Self-Assembled Hierarchical MoO_2/Graphene Nanoarchitectures and Their Application as a High-Performance Anode Material for Lithium-Ion Batteries

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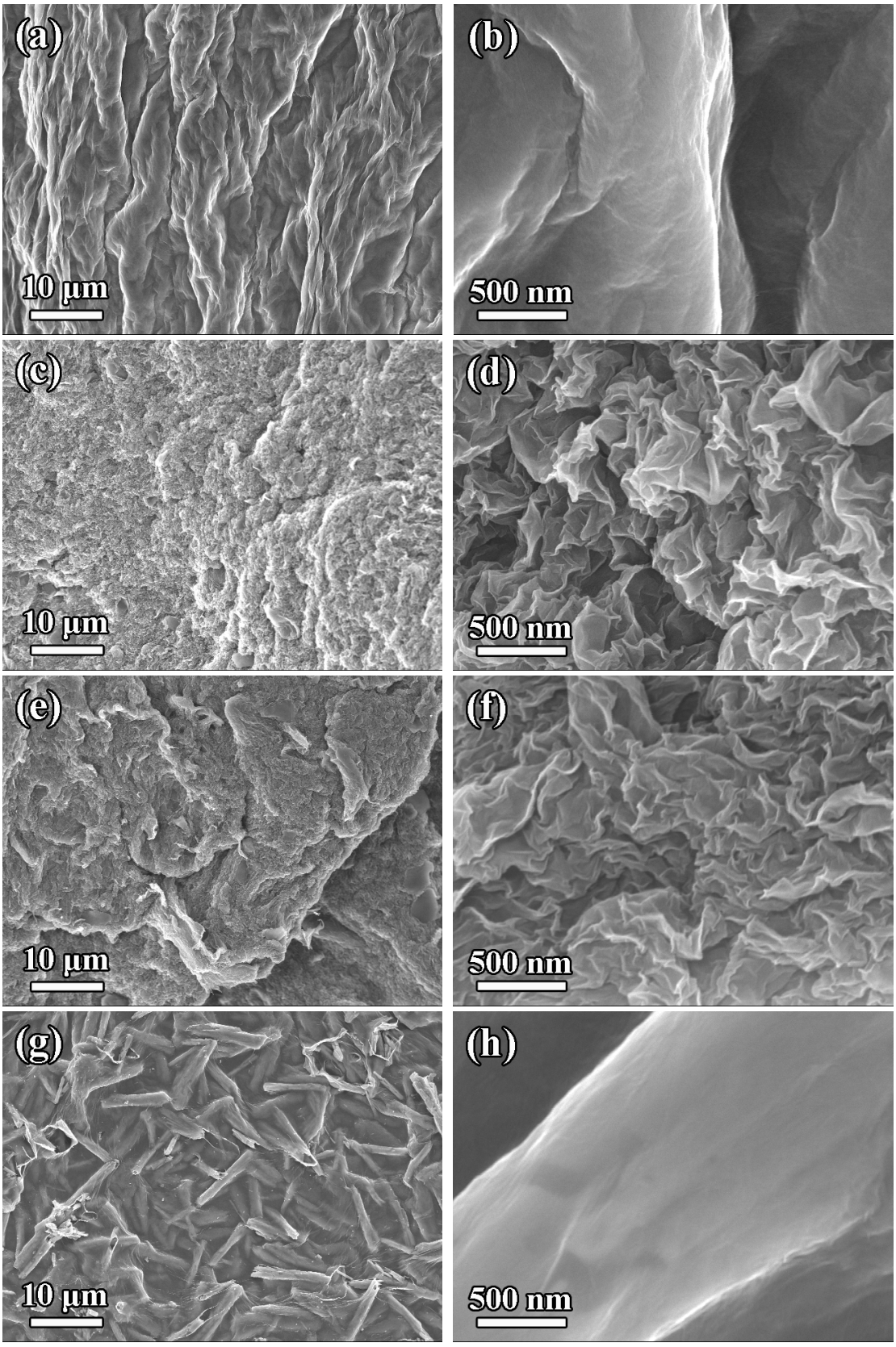
(a)
10 μm
(b)
500 nm
(c)
10 μm
(d)
500 nm
(e)
10 μm
(f)
500 nm
(g)
10 μm
(h)
500 nm

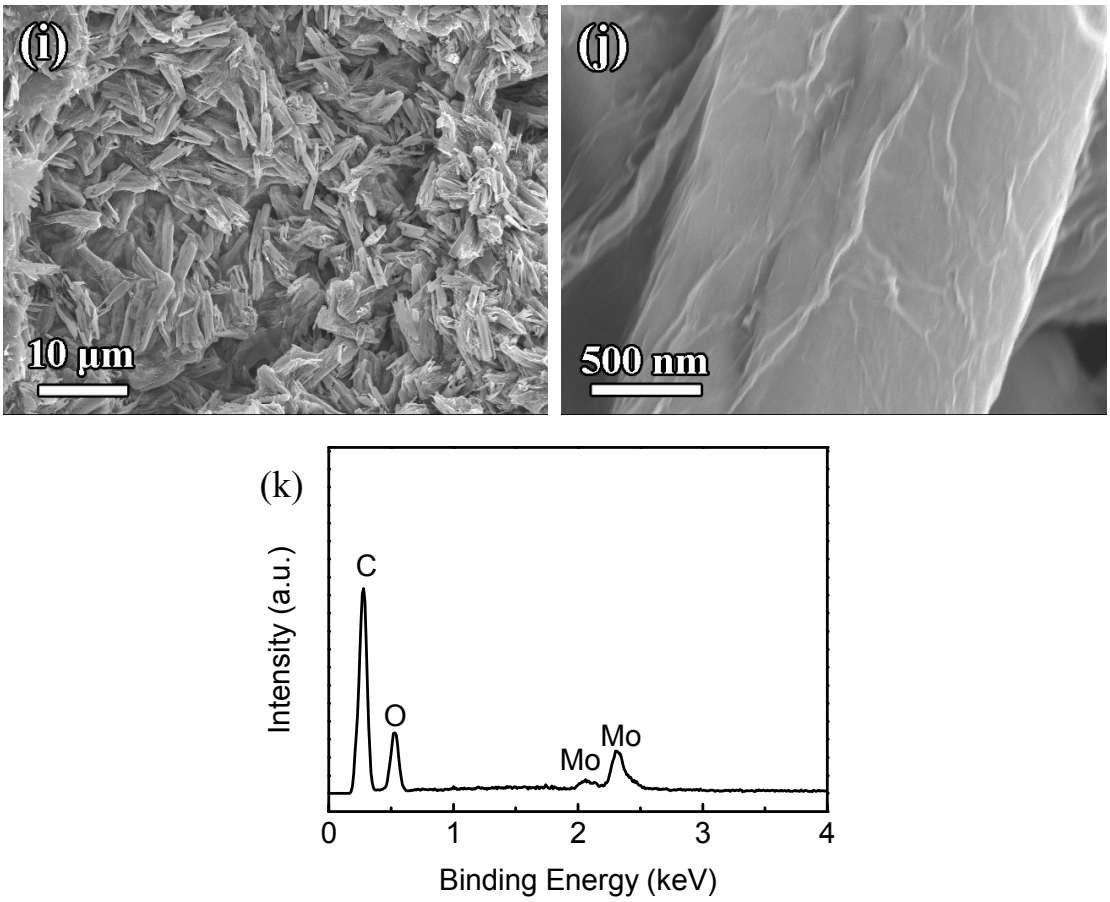

Figure S1. Representative FESEM images of the products for different reaction time: (a,b) 30 min; (c,d) 60 min; (e,f) 75 min; (g,h) 90 min; (i,j) 120 min. (k) A typical EDX spectrum of the product with the reaction time of 60 min.

With the reaction time of 30 min, the brown graphene oxide with smooth surface can be obtained after filtration (Figure S1a and S1b). The reaction solution was dark blue, indicating that the POM clusters were gradually reduced into "heteropoly blue" clusters (or HPB ions) by hydrazine hydrate.[1] After 60 min, a black graphene-based product with nanoporous structures and rough surfaces was obtained (Figure S1c and S1d). This product was also studied by EDX (Figure S1k). Three major peaks correspond to the elements of C, Mo, and O, indicating the formation of a graphene-based nanoporous material through assembling the graphene sheets mediated by the polyoxometalate nanoparticles.[1] When the reaction time was increased to 75 min, no obvious change was observed in the solid products (Figure S1e and S1f). However, the colour of the solution turns darker, suggesting the generation of more HPB ions in the reaction system. After ultrasonication for 90 min, a large number of hierarchical rods with diameters of ~1–3 μm and rough surfaces that are in-situ wrapped with graphene nanosheets were formed (Figure S1g and S1h). As the solubility of HPB ions is lower than POM, the solid HPB nanorods wrapped with graphene are immediately obtained when the HPB ions are saturated in the solution.[1] As the reaction time prolonged to 120 min, the morphology of the product was kept without

any further change (Figure S1i and S1j). Then, such a self-assembled product including the Mo-precursor and graphene was further treated in a reducing atmosphere of 5% H_2/Ar at 500 °C for 5 h, and the hierarchical MoO_2/graphene nanocomposite was finally obtained. Based on the above SEM and EDX results, we propose that three main steps may be included in formation process: (I) graphene/HPB clusters, (II) graphene wrapped HPB rods, and (III) graphene wrapped MoO_2 rods.

1. Zhou, D.; Han, B. H. Graphene-Based Nanoporous Materials Assembled by Mediation of Polyoxometalate Nanoparticles. *Adv. Func. Mater.* **2010**, *20*, 2717–2722.

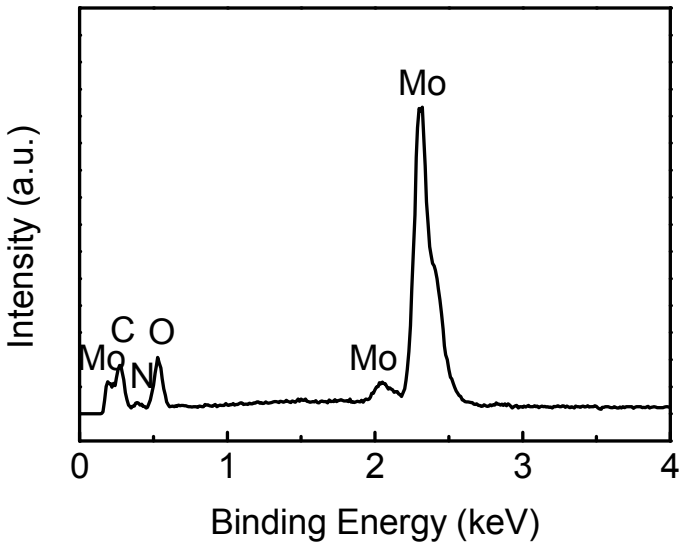

Figure S2. EDX spectrum of the Mo-precursor/graphene composite.

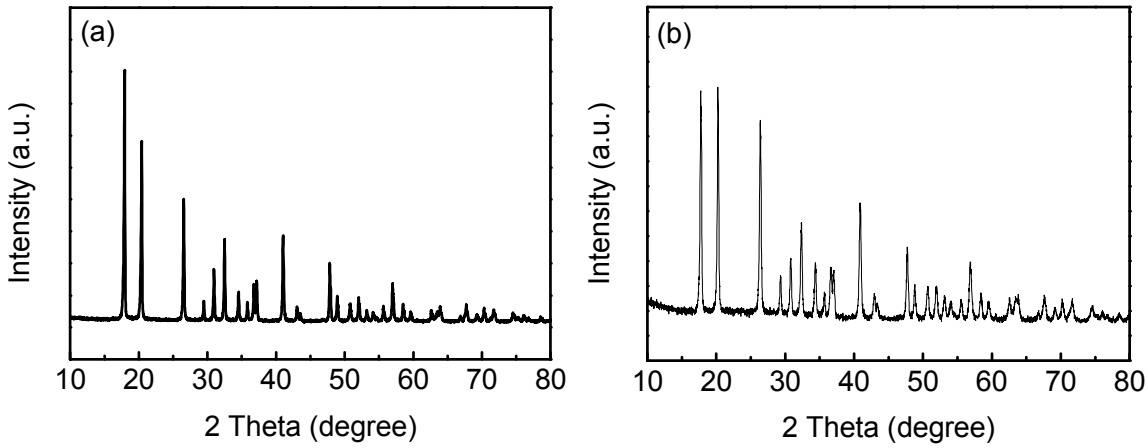

Figure S3. The XRD patterns of (a) the bare Mo-based precursor and (b) the Mo-precursor/graphene hybrid.

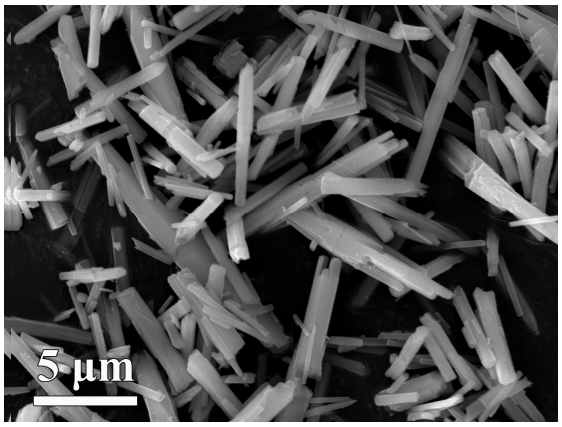

Figure S4. SEM image of the bare Mo-based precursor.

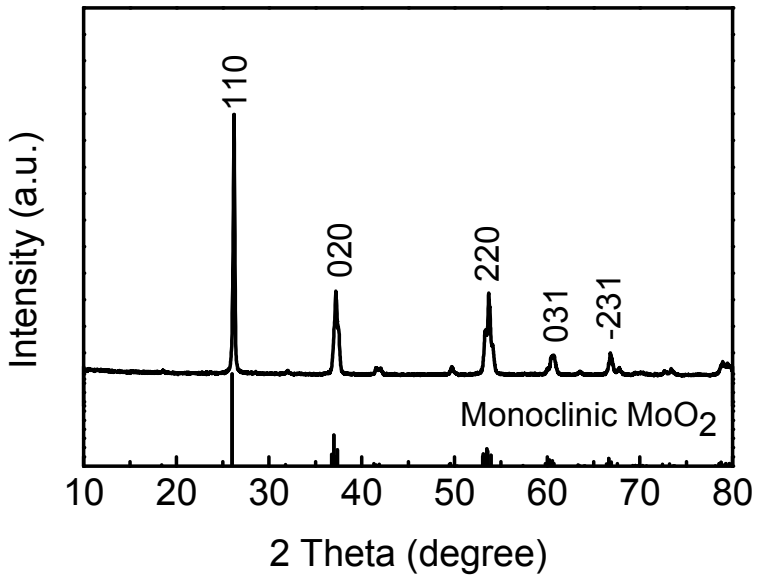

Figure S5. The XRD pattern of the bare MoO_2.

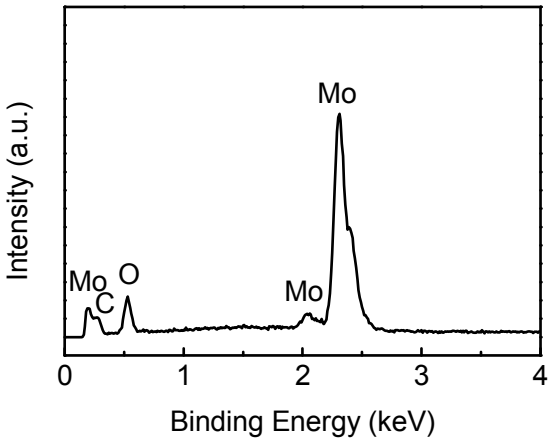

Figure S6. The corresponding EDX of the hierarchical MoO_2/graphene hybrid.

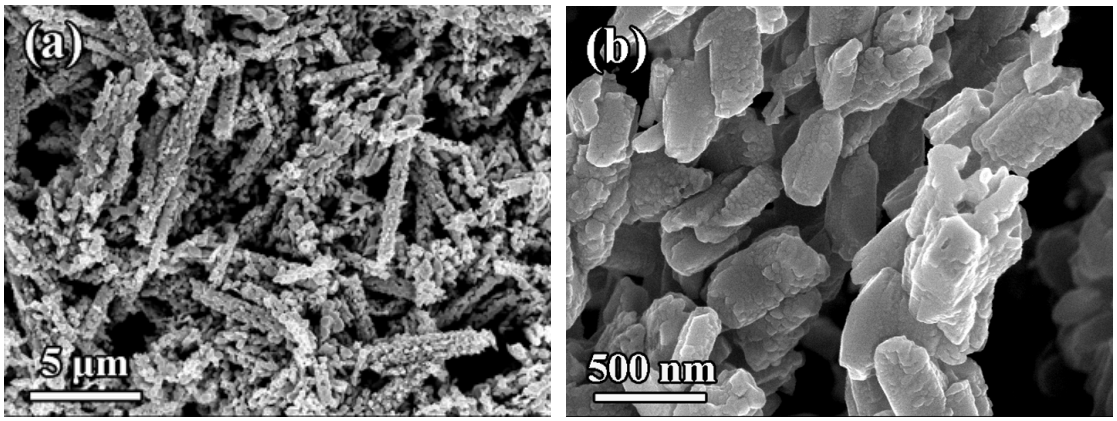

Figure S7. SEM images of the bare MoO_2 particles.

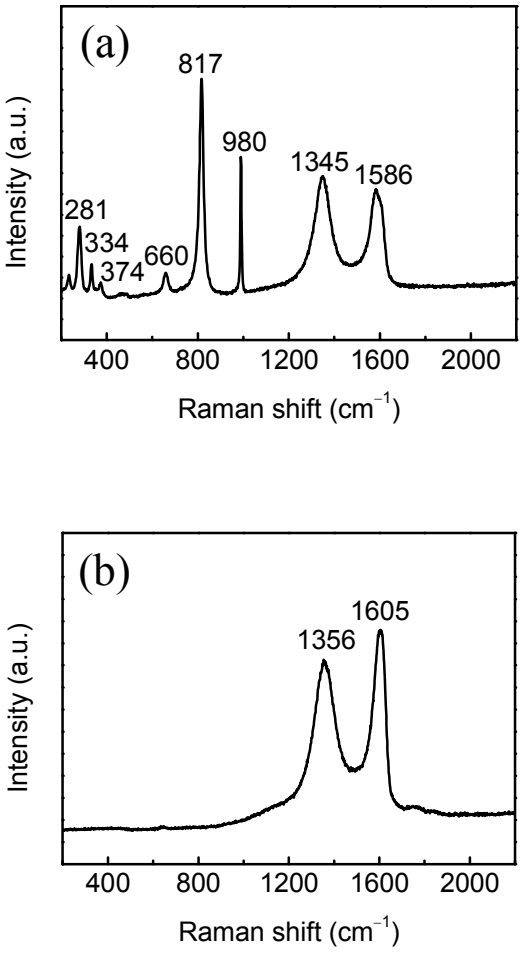

Figure S8. (a) Raman spectrum of the MoO_2/graphene hybrid. The peaks around 1345 and 1586 cm^{-1} are attributed to the characteristic D-band and G-band vibration modes of carbon, respectively. The peaks ranging from 300 to 1200 cm^{-1} are assigned to molybdenum oxide. (b) Raman spectrum of the graphene oxide. The peaks around 1356 and 1605 cm^{-1} are attributed to the characteristic D-band and G-band vibration modes of carbon, respectively.

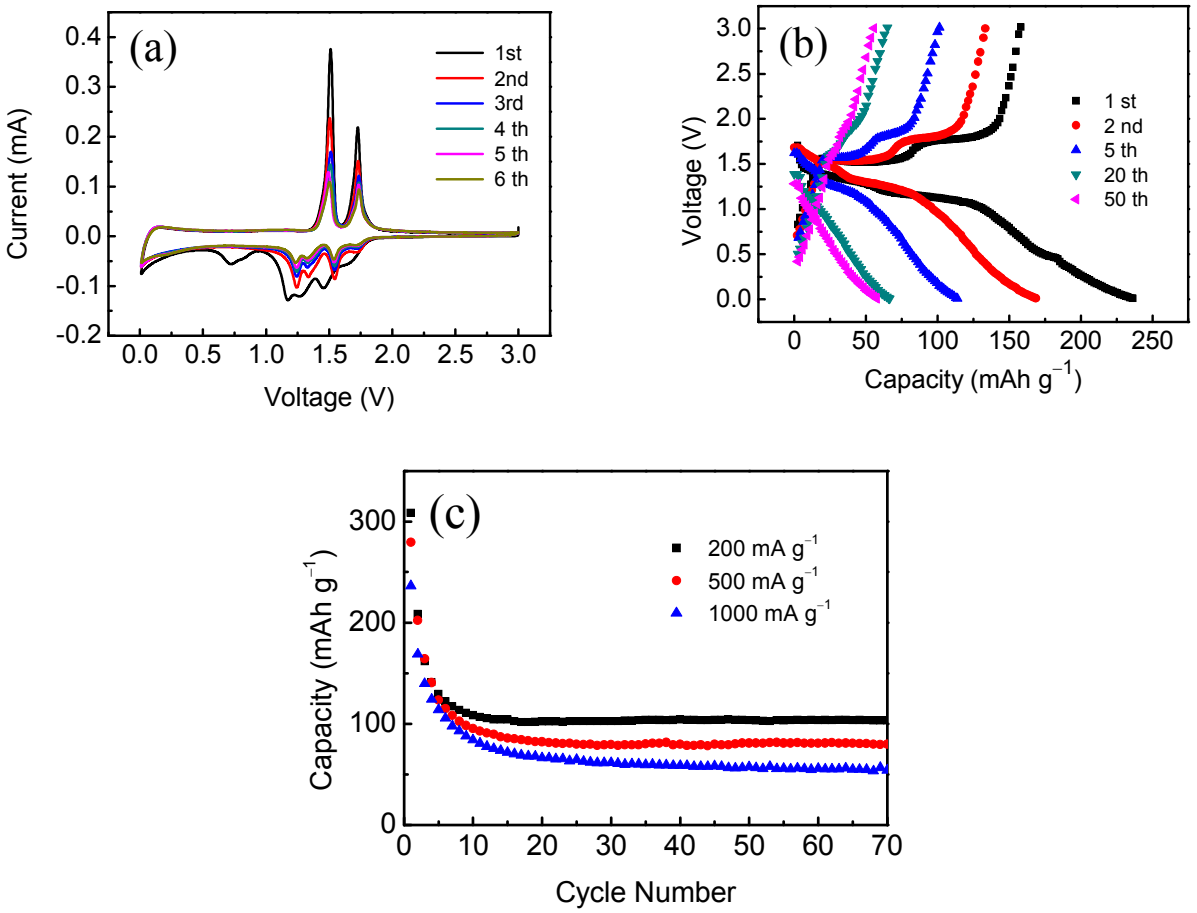

Figure S9. (a) Cyclic voltammograms of the free MoO_2 at a scan rate of 0.1 mV s^{-1} in the voltage range of 3–0.01 V vs Li. (b) Discharge and charge curves at a current density of 1000 mA g^{-1} cycled in the voltage range of 3–0.01 V vs Li. and (c) cycling performance of the electrodes in the voltage range of 3–0.01 V vs Li at various current densities of 200, 500 and 1000 mA g^{-1} in the voltage range of 3–0.01 V *vs* Li.

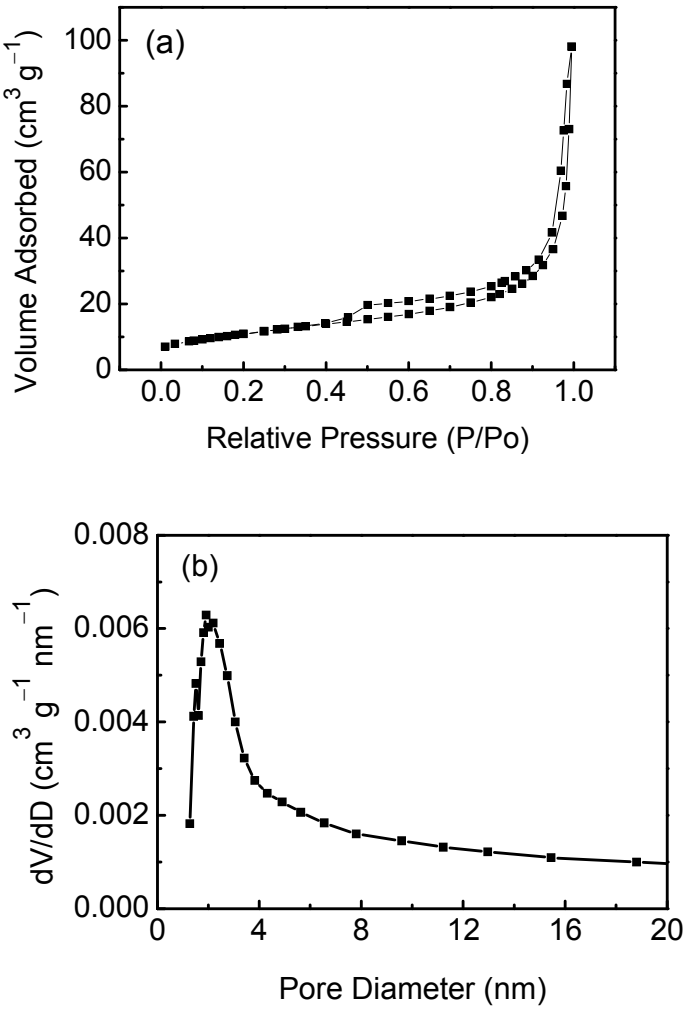

Figure S10. (a) Nitrogen isotherm adsorption-desorption curves and (b) the corresponding pore size distribution for the as-prepared MoO_2/graphene hybrid.

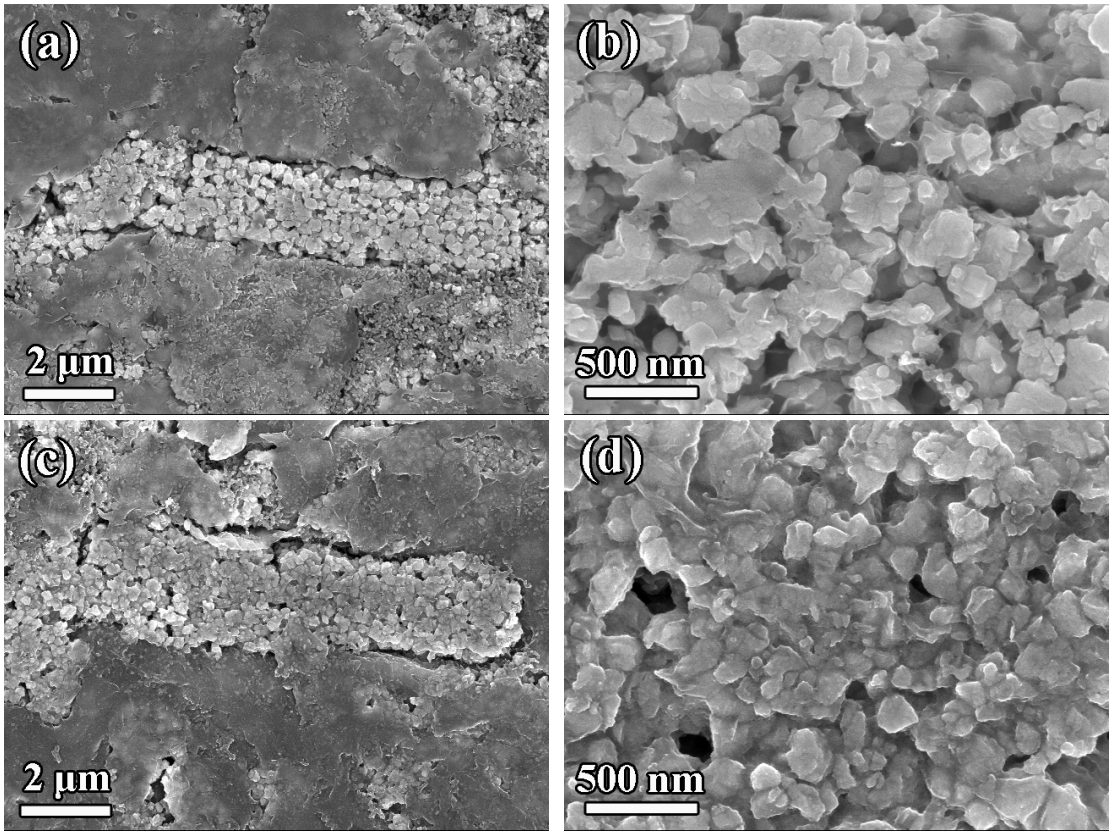

Figure S11. FESEM images of the MoO_2/graphene electrodes before (a,b) and after 70 discharge and charge cycles (c,d).

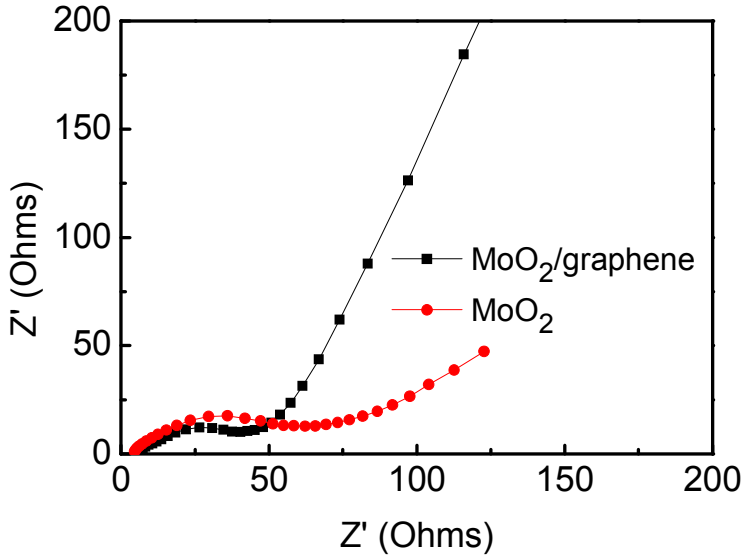

Figure S12. Electrochemical impedance spectra of the electrodes of the MoO_2/graphene hybrid and bare MoO_2.

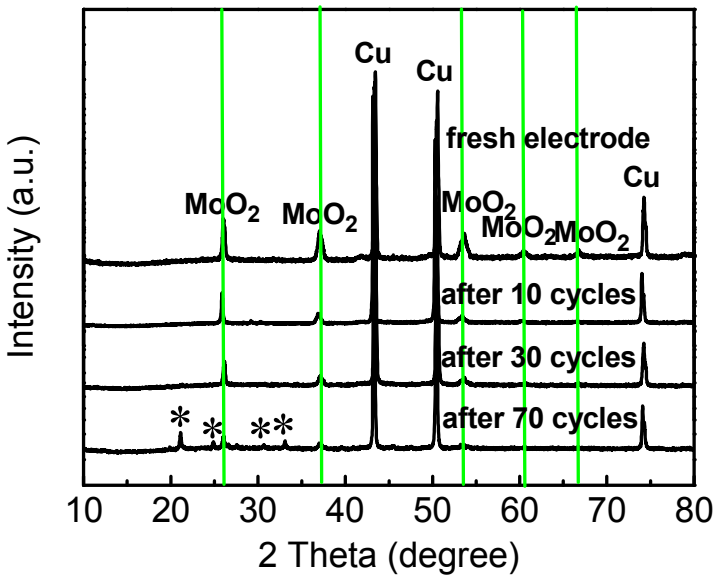

Figure S13. Ex-XRD patterns of the MoO_2/graphene electrodes after different discharge and discharge cycles. After 70 discharge and charge cycles, some new peaks (marked as star) appear, but cannot be easily assigned to one of the known Mo oxides.