Supporting Information

Construction and Performance Characterization of α -Fe₂O₃/rGO Composite for Long Cycling Life Supercapacitor Anode

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Figure S1. XPS results of the α -Fe₂O₃/rGO composite: high-resolution spectra of (a) Fe 2p and (b) C 1s.

XPS analysis was carried out to identify the structures and chemical states of the α -Fe₂O₃/rGO composite as shown in Figure S1. In the high-resolution Fe 2p spectrum, two major peaks at 710.9 and 724.3 eV ascribed to the Fe 2p_{3/2} and Fe 2p_{1/2} spin-orbit peaks of Fe₂O₃ can be observed. Moreover, two shake-up satellites at 719.4 and 734.1 eV also can be seen clearly, which is the fingerprint of the electronic structure of Fe₂O₃ [*Physical Review B*, 1999, 59: 3195]. Besides, the C 1s spectrum demonstrates the existence of some C–OH and C=O which are the possible interaction sites between α -Fe₂O₃/rGO. That is also the main reason why α -Fe₂O₃ can be well contacted with rGO.



Figure S2. CV curves of the α -Fe₂O₃/rGO composite electrodes with different mass

ratios (α -Fe₂O₃: rGO) at a scan rate of 50 mV s⁻¹.



Figure S3. Initial CV results of the α -Fe₂O₃/rGO (2:1) composite at different scan

rates.



Figure S4. Calculations of the specific capacitance of the $\alpha\mbox{-}Fe_2O_3/rGO$ (2:1) electrode

from a CV curve at a scan rate of 50 mV s^{-1} .



Figure S5. Ragone plot (power density vs energy density) of the $\alpha\text{-Fe}_2O_3/rGO$ (2:1)

electrode.



Figure S6. CV curves of pure α -Fe₂O₃ sample scanned to different negative potentials.



Figure S7. Electrochemical characterizations of α -Fe₂O₃/rGO electrode in 1 M KOH aqueous solution with a voltage window from 0 to -1.4 V (vs Ag/AgCl). (a) CV curve at a scan rate of 50 mV s⁻¹ and (b) Cycling stability measured at a scan rate of 50 mV s⁻¹.

Electrochemical properties of the α -Fe₂O₃/rGO in 1 M KOH with a potential window from 0 to -1.4 V (vs Ag/AgCl) were investigated (Figure S7). As expected, the electrode exhibit much better electrochemical properties in alkaline electrolyte with an obvious redox pair for the initial cycles. The specific capacitance is about 495 F g⁻¹ at a scan rate of 50 mV s⁻¹, about twice of that in neutral electrolyte. Yet, its cycling stability is very poor, only about 60% was remained after 1,000 cycles.



Figure S8. (a) CV and (b) GCD curves of a pure α -Fe₂O₃ electrode at different scan rates and current densities.



Figure S9. Electrochemical behavior of the α -Fe₂O₃/rGO // MnO₂ asymmetric supercapacitor. (a) Comparative CV curves of α -Fe₂O₃/rGO and MnO₂ electrodes recorded in a three-electrode cell in 1 M Na₂SO₄ aqueous solution at a scan rate of 50 mV s⁻¹; (b) CV curves at scan rates ranging from 5 to 200 mV s⁻¹; (c) GCD curves at different current densities, (d) Specific capacitance (based on the total mass of the two electrodes) variation with scan rates and current densities; (e) Long cycling performance measured at 4 A g⁻¹ with a potential window of 2 V; (f) Ragone plot

(power density vs energy density) of the α -Fe₂O₃/rGO // MnO₂ asymmetric supercapacitor.

To identify the performance of an asymmetric supercapacitor, our α -Fe₂O₃/rGO sample was used as anode and a common cathode material of MnO₂ was used as the other electrode in a CR 2032 coin cell. First, CV of the α -Fe₂O₃/rGO and MnO₂ electrode was investigated separately (Figure S9 a). The α -Fe₂O₃/rGO anode exhibits stable operating voltage ranging from -1 to 0 V, while the MnO₂ cathode shows a stable potential window from 0 to 1 V in 1 M Na_2SO_4 aqueous solution. As excepted, the α -Fe₂O₃/rGO // MnO₂ asymmetric supercapacitor emerged a high potential window (2 V) at different scan rates from 5 to 200 mV s⁻¹, shown in Figure S9 b. CV curves kept good rectangular shapes without obvious distortion even at a high scan rate of 200 mV s⁻¹, revealing the ideal capacitive characteristic and the rapid charge/discharge property. GCD measurements (Figure S9 c) were carried out at various current densities from 0.5 to 4 A g^{-1} , showing typical symmetrical triangular shapes. Figure S9 d shows specific capacitances (based on the total mass of the two electrodes) calculated from the CV and GCD curves. The specific capacitance was about 60 F g⁻¹ at a scan rate of 5 mV s⁻¹, 42 F g⁻¹ at 0.5 A g⁻¹ and still high as 30 F g⁻¹ at 10 A g^{-1} , exhibiting good rate capacitance. Long-term cycling performance of the asymmetric supercapacitor was also evaluated in the voltage window of 2 V at a current density of 4 A g^{-1} for 7000 cycles (Figure S9 e), exhibiting excellent cycling stability with 90% retention and almost no obvious loss during the last 4000 cycles. In addition, the energy density was about \sim 25 Wh kg⁻¹ at the power density of 0.5 kW kg⁻¹ and still as high as ~17 Wh kg⁻¹ at 10 kW kg⁻¹ based on total active mass of the two electrodes (Figure S9 f).



Figure S10 (a) SEM image and (b) Elemental mapping image accordingly, indicating the uniform distribution of iron, oxygen and carbon for the α -Fe₂O₃/rGO composite after long time cycling.



Figure S11. Schematic illustrations of the preparation and structural evolution for α -Fe₂O₃/rGO.

Calculation methods:

The specific capacitance (C_{sp} , F g⁻¹) of the single electrode was calculated from the CV and discharging curves according to the following equations:

1. Since the CV curves do not have an ideal rectangular shape, the voltammetric capacitance is calculated from the following equation (as shown in Figure S4):

$$C_{\rm sp} = \frac{\oint IdV}{m \times v \times \Delta V} \tag{1}$$

2. The specific capacitance from the discharge curves is calculated as following:

$$C_{\rm sp} = \frac{I \times \Delta t}{m \times \Delta V} \tag{2}$$

Where \oint IdV (A·V) stands for the cumulative charge during the measurements, which is the area under the CV curve; m (g), v (V s⁻¹), Δ V (V), I (A) and Δ t (s) stand for the mass of active material, the scan rate, the potential difference, the current, and the discharge period upon the potential change, respectively.

Energy density (E) and average power density (P) could be calculated according to the following equations:

$$E = \frac{1}{2} C_{sp} V^2$$
(3)
$$P = \frac{E}{t}$$
(4)

Where C_{sp} is the specific capacitance obtained from equation (2), V is the potential window and t is the discharge period upon the potential change.