# Supporting information

## Porous $MnO_2$ for use in a high performance supercapacitor: replication of a 3D graphene network as a reactive template

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## 1. Samples Preparation.

All chemicals used in this work are of analytical grade. In a typical synthesis, graphene oxide hydrogel was prepared from graphene oxide suspension (2 mg/mL) using a hydrothermal method. The as-produced hydrogel was immersed into 50 mL neutral and homogeneous $KMnO_4$ solution, and kept standing in a covered beaker at 80 °C until the purple color of the solution became black-brown (with overdosed graphene) or the hydrogel disappeared completely (with overdosed $KMnO_4$). The as–obtained products (P-$MnO_2$) were obtained by a simple centrifugation (separated from the soluble byproducts). The reaction rate was found to depend on the reaction temperature. The higher temperature is, the faster reaction rate is.

In a control experiment, C-$MnO_2$ nanoparticles, as a reference sample, were prepared by a co-precipitation method. 50 mL of 0.01 M $KMnO_4$ solution was mixed with 50 mL of 0.015 M $MnSO_4$ solution and stirred continuously for 6 h to obtain the dark-brown precipitate. And then the precipitate was washed several times with DI water and dried at 70 °C in air for overnight.

A graphene oxide hydrogel subjected to a freeze-drying has a hierarchical porous structure and is denoted PGM (porous graphene-based macroform), which is also used as a reference to investigate the structure of P-$MnO_2$.

## 2. Samples Characterizations.

Raman spectra were performed on LabRam HR (Horiba, French). The morphologies of the as-obtained samples were observed using field scanning electron microscopy (SEM, Hitachi S4800, Japan ) and transmission electron microscopy (TEM, JEM 2100F, JEOL, Japan). The specific surface area was estimated by Brunauer-Emmett-Teller (BET) method and pore texture was characterized by nitrogen cryo-adsorption (77 K) on a BEL mini instrument (BEL, Japan). All samples were first evacuated at 423 K in vacuum before measurement. X-ray photoelectron spectra (XPS) was performed on a Thermo Scientific ESCALAB 250XI photoelectron spectrometer with Al Kα (hν=1486.6 eV) as the X-ray source. Thermogravimetric analysis (TGA) was carried out using TG 8120 (Thermo Plus) with a heating rate of 10 $^{o}$C /min in a range of 25-800 $^{o}$C under air flow.

## 3. Electrodes Preparation and Electrochemical Measurements.

The electrochemical performance of $MnO_2$ samples were evaluated using a home-made three-electrode cell at room temperature with 1 M $Na_2SO_4$ aqueous solution as an electrolyte. The working electrodes were fabricated by homogenously mixing the active materials (80 wt. %) with PTFE (5 wt. %) and conductive super P (15 wt. %) in absolute ethanol under ultrasound. The resulting pastes were pressed at 10 MPa onto the stainless steel nets to make electrodes. Before the electrochemical test, the electrode was soaked in the electrolyte for at least 12 h. Platinum slice was used as counter electrode and a saturated calomel electrode (SCE) was chosen as reference electrode. Cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) measurements were used to determine the electrochemical performance of $MnO_2$ electrodes. CV and EIS tests were taken out on Autolab 128N electrochemical workstation (Metrohom, Switzerland). Galvanostatic charge-discharge tests were conducted on both Autolab 128N electrochemical workstation and Land testing system (Wu Han Lixing, China).

# 4. Supplementary figures (Figs. S1-5)

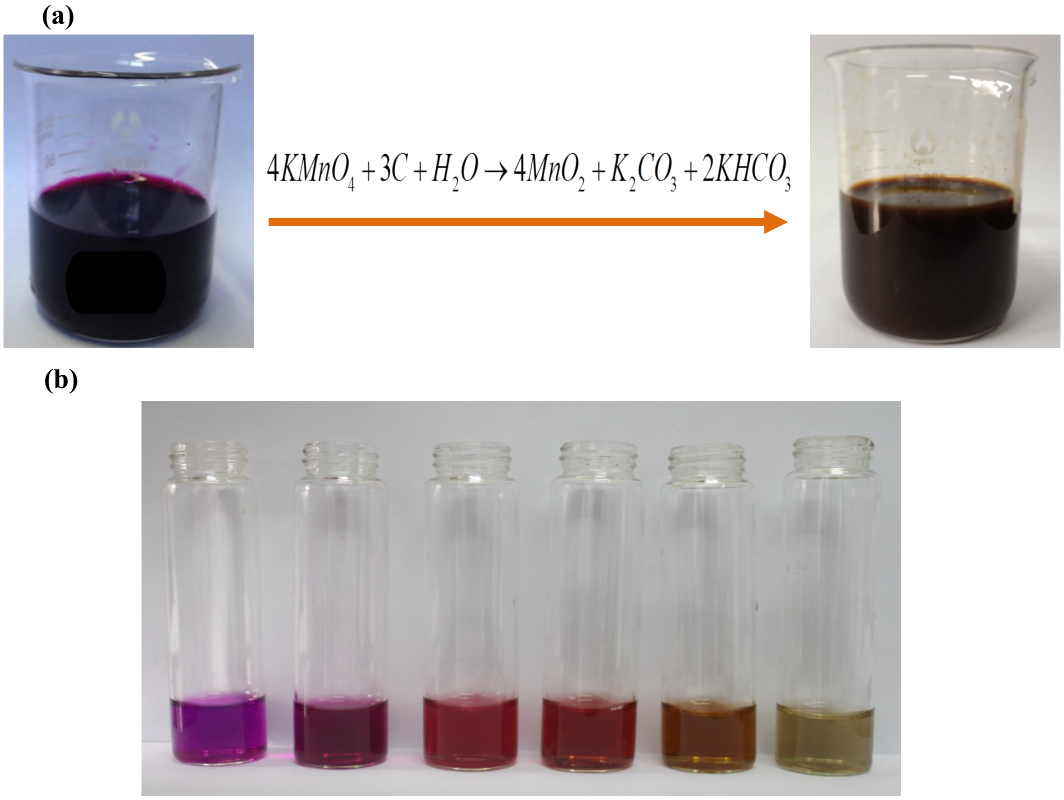

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**Fig. S1** Photographs demonstrating the reaction between graphene oxide hydrogel and $KMnO_4$ solution. (a) Purple color of the $KMnO_4$ solution changes to black-brown suspension containing $MnO_2$ nanoparticles after the reaction. (b) Color change of the solution at different reacting time (taking out every 10 min and diluting by 10 times).

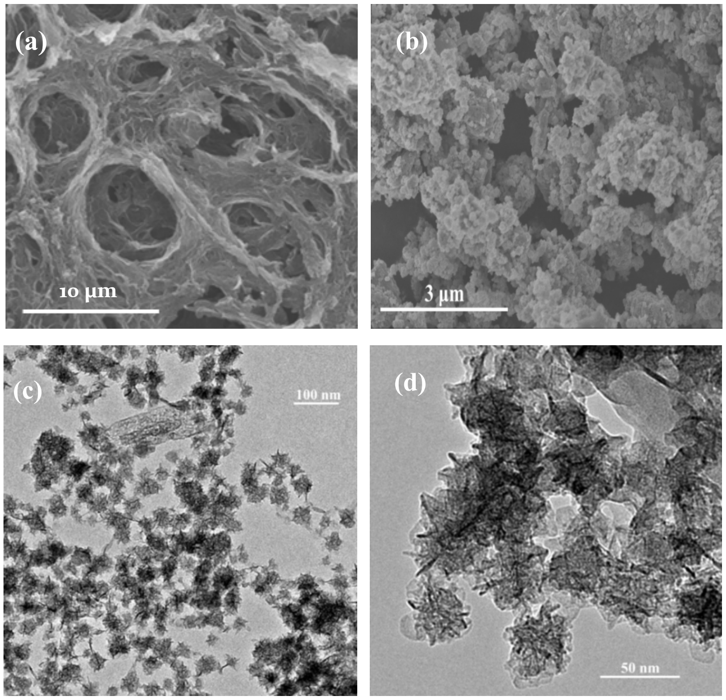

**Fig. S2** SEM images of (a) PGM and (b) P-$MnO_2$. (c) and (d) TEM images of P-$MnO_2$.

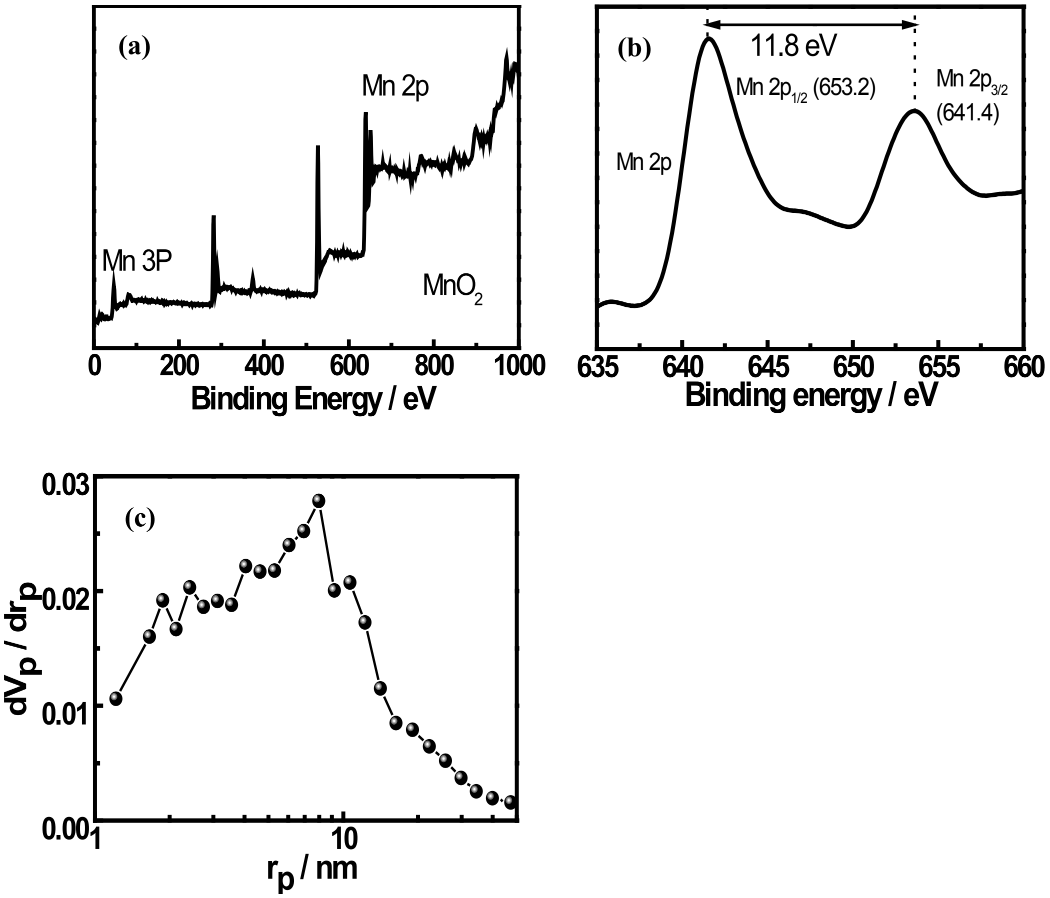

**Fig. S3** (a) XPS spectra of P-MnO$_2$ and (b) The Mn2p peak of P-MnO$_2$ in XPS analysis. (c) Pore size distribution (BJH) of P-MnO$_2$.

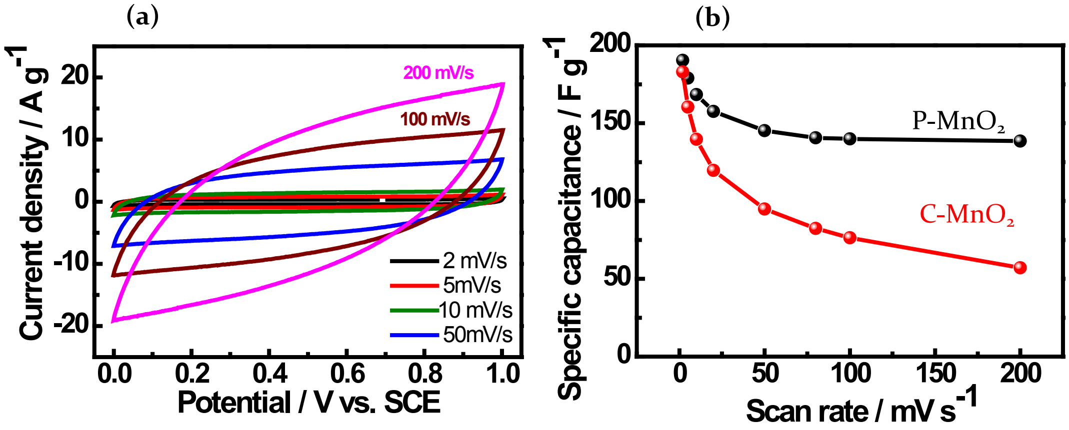

**Fig. S4** (a) CV curves of C-MnO$_2$ at different scan rates and (b) The capacitance retention obtained from cyclic voltammograms of P-MnO$_2$ and C-MnO$_2$.

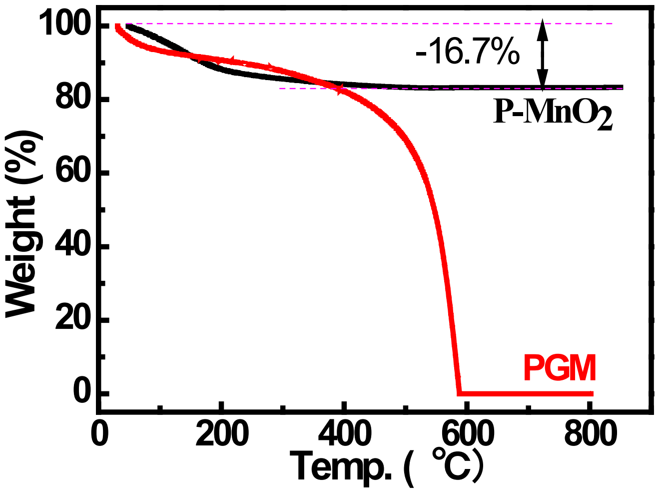

**Fig. S5** TG profiles of P-$MnO_2$ and PGM under air atmosphere. An obvious weight loss is observed for PGM in the range of 300-600 °C due to the carbon oxidation in air, while no notable weight loss is observed above 300 °C in the case of P-$MnO_2$. The results confirm that almost no carbon is contained in the final P-$MnO_2$. The weight loss (~16.7%) below 200 °C mainly comes from dehydration of the adsorbed water and the lattice water.[1]

Reference

1. S. Chen, J. Zhu and X. Wang, *ACS Nano*, 2010, **4**, 6212-6218.