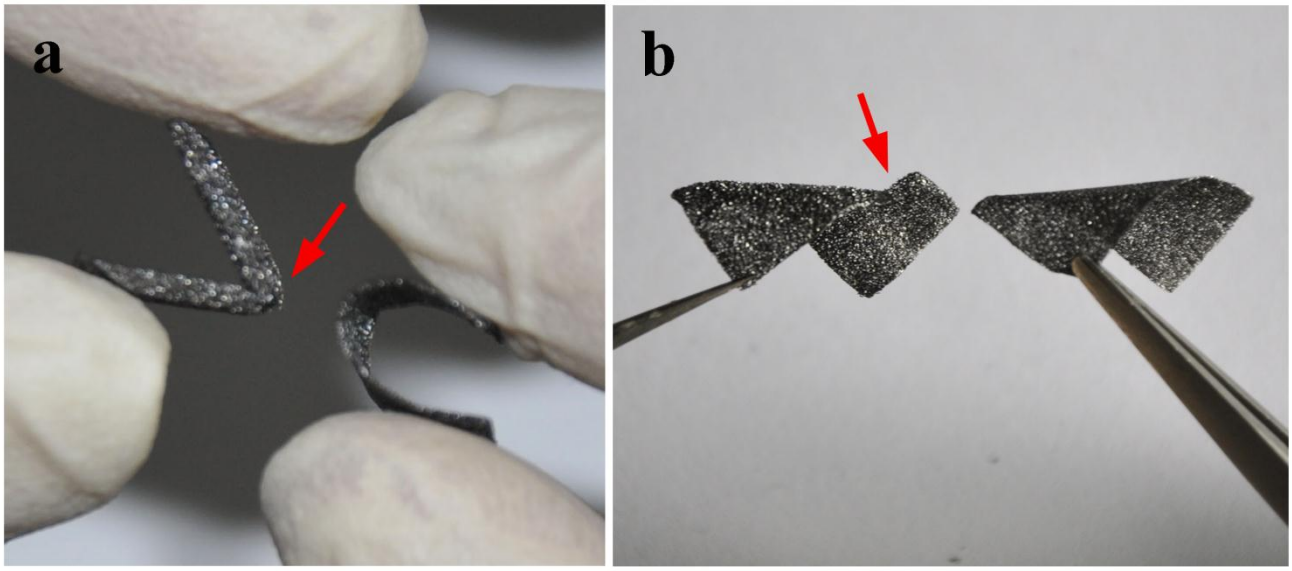

Figure S1. Digital photographs of the comparison between the 3D graphene networks from Ni foam (a) and the pressed Ni foam (b) under the same degree of mechanical deformation. As signed by the red arrows, obvious damage easily appeared on the 3D graphene network only from Ni foam.

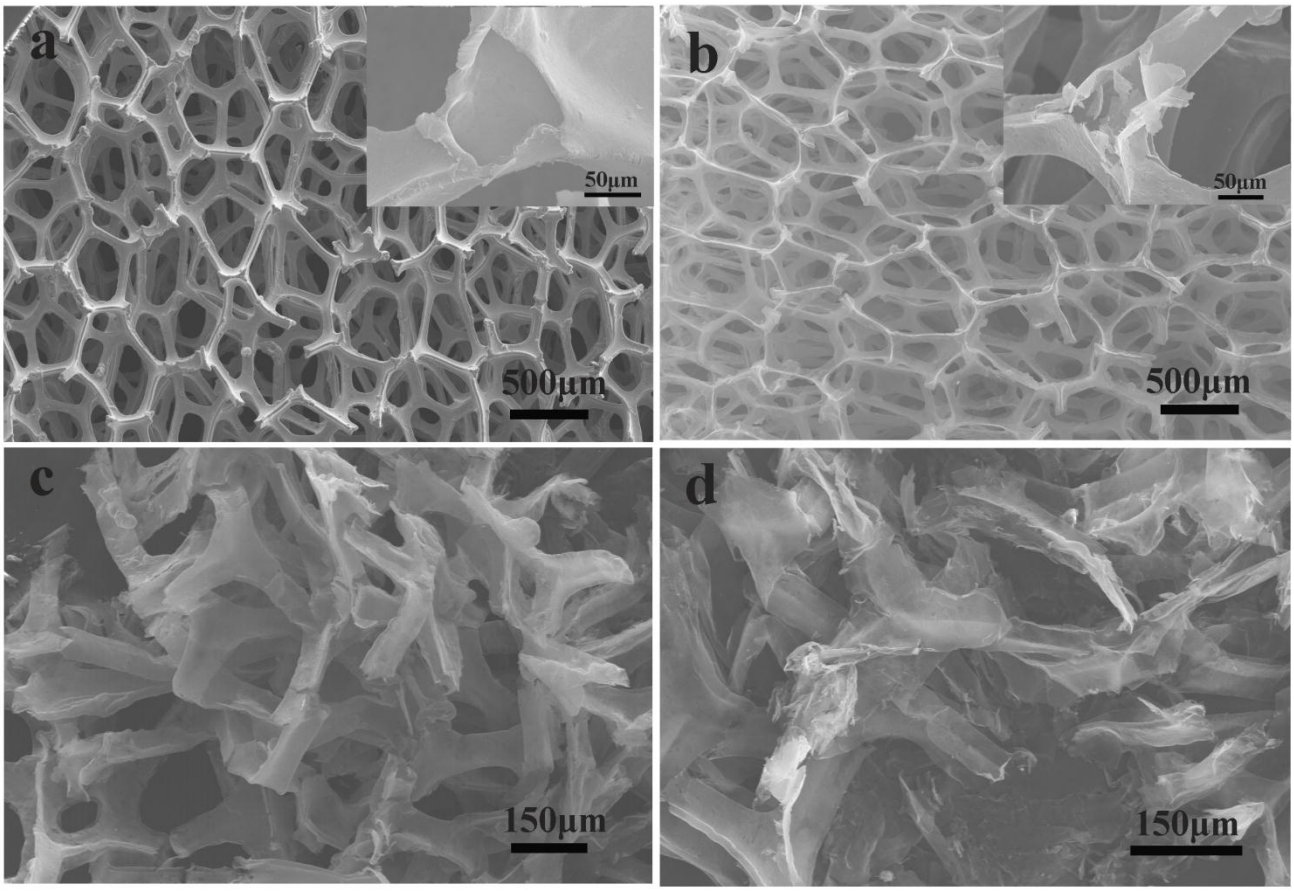

Figure S2. SEM images of Ni foam (a) and 3D graphene networks from Ni foam (b). The insets in (a) and (b) show the hollow internal structures of skeletons. (c), (d) SEM images of collapse and crack of 3D graphene networks during bending operation.

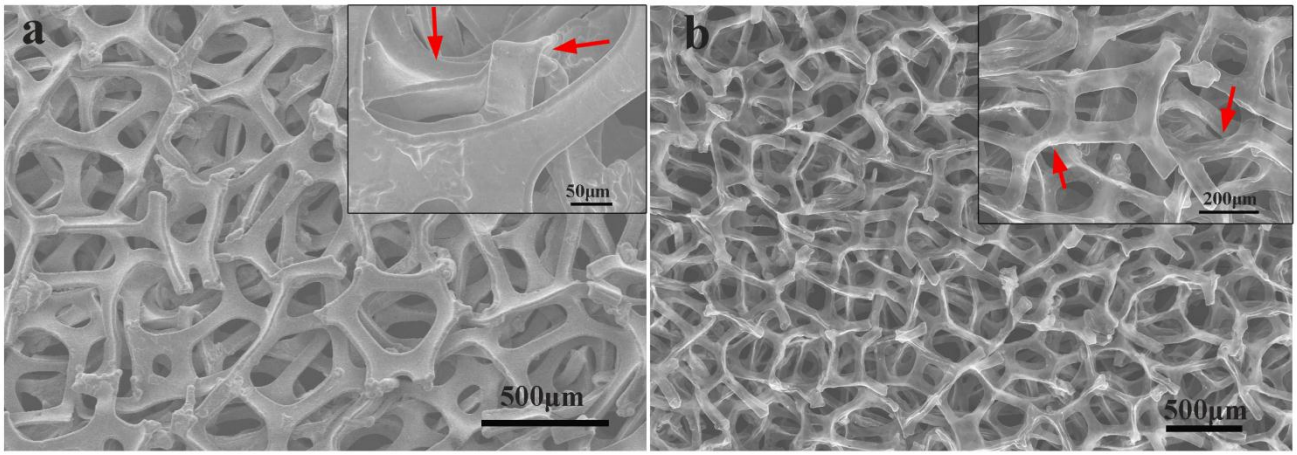

Figure S3. SEM images of pressed Ni foam (a) and 3D graphene networks from pressed Ni foam (b). (Inset) High-magnification SEM images show no collapses and cracks of both networks in the interconnected 3D scaffold, as signed by the red arrows.

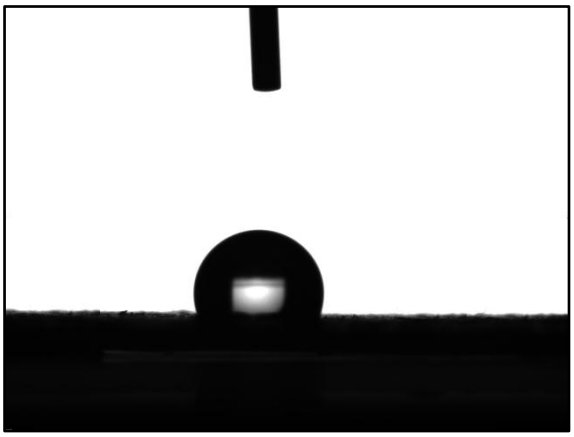

Figure S4. The contact angle for 3D graphene networks is about 112.3°.

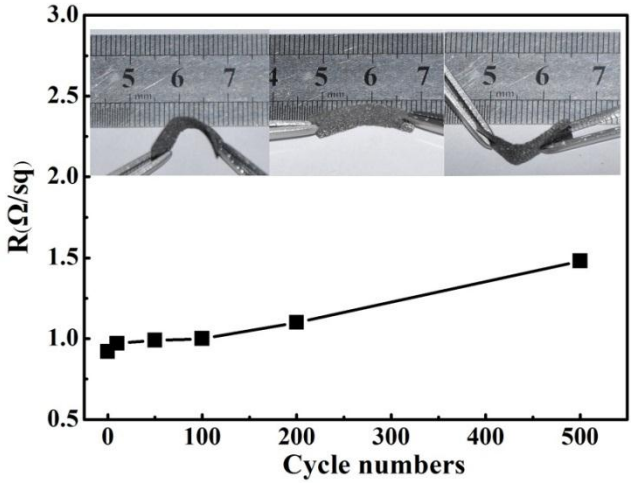

Figure S5. The electrical resistance of 3D graphene networks as a function of the number of bending cycles was measured. Under the degree of mechanical deformation used in this test (the inset of the Figure), the electrical resistance (a square resistance of 0.91 Ω/sq) was slightly increased, to ~1.5 Ω/sq, after 500 bending cycles.

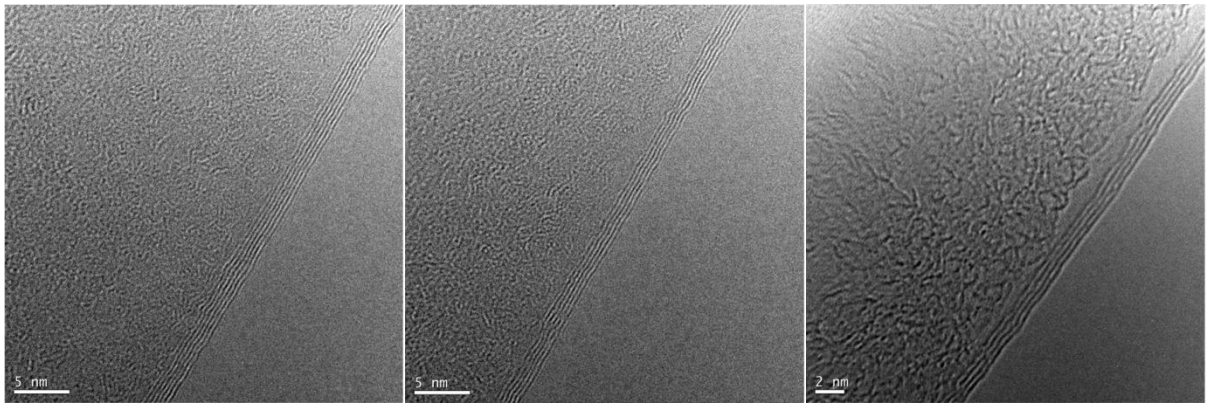

Figure S6. The number of graphene were examined by transmission electron microscopy (TEM) and the 3D graphene are multilayer (4-7 layers) in our experiment.

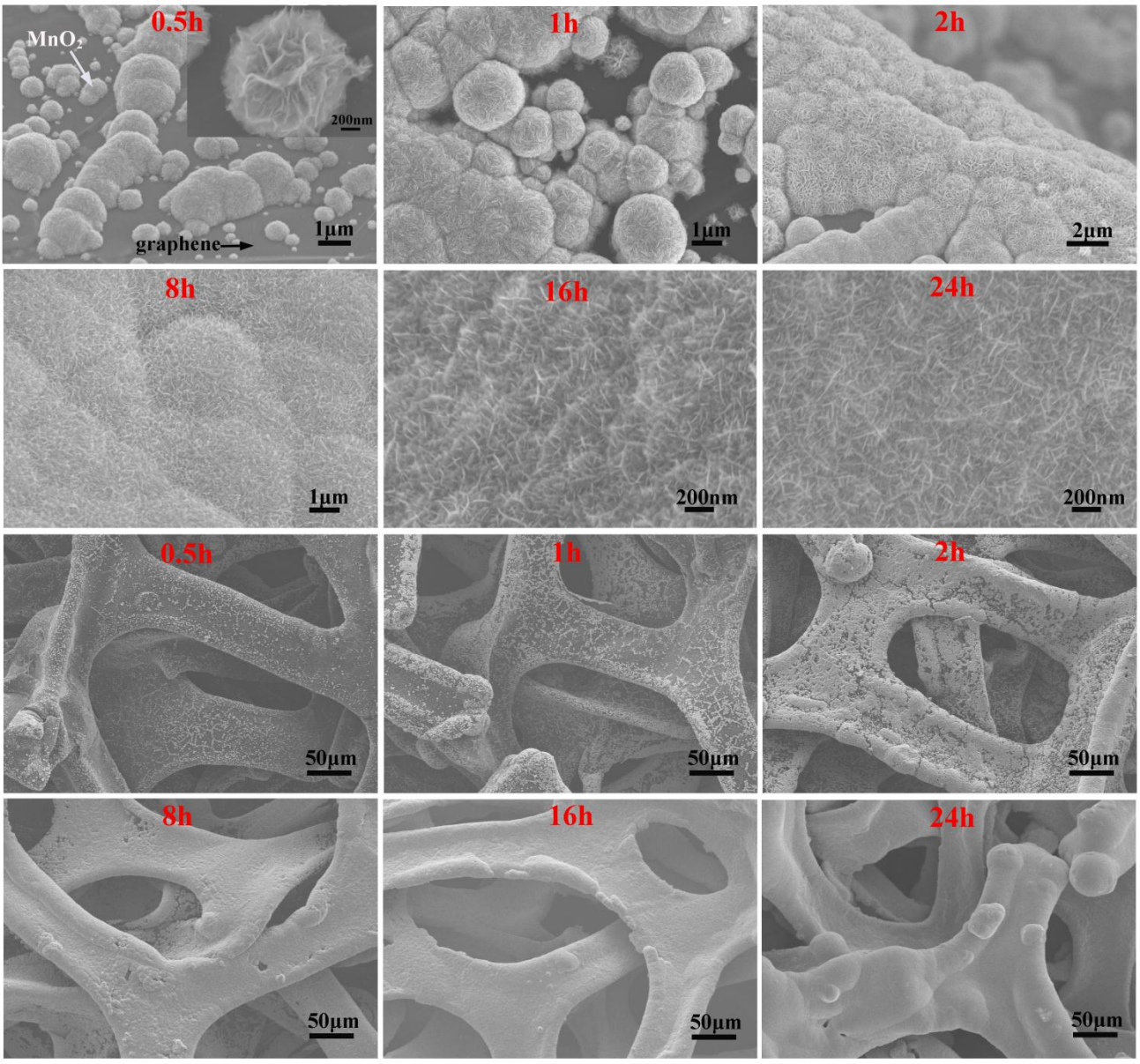

Figure S7. Low-magnification SEM images of MnO_2 with varied electrodeposition time from 15min to 1440 min show large-scale, uniform coating of MnO_2 nanomaterial on almost entire skeletons of 3D graphene networks. As can be seen from Figure S5, the morphology and structure of MnO_2 nanomaterial can be controlled by the electrodeposition time. In details, at short deposition time such as 15min, MnO_2 nanomaterial shows an individual nanoflower-like hierarchical structures decorated by many nanoscale mesopores. As the deposition time increases, the nanoflowers increase in size and connect with each other until a continuous thick MnO_2 layer is formed for 2h electrodeposition. Even for the longest depositing time of 1440 min, the 3D network structure of the graphene/MnO_2 composite is still maintained and covered by a uniform MnO_2 coating with no cracks, where its surface has many smaller nanopores.

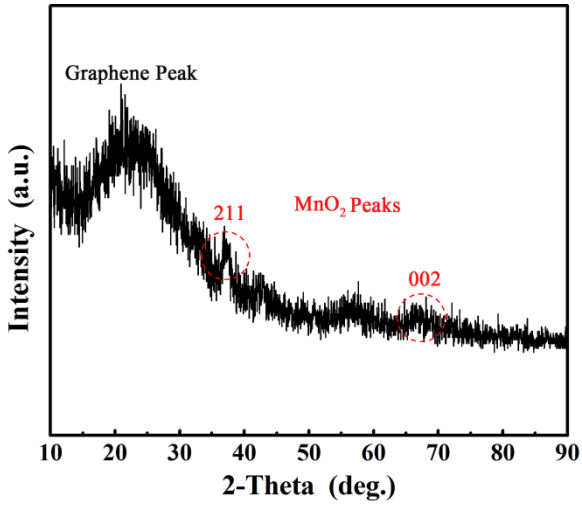

Figure S8. The two characteristic peaks at 37.1 and 66.3 ° in XRD analysis marked by an red circle indicates the presence of MnO_2, and the weak, broad signals suggest that MnO_2 is in amorphous nature, which is favorable for supercapacitor applications.

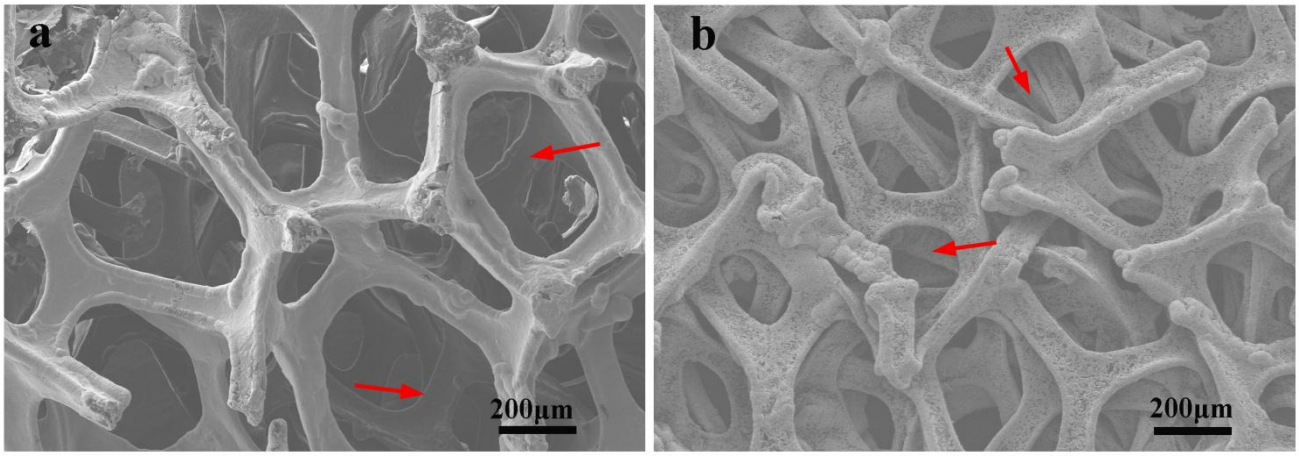

Figure S9. SEM images of two typical MnO_2-coated 3D graphene networks from Ni foam (a) and pressed Ni foam (b). The electrodeposition time was 120 min. As signed by the red arrows, uniform coating of MnO_2 on the entire skeletons of 3D graphene networks from pressed Ni foam was demonstrated comparing with only the outer surface coating on 3D graphene networks from Ni foam.

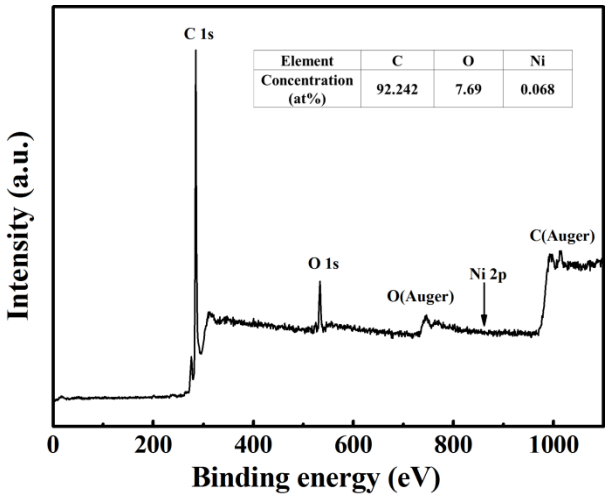

Figure S10. XPS spectra of a bare graphene network after etching Ni skeleton. There is 0.068 at% nickel in the 3D graphene network, and it suggests that nickel template should be completely removed after treating of 6M HCl solution for 6h.

Table S1. Surface area and specific capacitance(calculated for the entire electrode) of 3D graphene networks and graphene/MnO_2 composites with 2h and 24h electrodeposition, respectively. The specific capacitance of graphene/MnO_2 composites are from Figure 3f, and the specific capacitance of bare 3D graphene networks, due to its limited electro-active sites and less hydrophilic property, is as low as 4.7 F/g at 1 mV/s scan rate.

Samples	3D graphene networks	graphene/MnO_2 composite with 2h electrodeposition	graphene/MnO_2 composite with 24h electrodeposition
Surface area(m^2/g)	392	281	175
Specific capacitance (calculated for the entire electrode) (F/g)	4.7	125.2	133