Electronic Supplementary Information

Green interfacial synthesis of two-dimensional poly(2, 5-dimethoxyaniline) nanosheets as a promising electrode for high performance electrochemical capacitors

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Experimental Section

Materials Synthesis. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS), sodium chloride (NaCl), hydrogen peroxide (H_2O_2, 30 wt.%), acetonitrile, concentrated hydrochloric acid (HCl, 37 wt.%), ferric chloride ($FeCl_3$, 99%) and 2, 5-dimethoxyaniline (DMA, 98%) were purchased from Sigma Aldrich. And 1-ethyl-3-methyl imidazolium tetrafluoroborate ([Emim]BF_4, 95%) was purchased from Chengjie Chemical Co. LTD (Shanghai, China). Typically, the interfacial reaction was performed as follows. 0.05 g of DMA was added into 15 mL of [Emim]BF_4 to form a non-aqueous phase. Then, 0.2 mL of H_2O_2 and 1.2 g of NaCl were added into 15 mL of 1 M HCl, and the mixture solution was used as the aqueous phase, which was set above the ionic liquid phase to construct a green two-phase synthetic system. After polymerization reaction for 5 h, the resultant PDMA was collected, washed with copious amounts of 1 M HCl and acetonitrile to remove the unreacted monomer, oligomers and salt, and further dried in vacuum oven at 50 ºC for 12 h. In addition, 15 mL of 1 M HCl with 0.019 g of APS or 0.022 g of $FeCl_3$ were also used as oxidants for the interfacial polymerization of other PDMA samples, while other synthetic parameters were still kept the same. The resulting PDMA products were then denoted as PDMA-APS and PDMA-$FeCl_3$, respectively. For further comparison, a homogenous synthesis was carried out as follows: 15 mL of 1 M HCl with 1.2 g of NaCl and 0.2 mL H_2O_2 was added slowly into the 15 mL of [Emim]BF_4 with 0.05 g of DMA under stirring. After polymerization reaction for 5 h, the PDMA was also fabricated.

Materials Characterization. The samples were examined by powder X-ray diffraction (XRD) (Max 18 XCE, Japan) using a Cu K*a* source (λ = 0.154056 nm) at a scanning speed of 3° min^{-1} over a 2θ range of 5 - 35°. The morphologies and structures were observed with field-emission scanning electron microscopy (FESEM, JEOL-6300F, 15 kV) and Fourier transform infrared (FT-IR) spectra (360 Nicolet AVATAR FT-IR). Brunauer-Emmett-Teller (BET) measurement was carried out through measuring N_2 adsorption-desorption isotherms at 77 K by using an ASAP-2010 surface area analyzer. Round PDMA tablets was obtained by pressing (~20 MPa) 20 mg of the obtained PDMA samples using a tablet compression machine. And the thickness and diameter of the round tablet were measured by a vernier caliper. The as-fabricated round N-CNSs tablet was further used for the electronic conductivity measurement by a four-point probe meter (SDY-5, Guangzhou, China) at room temperature.

Electrochemical Measurements. The working electrode was prepared with the electroactive material

PDMA, acetylene black (AB) and polytetrafluoroethylene (PTFE) in a weight ratio of 5 : 1.5 : 0.5, which were smeared onto the graphite substrates for following electrochemical tests by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) measurements performed with an IVIUM electrochemical workstation (the Netherlands). The typical mass of the electroactive PDMA is 5 mg in the working electrode. All experiments were carried out in a three-electrode cell with a working electrode, a platinum plate counter electrode (1 cm^2) and a saturated calomel electrode (SCE) reference electrode at room temperature. The electrolyte used here was 1 M HCl aqueous solution. The cycling performance was carried out with a CT2001D tester (Wuhan, China). The specific capacitances of the PDMA electrodes can be calculated by using the following equation:

$$\mathrm{C} = \frac{It}{\Delta V} \qquad (1)$$

where C, I, t and ΔV are the specific capacitance (F g^{-1}), discharge current (A g^{-1}), discharging time (s), and discharge potential interval (V) of the PDMA electrodes, respectively. Another important parameter, coulombic efficiency (η) can be evaluated from the equation (2), where t_D and t_C are the discharging time and charging time, respectively.

$$\eta = \frac{t_D}{t_C} \times 100\% \qquad (2)$$

In addition, a quasi-capacitor was fabricated by using two PDMA NS electrodes face to face in 1 M HCl aqueous solution. The specific energy density (E) and specific power density (P) of the PDMA NS-based symmetric capacitor were calculated from the equations (3, 4) as follows.

$$E = \frac{1}{2}CV^2 \quad (3) \qquad\qquad P = \frac{E}{t} \quad (4)$$

where V and t are the electrochemical working potential range and discharge time of the PDMAbased symmetric device.

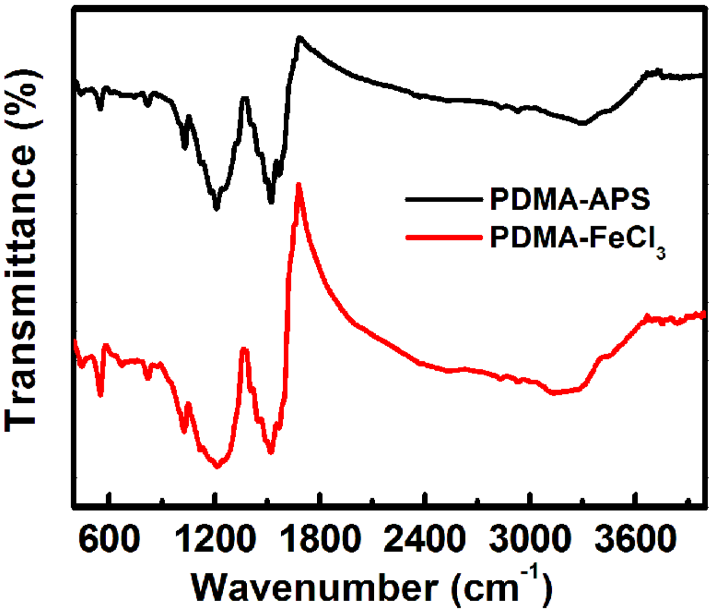

Fig. S1 FT-IR spectra of the as-obtained PDMA-APS and PDMA-$FeCl_3$ samples as indicated

As seen from the Fig. S1, the FT-IR spectra of the PDMA-APS and PDMA-$FeCl_3$ are greatly similar to that for the as-synthesized PDMA NSs.

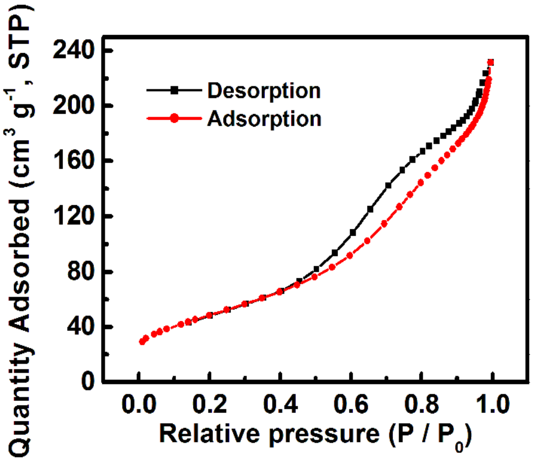

Fig. S2 N_2 adsorption-desorption isotherm of the as-obtained PDMA NS sample

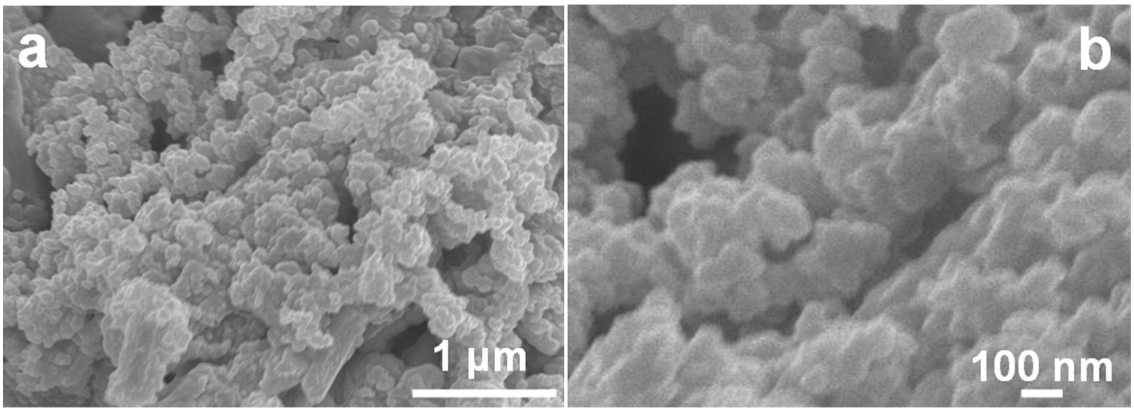

Fig. S3 FESEM images of the as-obtained PDMA *via* non-interfacial, *i.e.*, homogeneous synthesis by using H_2O_2 as an oxidant

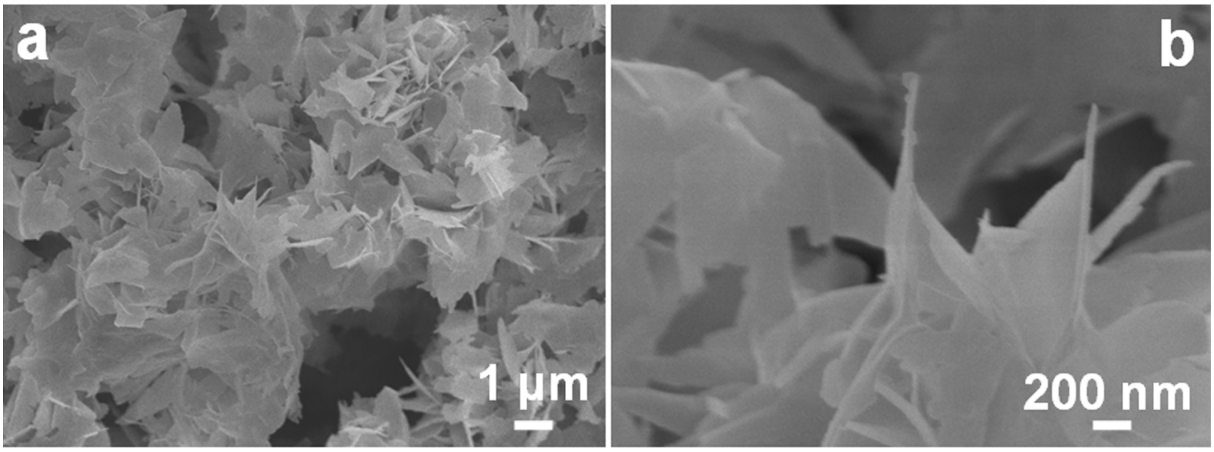

Fig. S4 FESEM images of the as-obtained PDMA *via* interfacial synthesis by using H_2O_2 as an oxidant without the NaCl during the synthetic procedure

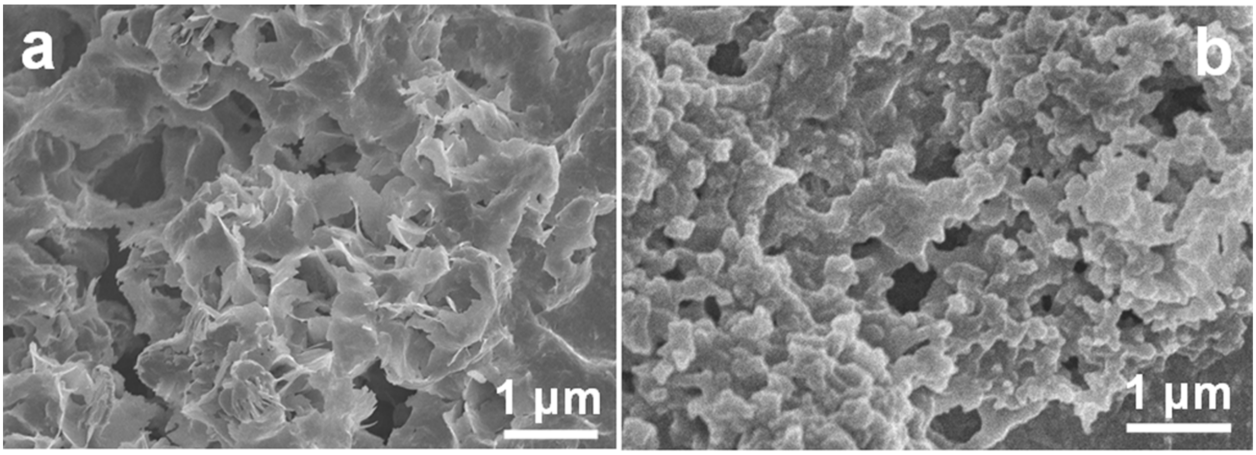

Fig. S5 FESEM images of the resulting PDMA-$FeCl_3$ (a) and PDMA-APS (b) samples

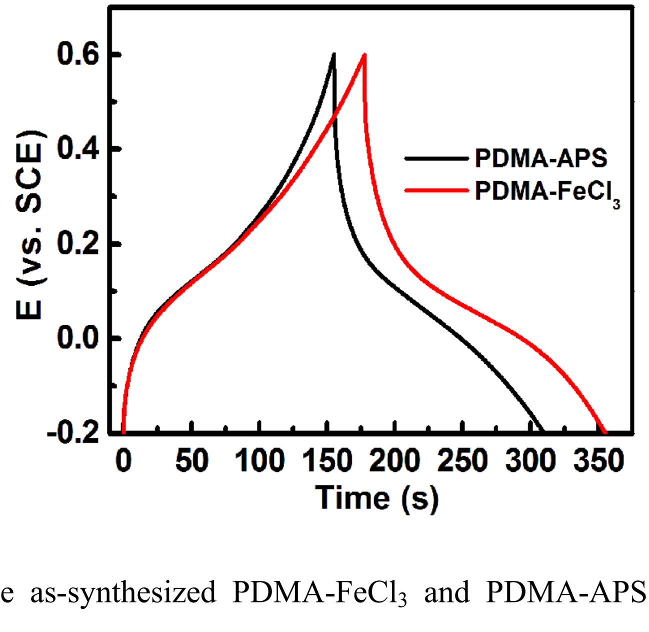

Fig. S6 CP plots of the as-synthesized PDMA-FeCl$_3$ and PDMA-APS electrodes at a current density of 0.5 A g^{-1} as indicated

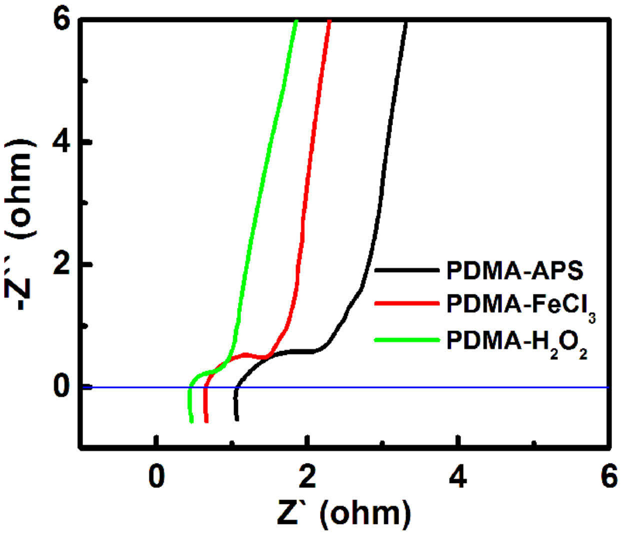

Fig. S7 EIS spectra of the as-synthesized PDMA-APS, PDMA-$FeCl_3$ and PDMA-H_2O_2 electrodes as indicated

Commonly, the intersection of the EIS plot at the X-axis demonstrates the solution resistance (R_s), which commonly includes the following three terms: the resistance of the KOH aqueous solution, the intrinsic resistance of the electroactive material itself, and the contact resistance at the interface between electroactive materials and current collector. Obviously, the R_s for the PDMA-H_2O_2, PDMA-$FeCl_3$, and PDMA-APS electrodes were observed as ~0.5, ~0.7 and ~1.1 ohm, respectively. And at the high-medium frequency region, a semicircle can be found and its diameter stands for the charge-transfer resistance (R_{ct}) during the electrochemical process. And the R_{ct} for the PDMA-H_2O_2, PDMA-$FeCl_3$, and PDMA-APS electrodes were observed as ~0.4, ~0.9 and ~1.3 ohm, respectively. In addition, in the low frequency region, the slope of the impedance plot almost tends to a vertical asymptote, indicating the typical electrochemical capacitance of the three PDMA electrodes in 1 M HCl aqueous solution.

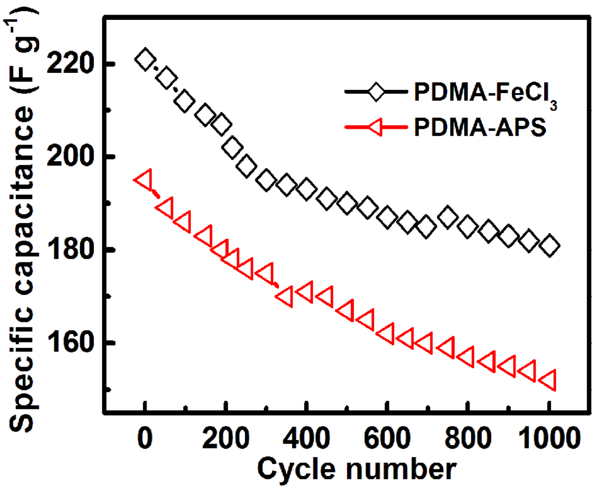

Fig. S8 Cycle performance (0.5 A g^{-1}) of the as-prepared PDMA-$FeCl_3$ and PDMA-APS samples as indicated

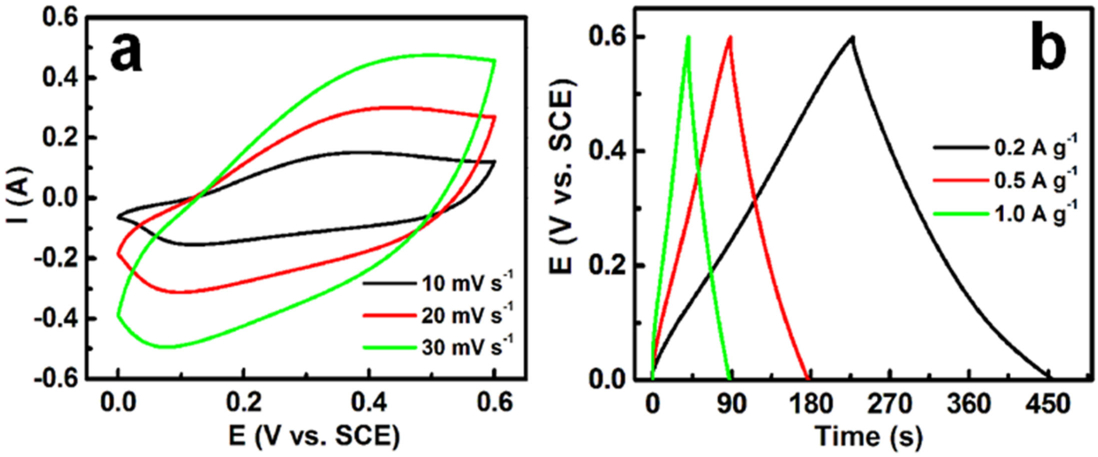

Fig. S9 Typical CV curves and CP plots of the as-fabricated PDMA NS-based supercapacitors