Supporting Information

Solution Etching Assisted Preparation of MOF-derived $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$ MXene Nanocomposite for High-performance Hybrid Supercapacitor

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Table of contents

EXPERIMENTAL SECTION

Preparation of ZIF-67

$Co(NO_3)_2 \cdot 6H_2O$ (1.746g) was dissolved in the mixture of 20 mL methanol and 20 mL ethanol. 2-Methylimidazole (1.979g) was dissolved in the mixture of 20 mL methanol and 20 mL ethanol. The above two solutions were then mixed under vigorous stirring for 30s, and the resulting solution was incubated at room temperature for 24h. The resulting purple precipitates were collected by centrifugation, washed by ethanol several times and finally vacuum-dried at 60℃.

Preparation of ZIF-67/$Ti_3C_2T_x$

$Co(NO_3)_2 \cdot 6H_2O$ (1.746g) and $Ti_3C_2T_x$ (1.0g) were added in the mixture of 20 mL methanol and 20 mL ethanol, marked A. 2-Methylimidazole (1.979g) was dissolved in the mixture of 20 mL methanol and 20 mL ethanol, marked B. Then the B solution was poured into A under vigorous stirring, and the resulting mixture was constantly stirred at room temperature for 24h. The resulting powder was collected by centrifugation, washed by ethanol several times and finally vacuum-dried at 60℃.

Preparation of $NH_4CoPO_4 \cdot H_2O$ and $NH_4CoPO_4 \cdot H_2O$/$Ti_3C_2T_x$

$(NH_4)_2 \cdot HPO_4$ (3.3g) was dissolved in 50 mL deionized water (DDW) to prepare 0.5M $(NH_4)_2 \cdot HPO_4$ solution. Then, 2g ZIF-67 or 2g ZIF-67/$Ti_3C_2T_x$ was added into 0.5M $(NH_4)_2 \cdot HPO_4$ solutions, respectively. The above resulting mixtures were constantly stirred at room temperature

for 6h. The resulting products were collected by centrifugation and finally dried at 60℃ to obtain $NH_4CoPO_4 \cdot H_2O$ and $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$.

Characterization

X-ray diffraction (XRD) data were obtained from a AXS D8 ADVANCE A25 with Cu Kα radiation (40 kV, 40 mA) of wavelength 0.154 nm (Germany). SEM images and Energy Dispersive Spectrometer (EDS) were collected from the ZEISS EVO18 scanning electron microscope at an accelerating voltage of 40 kV (Germany). XPS measurements were performed on a Thermo esca-lab 250Xi X-ray photoelectron spectrometer using Mg as the exciting source. The Raman spectra were collected on a Thermo Fisher Raman spectrometer under a backscattering geometry (λ= 532 nm). The Brunauer-Emmett- Teller (BET) nitrogen physisorption experiments were carried out on a Qutatachrome Autosorb-iQC system.

Electrochemical measurement

Electrochemical studies on $NH_4CoPO_4 \cdot H_2O$ and $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$ were carried out on a CHI 660E electrochemical working station (Shanghai Chenhua Instrument, Inc.) using a three electrode cell with 1M KOH as the electrolyte. The working electrode was made from mixing of active materials, carbon black, and PVDF (polyvinylidene fluoride) with a weight ratio of 8:1:1, coating on a nickel foam of about 1 cm^2. The typical mass load of electrode material is 2 mg.

The saturated calomel electrode (SCE) was used as reference electrode and platinum plate electrode as the the counter electrode. Cyclic voltammetry and galvanostatic charge-discharge methods were used to investigate capacitance of electrode materials. And electrochemical impedance spectroscopy measurements were conducted at open circuit voltage.

Fabrication of asymmetric supercapacitor (ASC)

The asymmetric supercapacitor was assembled by using as prepared $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$ as positive electrode and active carbon (AC) working electrode as negative electrode. For fabrication of AC working electrode, AC mixed with carbon black and PVDF in a mass radio of 8:1:1 to form a paste and then was pasted onto a nickel foam. To get the best performance of ASC, the charge balance the relationship between the two electrodes should follow $q^+ = q^-$. To satisfy $q^+ = q^-$, the mass balancing between the two electrodes could be shown in the following the equation:

$$q = C \times \Delta V \times m \qquad \text{(Formula S1)}$$

$$m^+ / m^- = (C^- \times \Delta V^-)/(C^+ \times \Delta V^+) \qquad \text{(Formula S2)}$$

Where C (F g^{-1}) is specific capacitance of electrode, m (g) is the active material mass on the electrode, and the ΔV (V) is the potential window. According to the results of the GCD curves of $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$ and AC, the optimal mass ratio between the two electrodes was calculation to be about $m(NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x)/m(AC)$ = 1:3.3 in the ASC.

Usually, the mass of AC is 5 mg and $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$ is 1.5 mg in fabricated ASC.

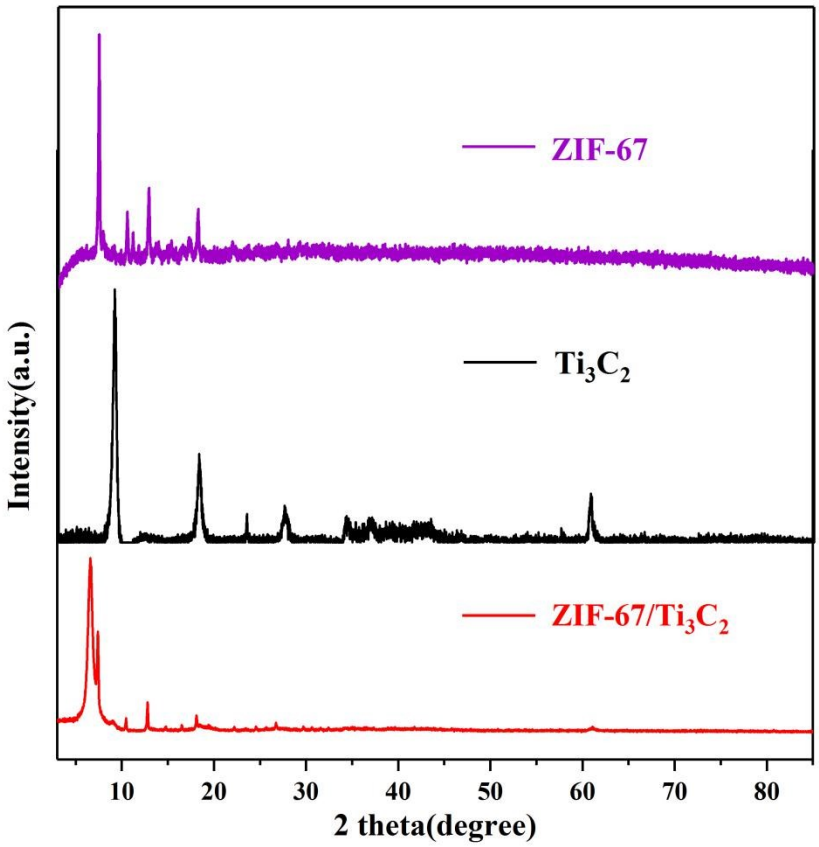

Fig. S1 XRD pattern of ZIF-67, $Ti_3C_2T_x$ and ZIF-67/$Ti_3C_2T_x$.

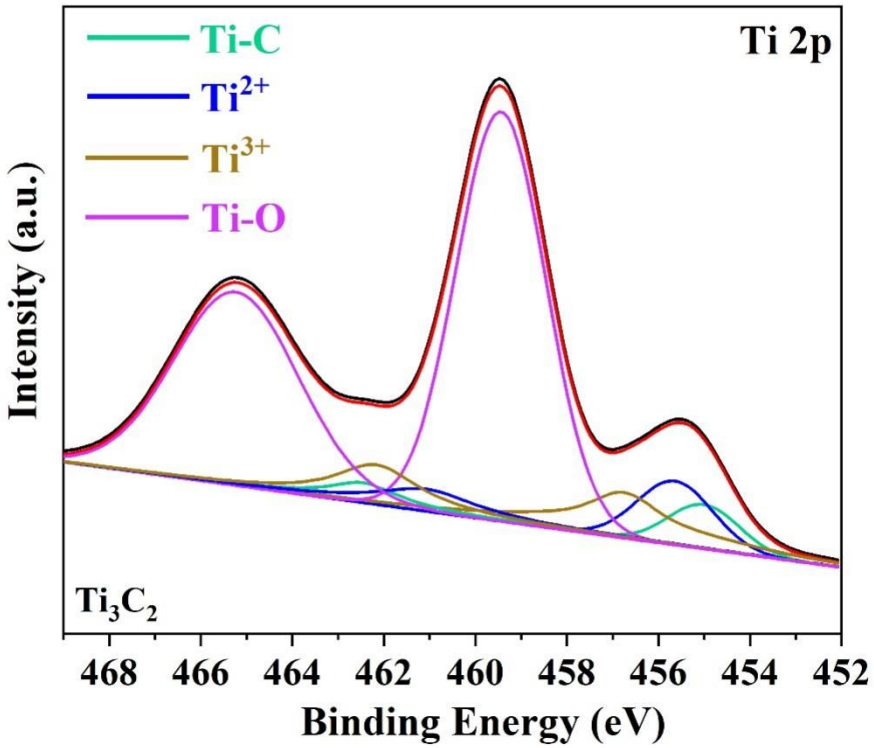

Fig. S2 Ti 2p XPS spectra of $Ti_3C_2T_x$.

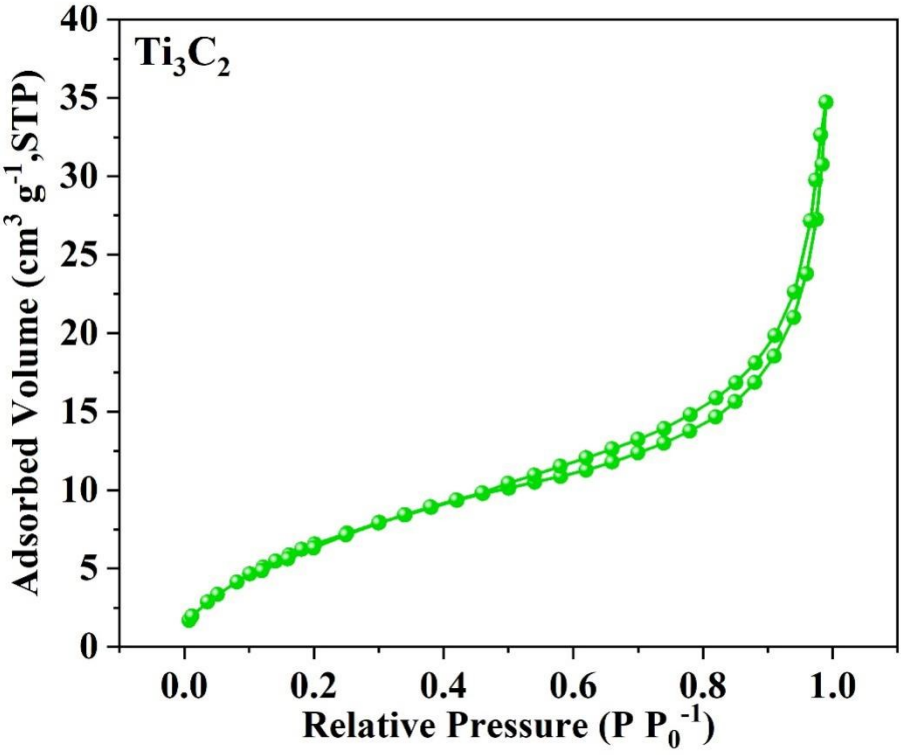

Fig. S3 BET curve of $Ti_3C_2T_x$.

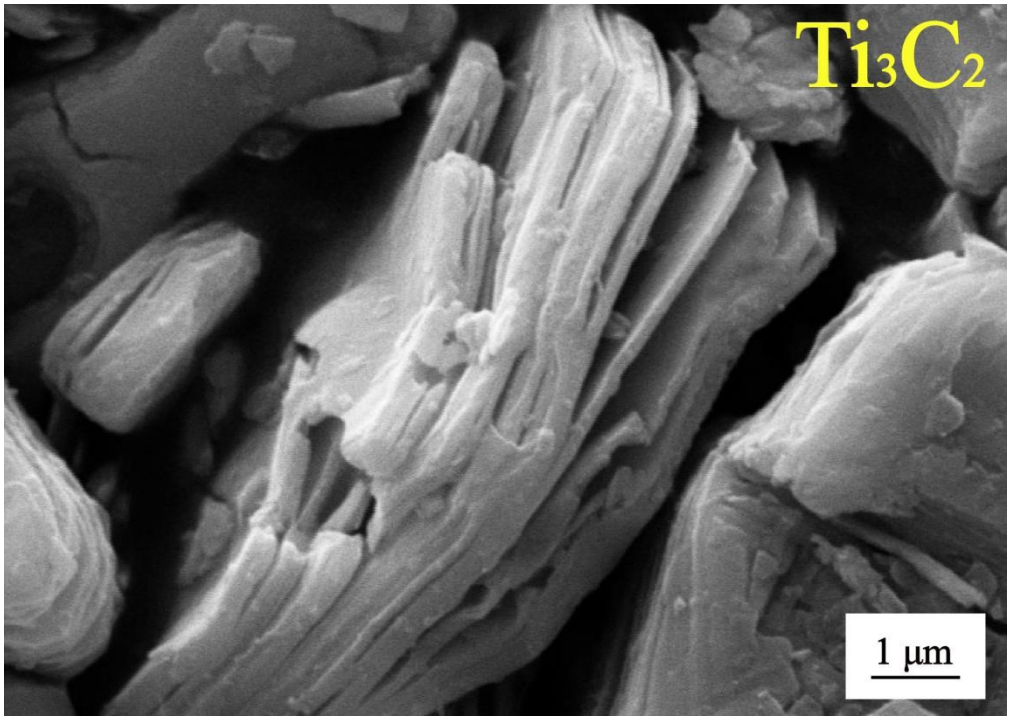

Fig. S4 SEM image of $Ti_3C_2T_x$.

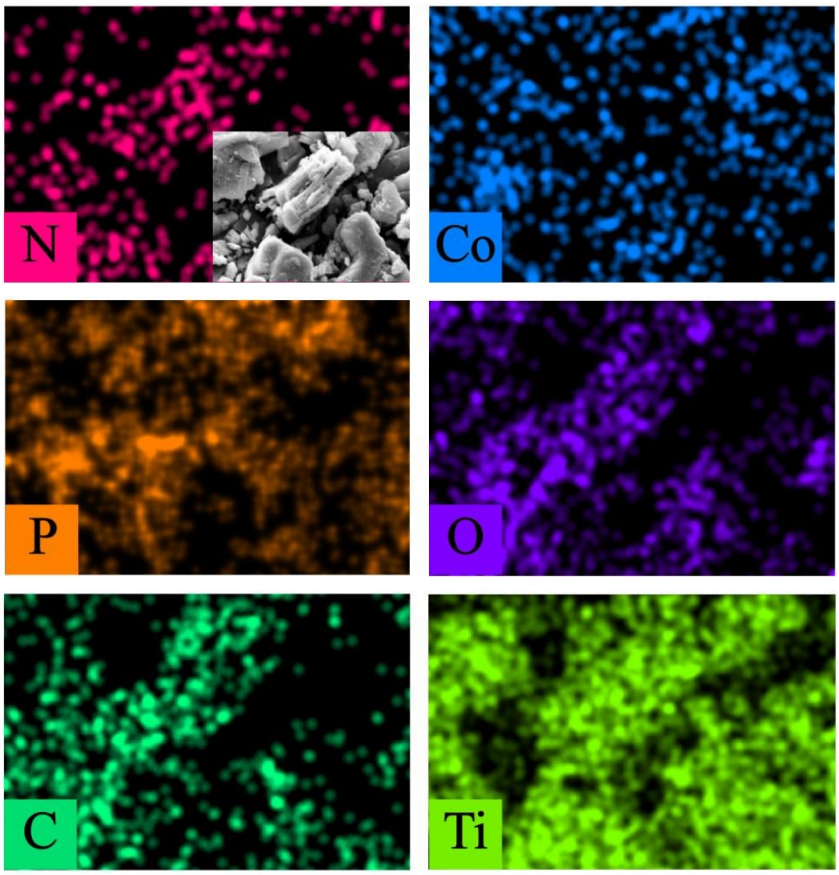

Fig. S5 EDX elemental mapping (N, Co, P, O, C and Ti element) of $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$.

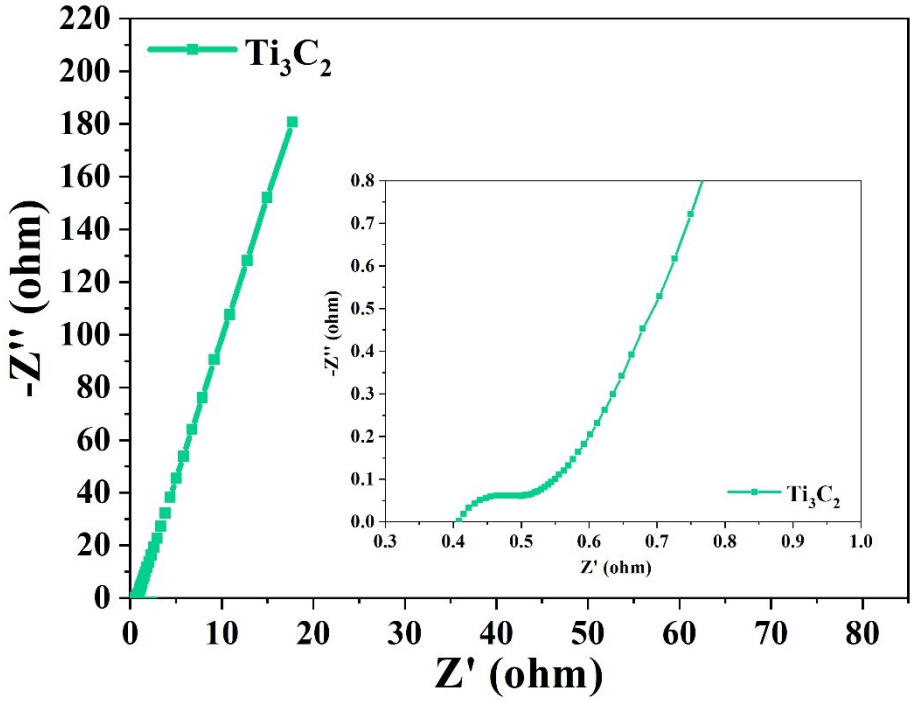

Fig. S6 EIS plot of $Ti_3C_2T_x$.

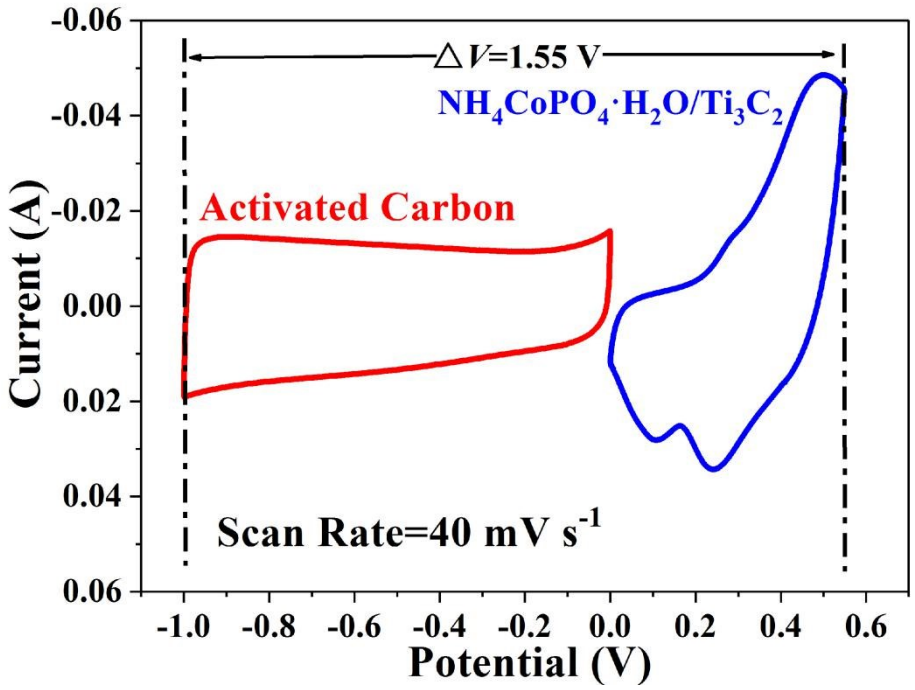

Fig. S7 CV curves of activated carbon and $NH_4CoPO_4 \cdot H_2O/Ti_3C_2T_x$ at 40 mV s^{-1} in a three-electrode system.

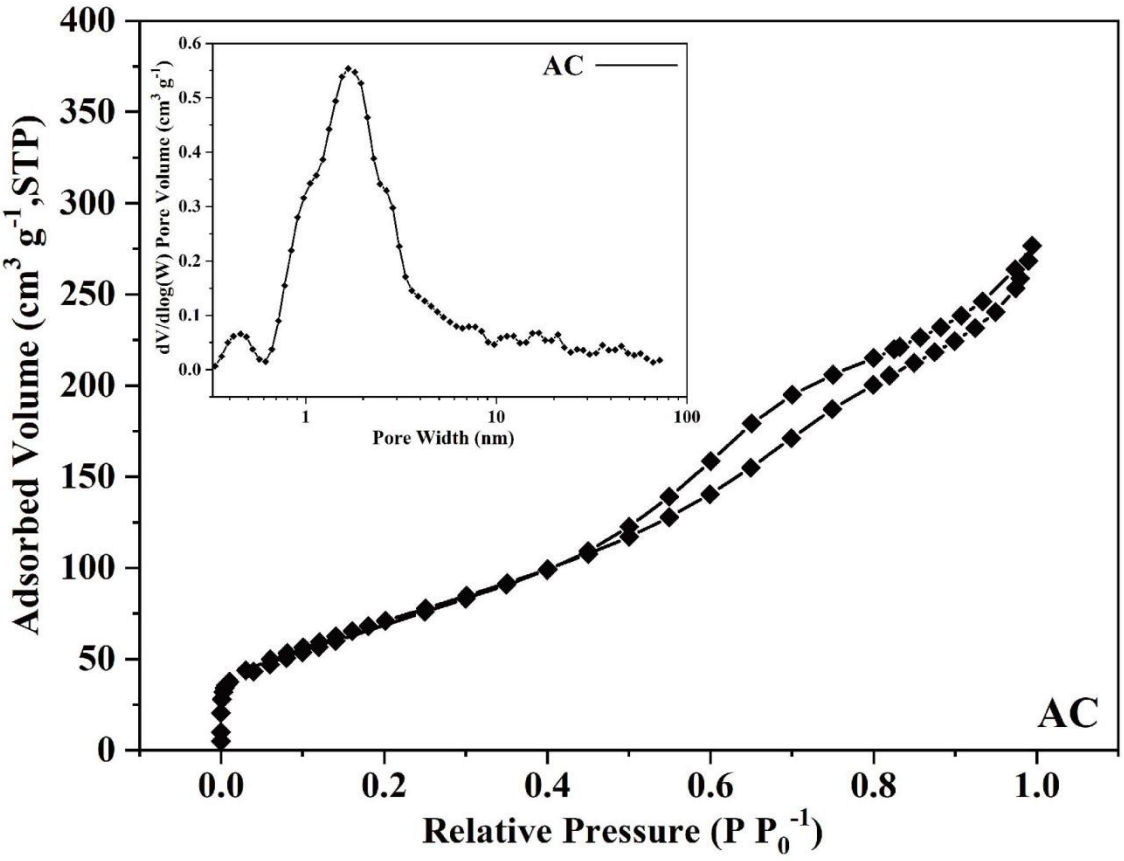

Fig. S8 BET curves of AC.

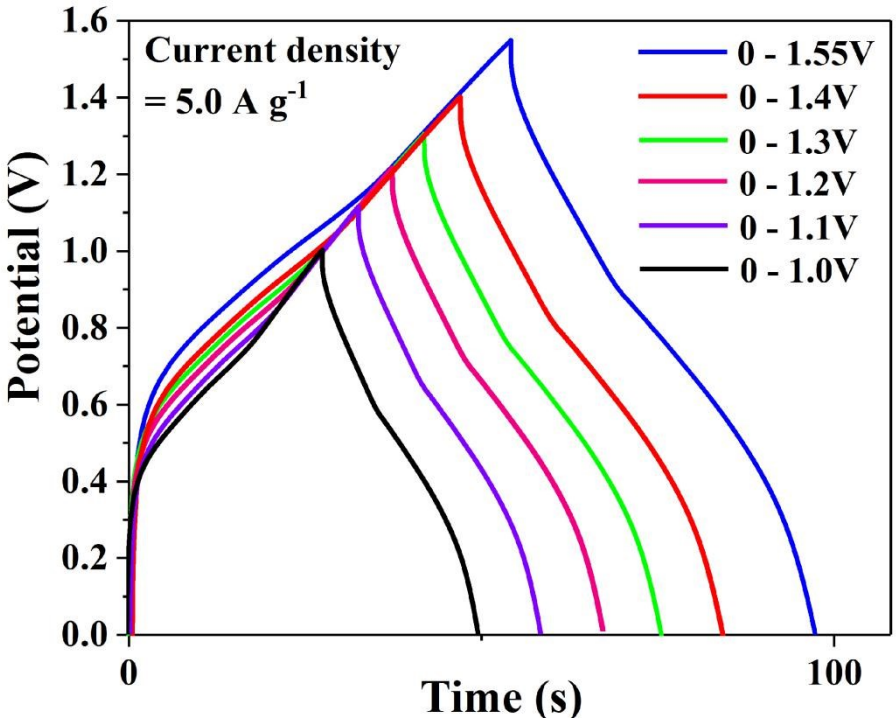

Fig. S9 GCD curves of ASC at different voltage window at 5 A g^{-1}.

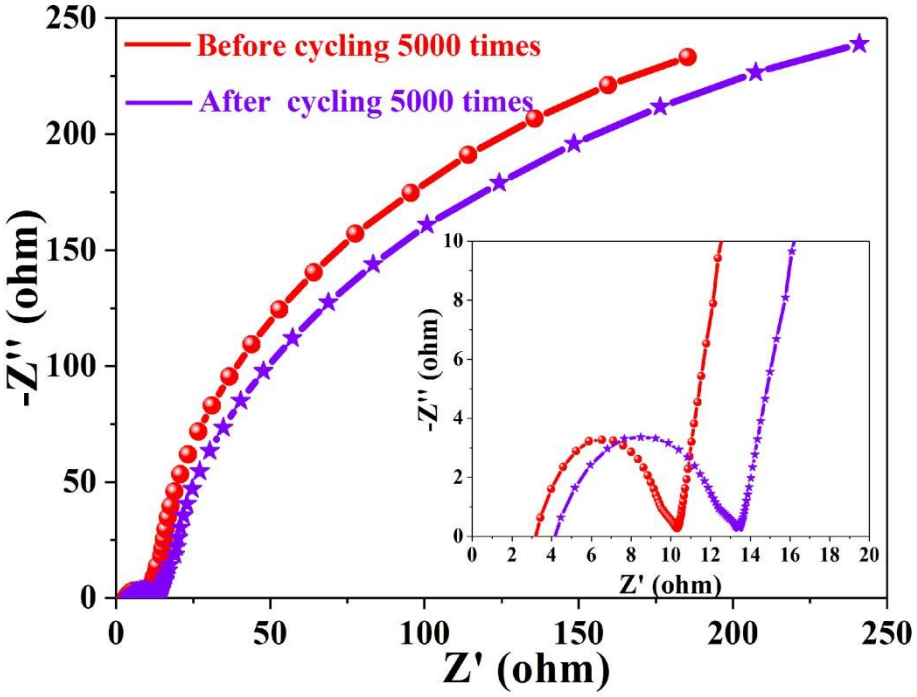

Fig. S10 EIS plots of ASC before and after 5000 cycles.

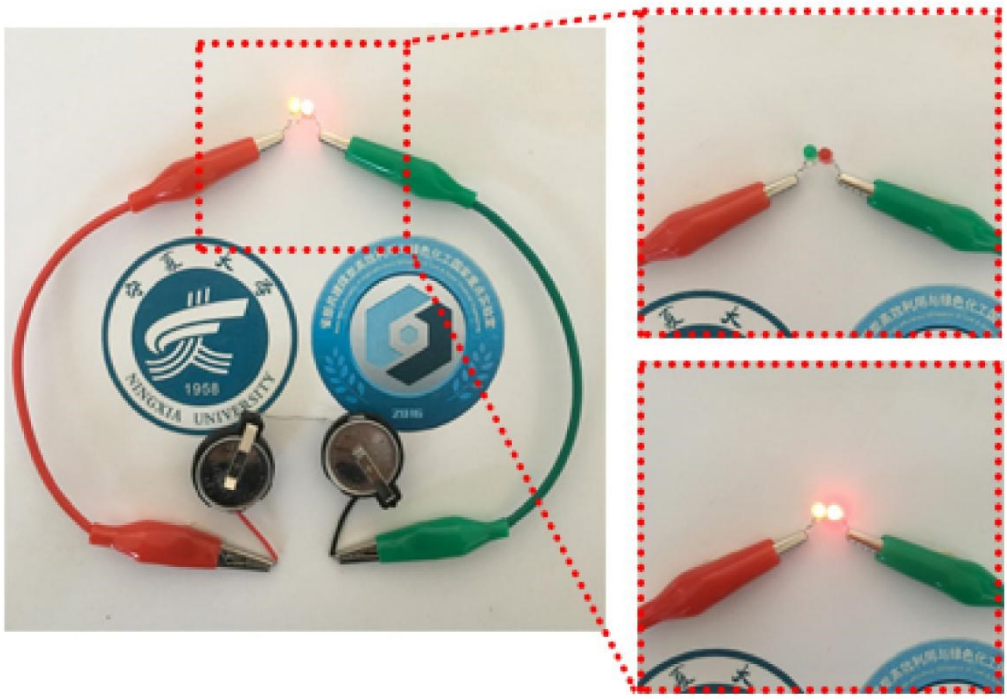

Fig. S11 Images of a LED driven by two serried ASCs.

Formula S3 is used to calculate the electrode density of ASC.

$$\rho = \frac{m}{V} = \frac{m}{S \cdot h} = \frac{m}{\pi r^2 \cdot h} \qquad \text{(Formula S3)}$$

where *m*, *r*, and *h* are the mass (g), radius (cm) and height (cm) of electrode, repectively. The electrode density of ASC calculated was 0.36 g cm^{-3} by using formula S3.