

Supplementary Information

Electrostatic layer-by-layer self-assembly multilayer films based on
graphene and manganese dioxide sheets as novel electrode materials for
supercapacitors

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1. Preparation and characterization of GO

In a typical synthesis, expandable graphite (EG) was first treated at 1050 °C in air for 15 s to split the EG. Thermally treated EG powder (1 g) was added to 98% H₂SO₄ (23 mL) in an ice bath, and then KMnO₄ (3 g) was added gradually under stirring and the temperature of the mixture was kept to be below 20 °C by cooling. The above mixture was kept at 35 °C for 30 min. Then, deionized water (46 mL) was gradually added keeping the reaction in an ice bath. After 15 min, the mixture was further treated with deionized water (140 mL) and 30% H₂O₂ solution (12.5 mL). The GO was firstly washed with 5% HCl solution until pH 7 was reached, and then dialyzed at 60 °C with stirring until SO₄²⁻ anions could not be detected. The GO slurry was dried in a vacuum oven at 60 °C and purified by dialysis for one week.

Fourier transformation infrared (FTIR) spectrum of GO were recorded using a Bruker IFS66V FTIR spectrometer. X-ray diffraction (XRD) patterns were carried out by an X-ray diffraction using Cu K α_1 radiation (XRD, Philips X'Pert Pro.) The morphology and microstructure of the prepared samples were observed TEM (JEOL JEM-3010).

[Figure S1](#) shows the FT-IR spectrum of GO, the broad bands at 3412 and 1614 cm⁻¹ are caused by the stretching vibration of O–H bond and the bending vibration of H–O–H of the absorbed water, but may also contain the stretch of aromatic C=C bond. The peak at 1718 cm⁻¹ can be attributed to the characteristic C=O stretch of the carboxylic group. [Figure S2](#) shows the XRD patterns of natural graphite and GO. In

comparison to the natural graphite, a wide peak at $2\theta = 11.7^\circ$ corresponds to the (001) diffraction is observed for GO, and it clearly indicates the damage of the regular crystalline of natural graphite during the oxidation.

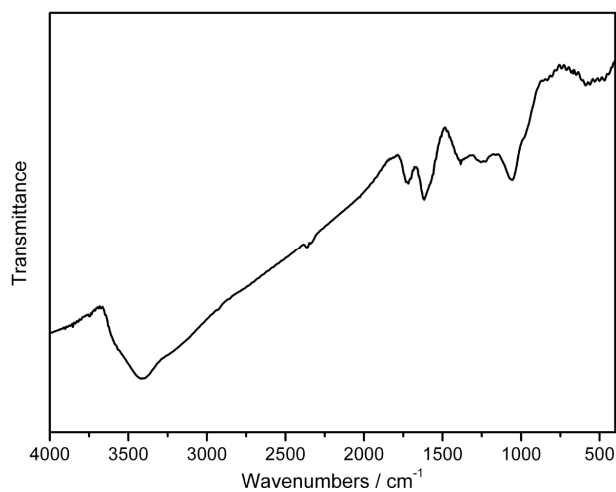


Figure S1. FTIR spectrum of GO.

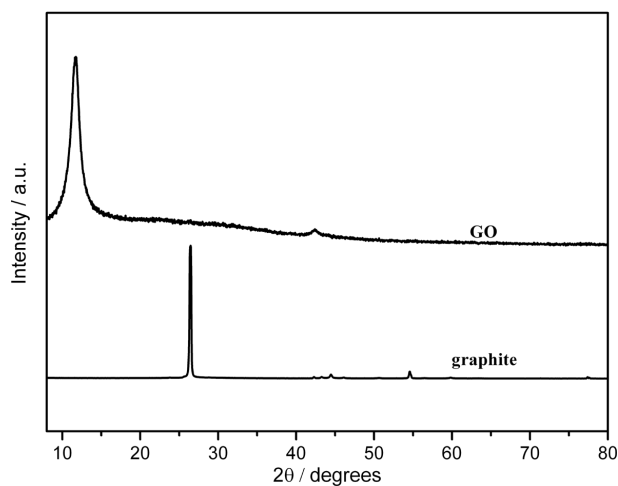


Figure S2. XRD patterns of natural graphite and GO.

2. Characterization of PSS-GS

[Figure S3A](#) gives the TEM images of GS, which reduced GO by hydrazine hydrate

at 100 °C for 24 h without adding PSS. Large scale graphene sheets are observed, and they entangle with each other, showing a crumpled silk veil-like structure. From the high resolution TEM image, the few layer graphene in the outer edges of the graphene sheets can be clearly seen (Figure S3C). Figure S3B shows a typical low-magnification TEM image of the PSS-GS, which obtained by reducing GO by hydrazine hydrate at 100 °C for 24 h with PSS. It can be found that there are some polymers particles on the surface of the PSS-GS, indicating the PSS molecules were attached in the surface of the GS in the chemical reduction process. A high-magnification TEM image shows that the thickness of PSS layer is about 2-5 nm and indicates that the thin PSS coating layer is successfully adsorbed on the GS platelets surface. (Figure S3D).

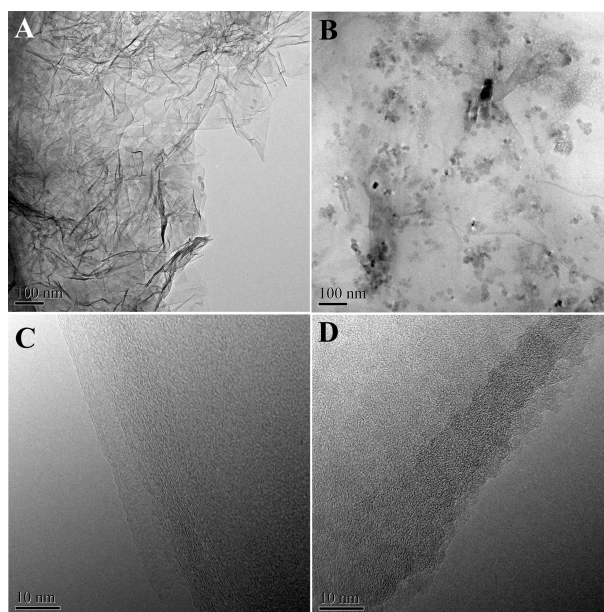


Figure S3. TEM images of GS (A and C) and PSS-GS (B and D).

3. Structural characterization of as-prepared MnO₂ sheets.

Figure S4 presents the XRD pattern of as-prepared H-birnessite MnO₂. It can be

seen that two peaks corresponding to the (001) and (002) lattice plane at $2\theta = 12.3^\circ$ and 25.1° , which are in good agreement with the value reported in literature.¹

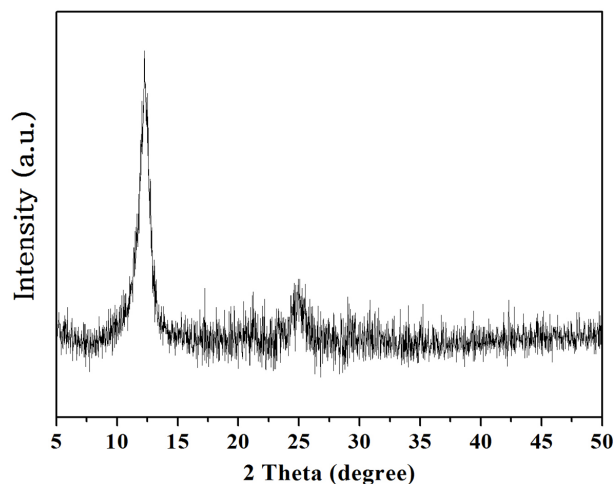


Figure S4. XRD pattern of the as-prepared H-birnessite MnO₂.

4. Electrochemical performances of uniformly dispersed PSS-GS/MnO₂ mixture, pure PSS-GS, pure MnO₂, and ITO/(PDDA/PSS-GS/PDDA/MnO₂)₁₀ multilayer film electrode.

The working electrodes were fabricated by mixing the electroactive materials, acetylene black and poly(tetrafluoroethylene) in a mass ratio of 80:15:5 and dispersed in ethanol to produce homogeneous mixtures. Then the resulting mixture was pressed onto the nickel foam current collectors (1 cm × 1 cm) under 10 MPa. The masses of PSS-GS/MnO₂ mixture (the mass ratio of PSS-GS and MnO₂ = 15:85), pure PSS-GS and pure MnO₂ are 2.8, 1.6 and 2.7 mg, respectively. The electrochemical performances of uniformly dispersed PSS-GS/MnO₂ mixture, pure PSS-GS and pure MnO₂ were evaluated in a three-electrode cell system with 0.1 M Na₂SO₄ aqueous solution as

electrolyte. Platinum wire and Ag/AgCl (KCl-saturated) electrode were used as counter and reference electrodes, respectively.

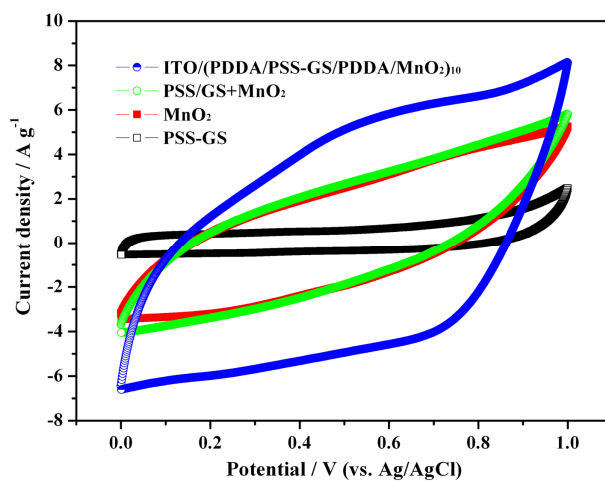


Figure S5. CV curves of ITO/(PDDA/PSS-GS/PDDA/MnO₂)₁₀, uniformly dispersed PSS-GS/MnO₂ mixture, pure MnO₂, and pure PSS-GS electrodes at a scan rate of 40 mV s⁻¹.

Reference

1. Z. Liu, K. Ooi, H. Kanoh, W. Tang and T. Tomida, *Langmuir*, 2000, 16, 4154-4164.