Electronic Supplementary Information

Three-dimensional metal/oxide nanocone arrays for high-performance electrochemical pseudocapacitors

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Experimental Section

Preparation of the molds with an inverted nanocone hole array. Aluminum (Al) foil was cut into 3 cm by 5 cm pieces and cleaned in acetone and isopropyl alcohol. The sheets were electrochemically polished in a 1:3 (v:v) mixture of perchloric acid and ethanol for 2 min at 10 °C. The polished Al sheets were imprinted by silicon mold (Squarely ordered pillar array with height of 200 nm and with a pitch of 1.2 μm with a pressure of ~2×10^4 N cm^{-2} to initiate the perfectly ordered anodic alumina membrane (AAM) growth. Then the Al sheets were placed in a home-built anodization setup. The sheets were anodized at a 160 V voltage in the solution of 2% citric acid and ethylene glycol (v/v = 1:1), 9 mL of 0.1% H_3PO_4 for 30 min. The first anodization layer was then etched away in a mixture of phosphoric acid (6 wt.%) and chromic acid (1.8 wt.%) at 63 °C for 15 min. After etching, the second anodization was carried out under the same solution at a 480 V voltage for 20 min to obtain approximately 550 nm thick AAM. Afterward, desired pore diameters of AAMs were obtained by wet etching with 5% phosphoric acid at 53°C for 13 min. In order to

achieve AAM with an inverted nanocone hole array, the sheets were thirdly anodized for the same time using the same anodization conditions and etched in 5% phosphoric acid at 53°C for 13 min. Finally, the sheets with inverted nanocone hole arrays were anodized for 25 min using the same anodization conditions. The fabrication process can also be referred to ref. 22 and 23 and Figure S1 (Supplementary Fig. S1).

Preparation of PFPE nanocone array electrode. Perfluoropolyether (PFPE) solution was spin-coated on the mold substrate with inverted nanocone hole array. After spin-coating, the substrate was cured by a 4-W UV lamp for 10 min. PFPE nanocone array films could be directly peeled off from the mold substrate. And then the conductive electrode films were obtained from magnetron sputtering 100 nm thick Au on PFPE nanocone array.

Preparation of Au/MnO_x nanocone array electrode. An aqueous solution of 0.05 M $MnSO_4$ and 0.05 M CH_3COONa was prepared. Anodic pulses (0.7–1.4 V; 1 s on, 5 s off) were applied to deposit MnO_x on the electrode using this solution and a platinum counter-electrode.

Preparation of CCG electrode. Chemically converted graphene (CCG) was prepared according to our previous report [31]. Briefly, 30 mL as-obtained CCG dispersion was vacuum filtrated through a mixed cellulose ester filter membrane (0.05 μm pore size). The vacuum was disconnected immediately once no free CCG dispersion was left on the filtrate cake. The CCG hydrogel films were then carefully peeled off from the filter membrane, immediately transferred to a Petri dish and

immersed in water overnight to further remove the remaining ammonia and hydrazine. The as-obtained gel films contained ~1.0 mg/cm^2 of CCG.

Characterization. Morphologies of the films were directly examined by SEM using a JEOL6700F at an accelerating voltage of 5 kV. Electrochemical experiments were carried out using a classical two-electrode or three-electrode configuration (CHI660D). Cyclic voltammetry and galvanostatic charge/discharge tests were used to characterize the electrochemical behaviour of the supercapacitor devices.

The loading mass of the electrode was calculated by the following equation:

$$m = \frac{\left(\int I \mathrm{d}U\right) M}{nFv}$$

where I is the current, U is the potential window, v is the scan rate, m is the electrodeposition mass of MnO_x, n is electron number per mole, F is Faraday constant (96485.2 C mol^{-1}), and M is molar mass of MnO_x, the appropriately MnO_x mass is directly proportional to the amount of charge flow through the circuit in deposition process, and thus is closely related to the scan rate and deposition current. See our previous work in ref. 17. The mass of the negative electrode made of only CCG hydrogel film was obtained by weighing.

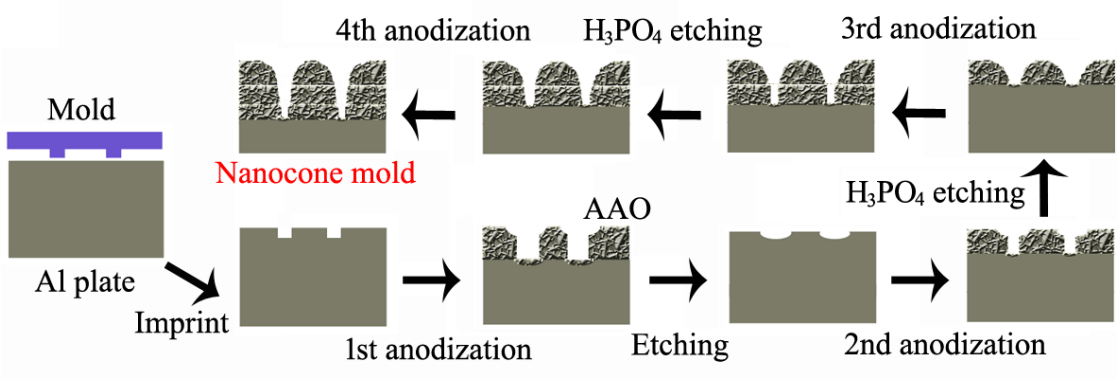

Figure S1, The mold with an inverted nanocone hole array. The detailed processes for preparation of AAM with an inverted nanocone hole array.

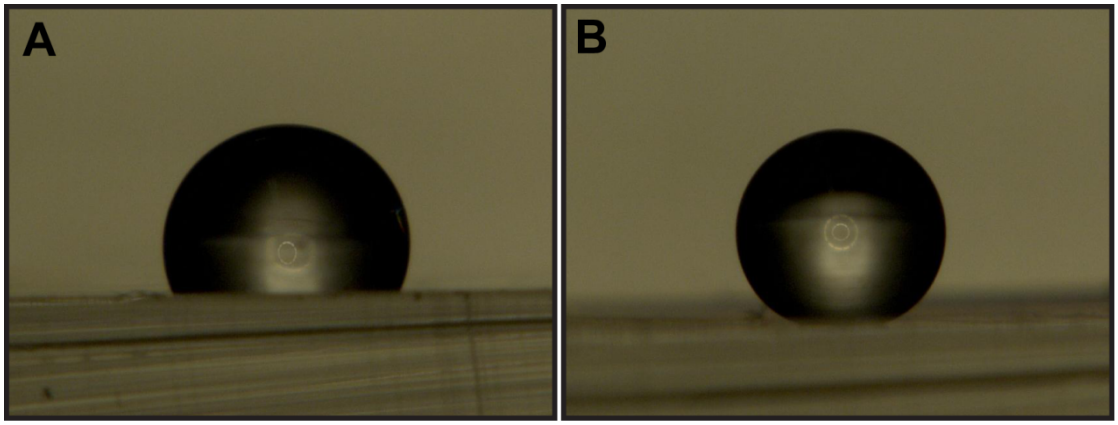

Figure S2, Contact angle tests. The water droplet on the PFTE surface without (A) and with a nanocone array.

PFPE is a perfluopolyether, Fig. S2A shows a contact angle of ~107˚, which indicates that the flat PFPE surface is hydrophobic. However, the nanopatterned PFPE replicated from the AAM shows a contact angle of ~154˚, which means that the surface of the nanopatterned PFPE is superhydrophobic. This wettability change can be explained using Cassie-Baxter equation:

$$\cos\theta' = f\cos\theta - (1-f)$$

In which θ is the intrinsic contact angle on a flat surface, θ' is the apparent contact angle on a rough surface, f is the fraction of the solid/water interface, while (1-f) is that of the air/water interface. When we introduce nanocone array onto the surface of PFPE, air trapping on groove area around nanocone happens, which contributes greatly to the increase of hydrophobicity.

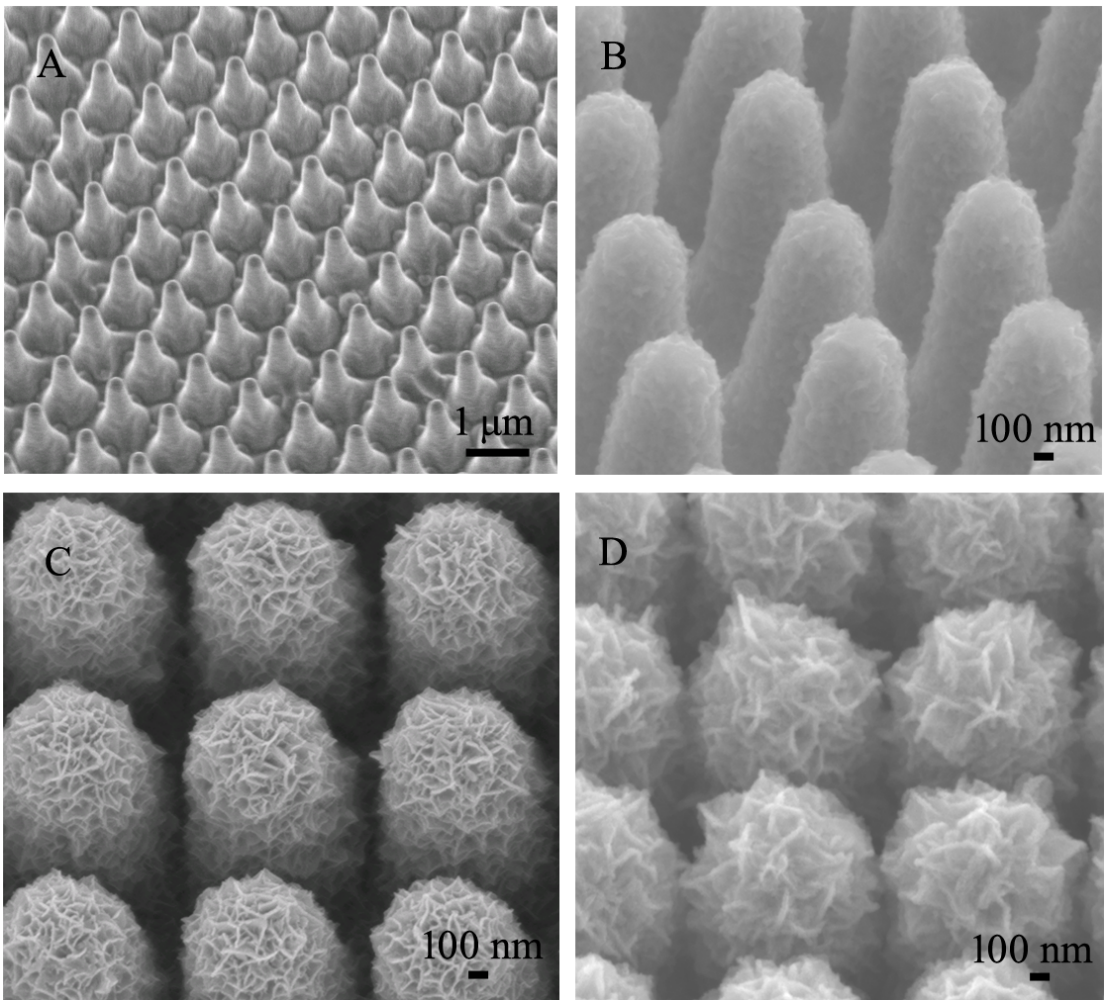

Figure S3, Microscopy measurements of metal/oxide nanocone array electrode. A, High-magnification SEM image of the Au nanocone array electrode. B-D, High-magnification SEM image of electrodepositing MnO_x on Au nanocone array electrode in different time of 175 s, 350 s and 700 s, respectively.

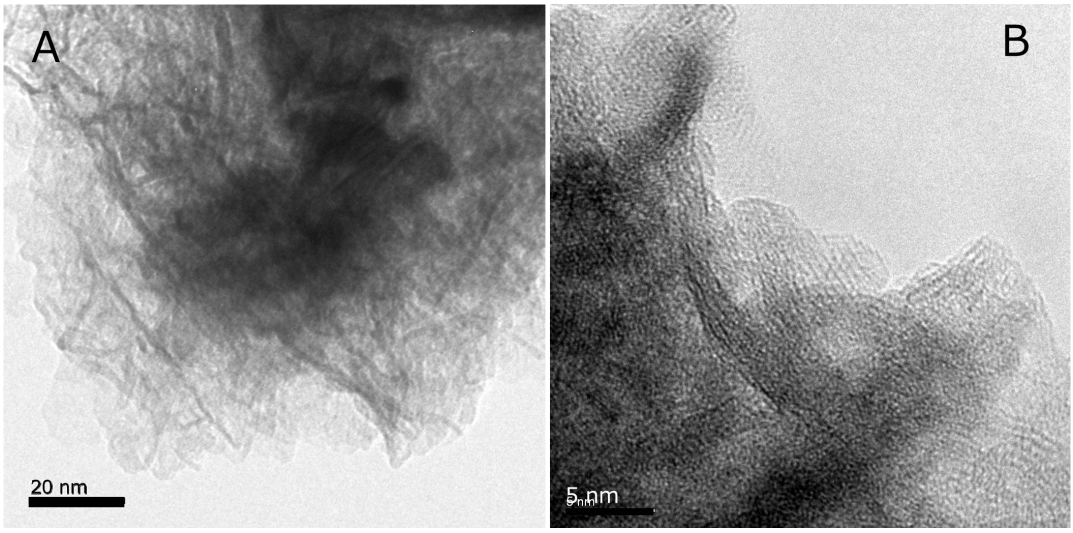

Figure S4, Microscopy measurements of metal/oxide nanocone array electrode. Low-magnification (A) and High-magnification (B) TEM images of the Au/MnO_x nanocone array electrode taken from the sample with a deposition time of 175 s.

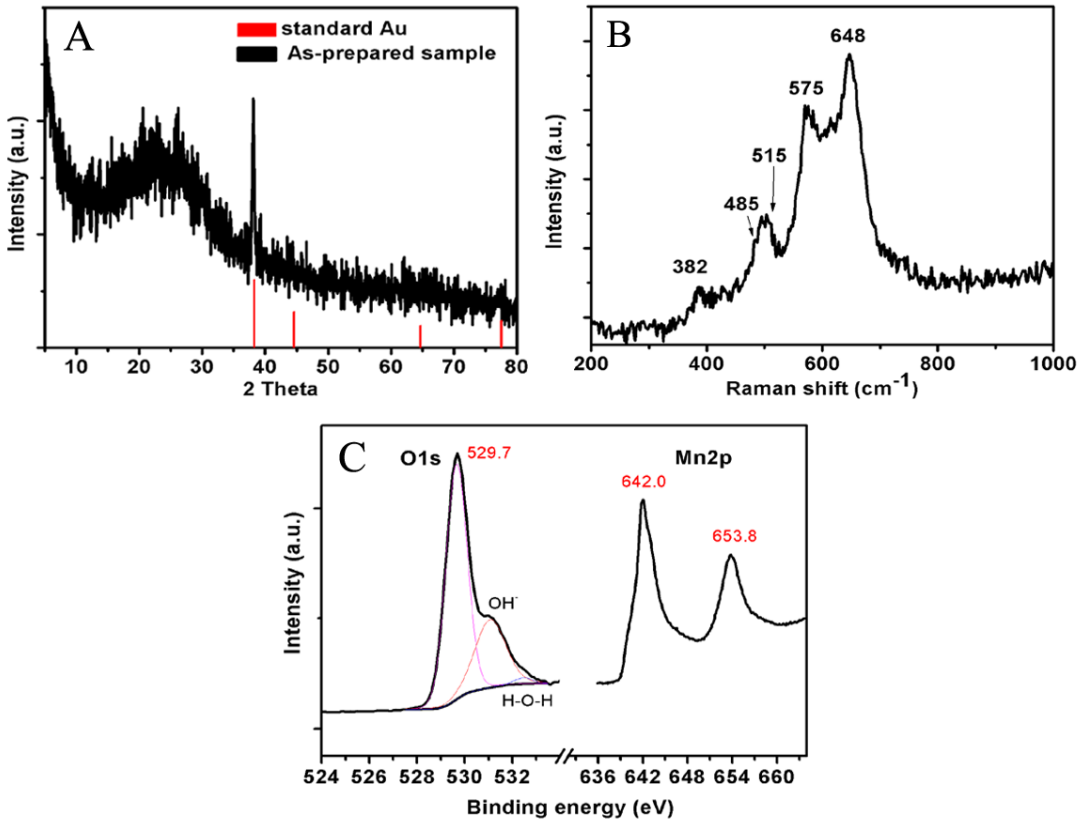

Figure S5, Characterizations. A, Glancing angle XRD pattern, (B) Raman spectra and (C) high-resolution XPS spectra of the as-prepared sample.

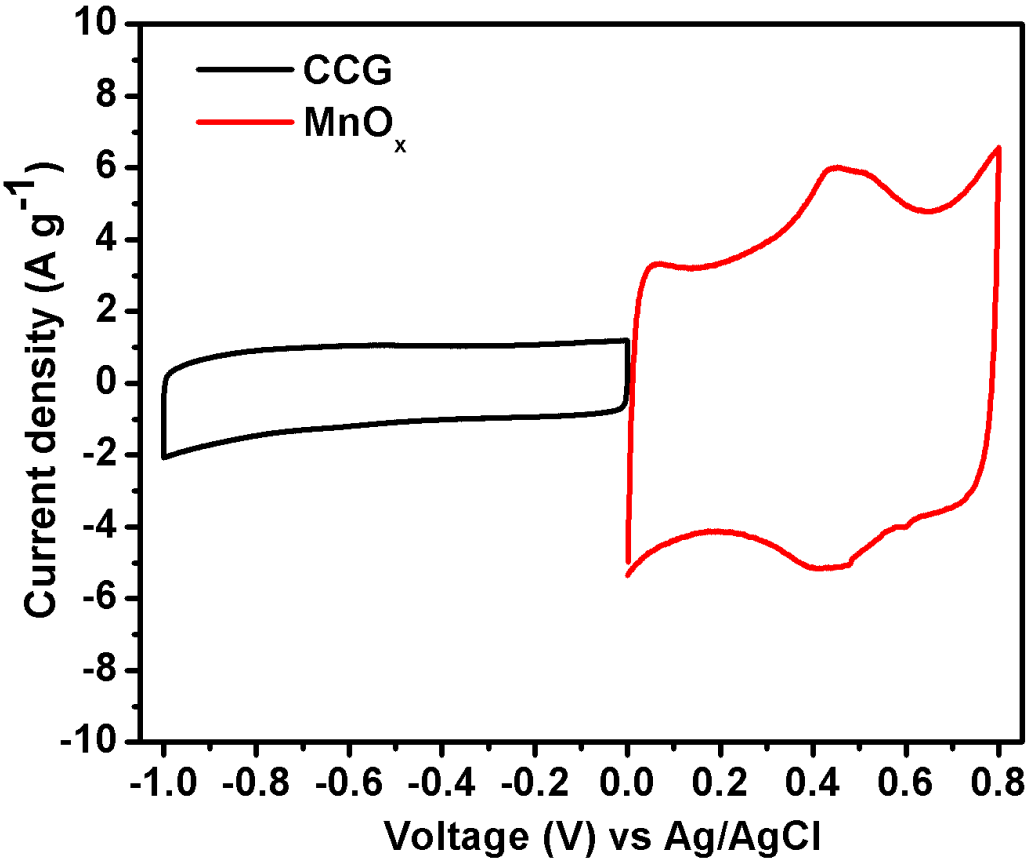

Figure S6, CV curves of RGO and MnO_x at a scan rate of 5 mV s^{-1}.

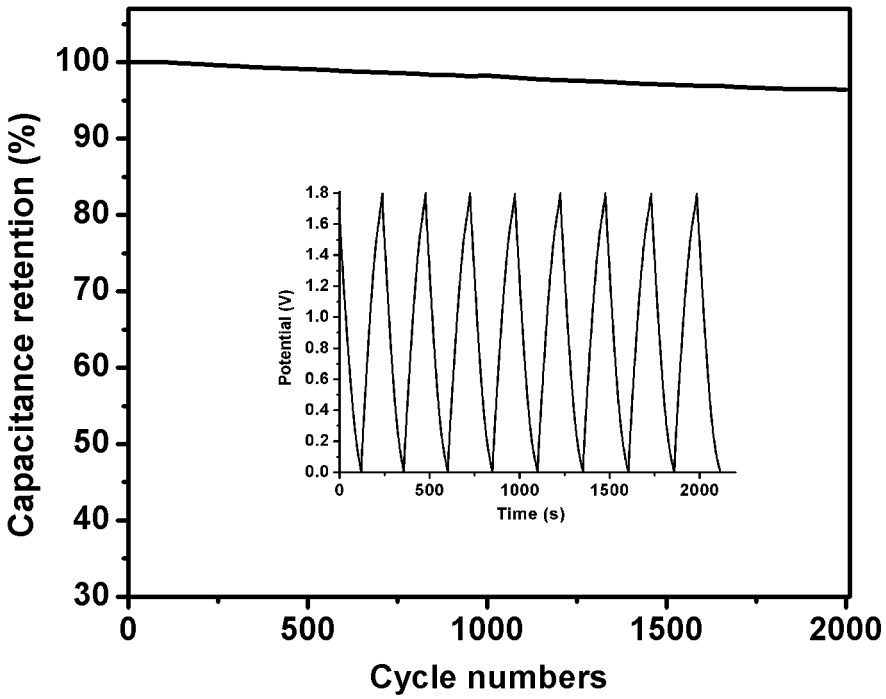

Figure S7, Stability test over 2000 cycles of the asymmetric capacitor at a current density of 2 A g^{-1}. Inset: Corresponding discharge-charge curves.