Supporting Information

Carbon with ultrahigh capacitance when graphene paper meets $K_3Fe(CN)_6$

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Experimental

Graphene paper was synthesized according to our previous work.[22] First, solid graphene oxide was dispersed in deionized water. Then, the as-formed graphene oxide dispersion was transferred into a Petri dish and frozen at −50 °C for 2 h. The graphene oxide aerogel was obtained by freeze-drying of the ice solid under vacuum for 24 h. The graphene aerogel was formed by directly heating graphene oxide aerogel at 200 °C in air for 1.5 h. Graphene paper can be obtained by pressing the graphene aerogel at 10 MPa using a compression machine. By pressing the graphene aerogel at 10 Mpa, graphene paper with a uniform thickness and strong structural integrity was obtained, which is freestanding and highly flexible.The graphene paper was characterized by field-emission scanning electron microscopy (FESEM, Hitachi-S4800) and a Bruker D8 focus powder X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm).

For supercapacitor tests, a small piece of graphene paper (1×1 cm^2) was attached between two nickel foils (1×1 cm^2) and the sandwich structure was pressed at 10 MPa. In order to better evaluate the inherent electrochemical properties of graphene-electrodes/redox-electrolyte supercapacitor system, we selected nickel foam as current collector to reduce the internal resistance of supercapacitor to a minimum value. Previously, nickel foam has been often applied as current collector in alkaline and neutral electrolytes by others. The loading of each electrode is about 1.5 mg. Cyclic voltammetry and galvanostatic charge–discharge measurements were performed in two different redox-electrolytes, viz., 1 M Na_2SO_4 with different concentrations of $K_3Fe(CN)_6$ at the potential range of –0.8–0.8 V. Classical three-electrode configuration was used to carry out electrochemical experiments. The saturated calomel electrode (SCE) was used as the reference electrode while Pt wire served as a counter electrode. All tests were performed using a CHI660D electrochemical workstation. The specific capacitance of the system was calculated through integration of galvanostatic discharge curves according to the equation:

$$S_c = \frac{2I \cdot \int V dt}{A \cdot \Delta V^2} \tag{1}$$

where I(A) is the current used for charge/discharge, Δt(s) is the time elapsed for the discharge cycle, A (cm^2) is the area of the graphene paper, and ΔV is the voltage interval of the discharge. The energy density (E) in supercapacitor is related to the capacitance (S_c) and voltage (V) according to the formula: $E=0.5S_cV^2$.

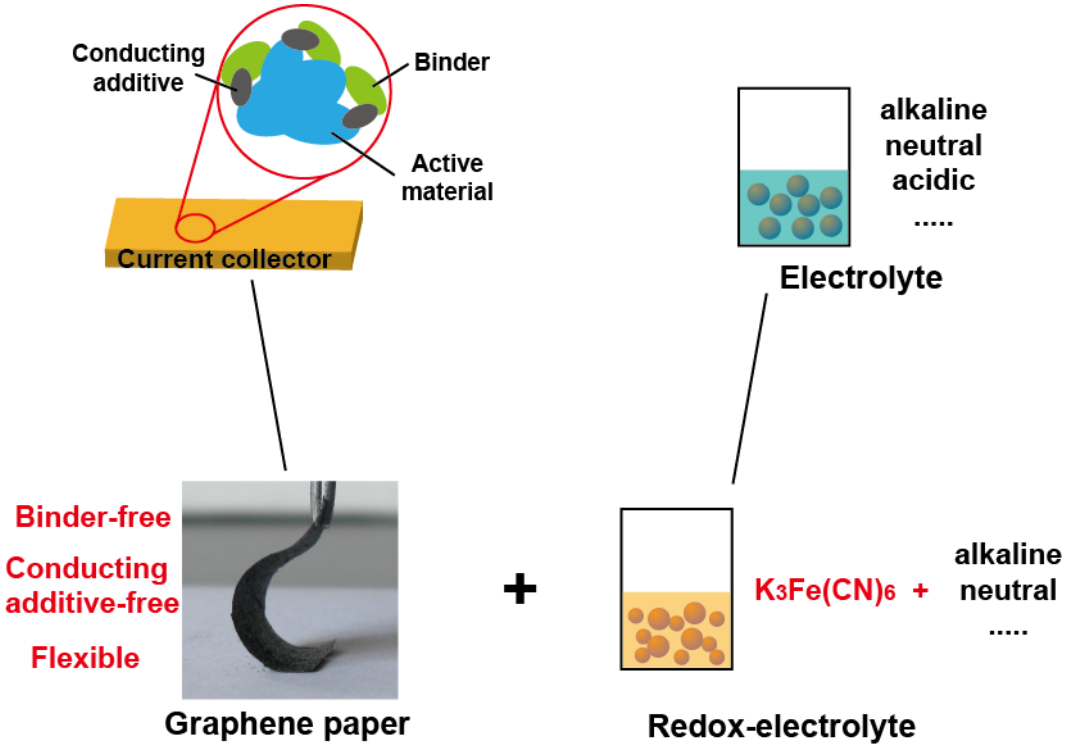

Figure S1 The proposed graphene paper electrode and redox-electrolyte system. Schematic of a supercapacitor with a zoomed-in view of the electrode material to show its composite nature, it is made of (i) an electrochemical active material, (ii) a binder for mechanical cohesion and (iii) a carbon additive to provide electronic percolation through the electrode. Traditional electrolytes for supercapacitors included alkaline, neutral and acidic solutions. Novel electrolyte consists of a redox-active component added to electrolyte. The novel electrode and electrolyte system can significantly increase the supercapacitor performance.

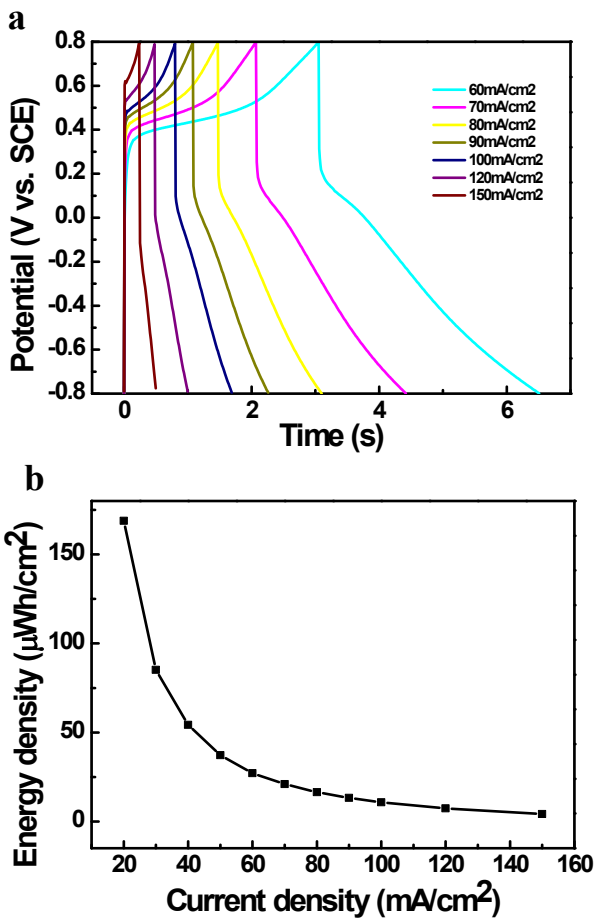

Figure S2 (a) Charge/discharge curves at various current densities of graphene paper electrode in redox-electrolyte of 1M Na_2SO_4 and 0.3 M $K_3Fe(CN)_6$. (b) Energy density as a function of current density.

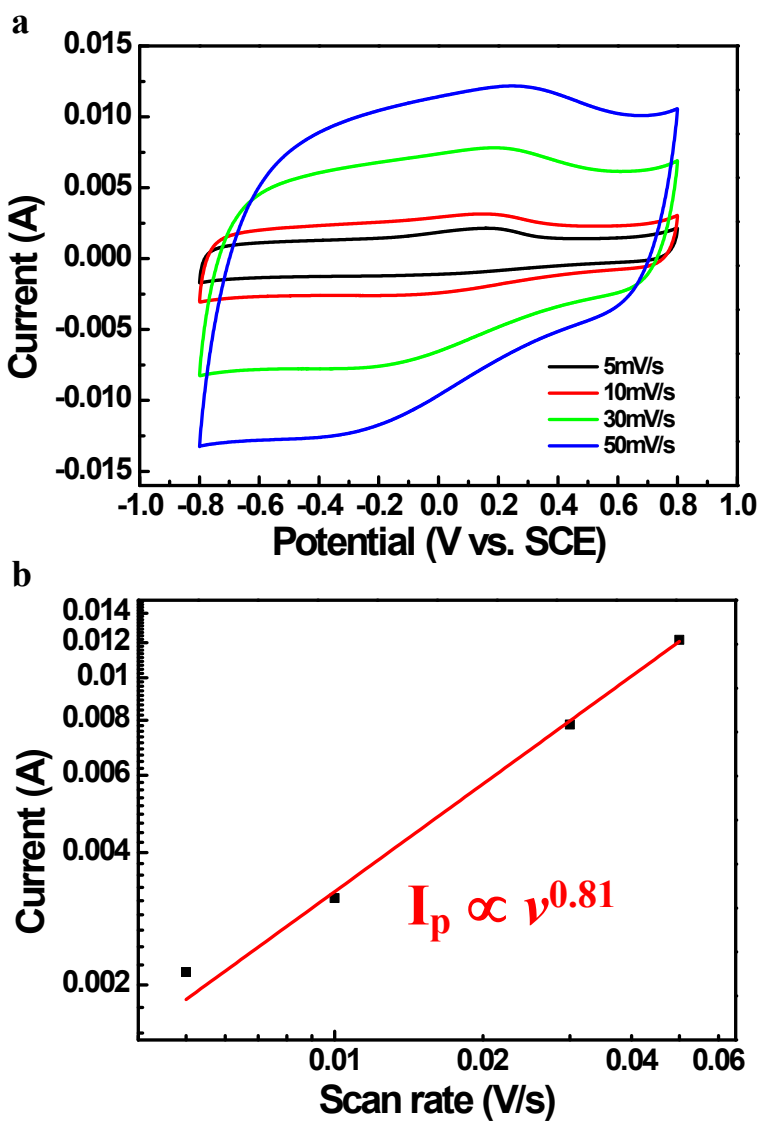

Figure S3 (a) CV curves and (b) the current of graphene paper electrode in Na_2SO_4 electrolyte at various scan rates. The best fit of the data to an apparent power-law dependence yields $I_p \propto \nu^{0.81}$, which suggests that the charge storage mechanism of graphene paper is mainly electric double layer capacitance.