

Electronic Supplementary Material

Advanced Asymmetrical Supercapacitors Based on Graphene Hybrid Materials

Hailiang Wang, Yongye Liang, Tissaphern Mirfakhrai, Zhuo Chen, Hernan Sanchez Casalongue, and Hongjie Dai (✉)

Department of Chemistry, Stanford University, Stanford, CA 94305, USA

Supporting information to DOI 10.1007/s12274-011-0129-6

Synthesis of graphene hybrid materials

Synthesis of Ni(OH)₂/graphene: Typically, ~5 mg of graphene sheets (GS, prepared following Refs. [22, 23, 25, 35] in the main text) was dispersed in 20 mL of anhydrous *N,N*-dimethylformamide (DMF). The suspension was heated to 80 °C, after which 2 mL of 0.2 mol/L nickel acetate (Ni(OAc)₂) aqueous solution was injected in. The mixture was kept at 80 °C with stirring for 1 h. After that, the intermediate product was transferred to ~20 mL of water and sealed in 40 mL Teflon-lined stainless steel autoclaves for hydrothermal treatment at 180 °C for 10 h.

Synthesis of RuO₂/graphene: ~1 mg of GS was dispersed in 1 mL of DMF and 9 mL of H₂O. After adding ~10 mg of RuCl₃, the mixture was bath-sonicated for ~20 min to make a homogeneous suspension. The suspension was then heated at 80 °C with stirring for 1 h. After that, the intermediate product was transferred to ~10 mL of water and sealed in 40 mL Teflon-lined stainless steel autoclaves for hydrothermal treatment at 180 °C for 10 h.

Supercapacitor electrode preparation

To prepare a RuO₂/graphene electrode, ~1 mg of hybrid material was first mixed with polytetrafluoroethylene (from 60 wt% water suspension, Aldrich) in a ratio of 100:2 by mass, and then dispersed in ethanol. Then the suspension was drop-dried into a 1 cm × 1 cm Ni foam (2 mm thick, 100 pores per inch (ppi), 95% porosity, Marketech) at 80 °C followed by a post-baking at 200 °C for 1 h. The foam with sample loaded was compressed before measurement. Control experiments confirmed that the capacitance contribution from the Ni foam was negligible.

The Ni(OH)₂/graphene electrode was prepared in the same way as the RuO₂/graphene electrode except that the Ni foam was coated by carbon (from decomposition of CH₄ at 800 °C) before deposition of Ni(OH)₂/graphene to prevent the Ni foam being in direct contact with the KOH electrolyte. Control experiments confirmed that the capacitance contribution from carbon-coated Ni foam was negligible (less than 2%) for our Ni(OH)₂/graphene electrodes.

To prepare an RGO electrode, ~3 mg of GO (made by following Refs. [34–36] in the main text, and then degassed at 120 °C in a Micromeritics ASAP 2010 surface area and porosity analyzer) was dispersed in ~6 mL of ethanol and deposited into a 3 cm × 1 cm Ni foam at 80 °C. The sample was then treated by hydrazine vapor for 72 h to reduce the GO.

Address correspondence to hdai@stanford.edu



Electrochemical measurements

Electrochemical measurements were carried out in a beaker cell with 1 mol/L KOH aqueous solution as the electrolyte. In a three-electrode configuration, a Ag/AgCl electrode filled with 1 mol/L NaCl was used as the reference electrode and a platinum wire was used as the counter electrode. In a two-electrode configuration, the reference electrode lead was connected to the counter electrode lead. The Ni(OH)₂/graphene electrode was pre-scanned against the Ag/AgCl reference electrode at 40 mV/s for 200 cycles to stabilize the capacitance before further measurements. Specific capacitance values were calculated from the CV curves using the following equation:

$$C = \frac{\int Idt}{m\Delta V}$$

where I is the oxidation or reduction current, dt is the time differential, m indicates the mass of the electrode materials, and ΔV indicates the voltage range of one sweep segment. Specific capacitances were also calculated from the galvanostatic charge and discharge curves, using the following equation:

$$C = \frac{I\Delta t}{m\Delta V}$$

where I is the charge or discharge current, Δt is the time for a full charge or discharge, m indicates the mass of the electrode materials, and ΔV represents the voltage range. Energy density (d_e) was derived from the CV curves using the following equation:

$$d_e = \frac{1}{2}C(\Delta V)^2$$

where C is the specific capacitance of the supercapacitor, and ΔV is the voltage range of one sweep segment. Power density (d_p) was calculated from the following equation:

$$d_p = \frac{d_e}{\Delta t}$$

where d_e is the energy density, and Δt is the time for a sweep segment. Energy and power densities could also be derived from galvanostatic charge and discharge measurements using

$$d_e = \frac{\int IVdt}{m}$$

and

$$d_p = \frac{d_e}{\Delta t}$$

where I is the charge or discharge current, V is the voltage of the supercapacitor, dt is the time differential, m indicates the mass of the electrode materials, and Δt is the time for a full charge or discharge.

Supplementary Figures

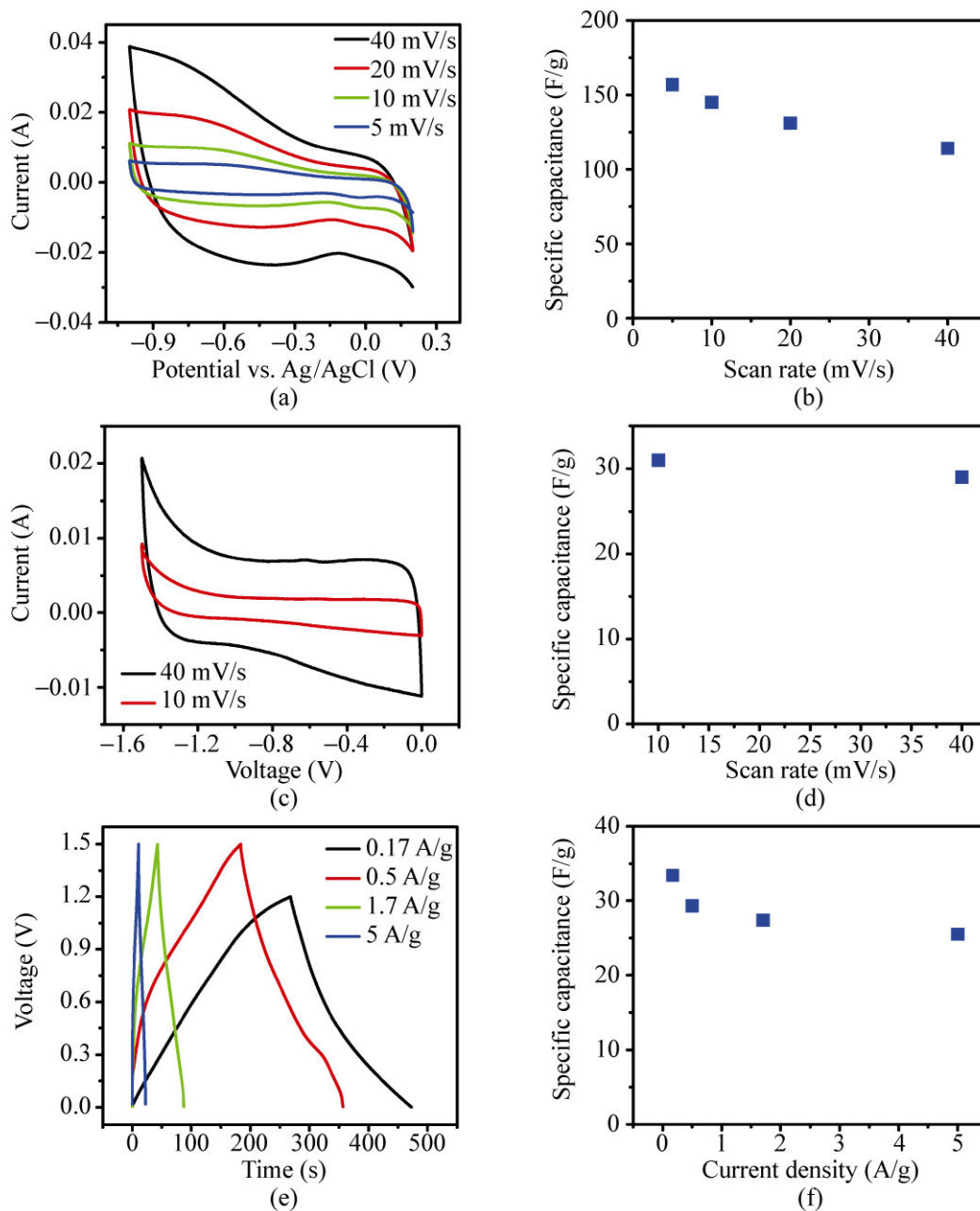


Figure S-1 Symmetrical RGO supercapacitor: (a) CV curves of a RGO electrode at various scan rates against a Ag/AgCl reference electrode; (b) average specific capacitance of the RGO electrode at various scan rates; (c) CV curves of the symmetrical RGO supercapacitor at various scan rates; (d) average specific capacitance of the RGO supercapacitor at various scan rates; (e) galvanostatic charge and discharge curves of the RGO supercapacitor at various current densities; (f) average specific capacitance of the RGO supercapacitor at various discharge current densities

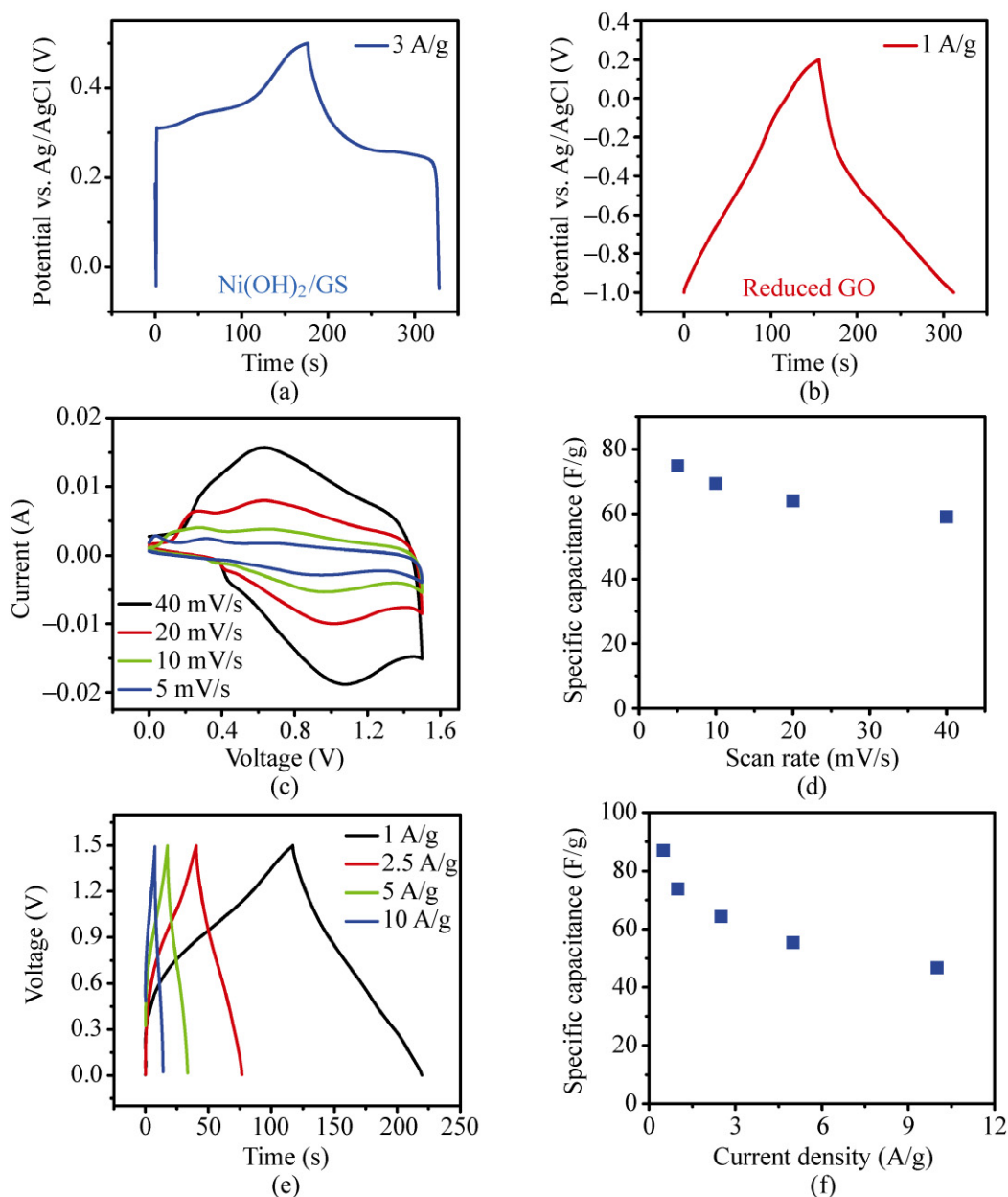


Figure S-2 Asymmetrical supercapacitor made of Ni(OH)₂/graphene and RGO: (a) charge and discharge curve of the Ni(OH)₂/graphene electrode at 3 A/g against a Ag/AgCl reference electrode; (b) charge and discharge curve of the RGO electrode at 1 A/g against a Ag/AgCl reference electrode; (c) CV curves of the asymmetrical supercapacitor at various scan rates; (d) average specific capacitance of the asymmetrical supercapacitor at various scan rates; (e) galvanostatic charge and discharge curves of the asymmetrical supercapacitor at various current densities; (f) average specific capacitance of the asymmetrical supercapacitor at various discharge current densities

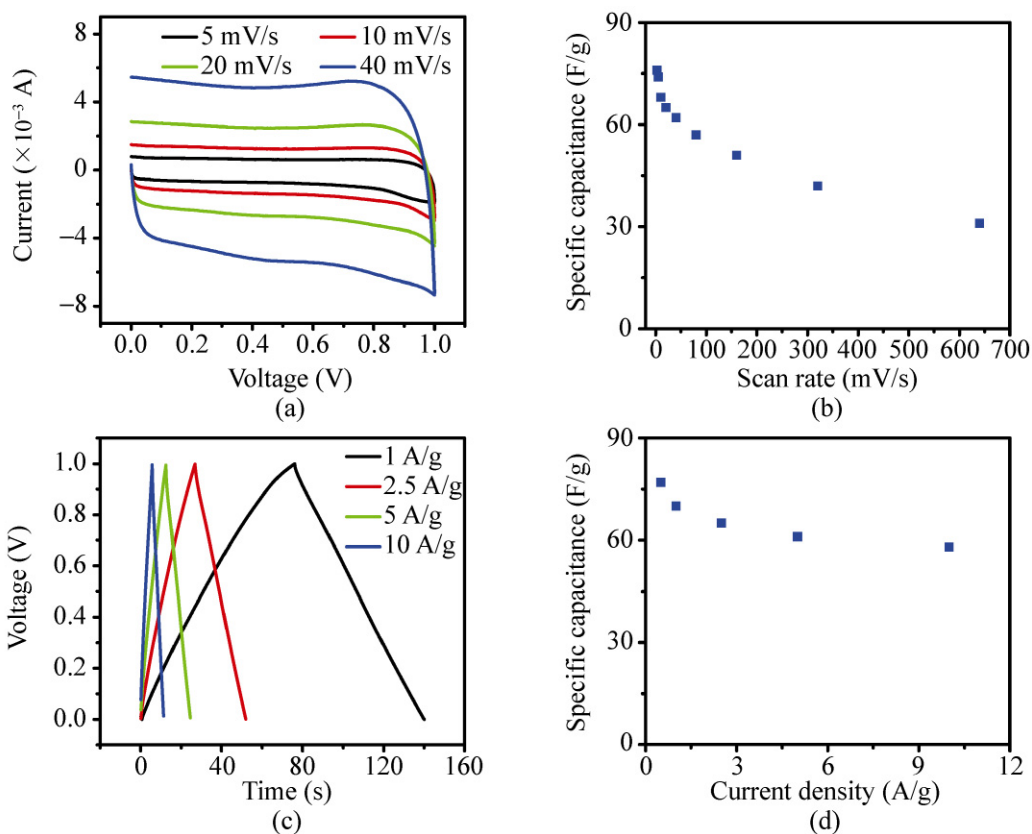


Figure S-3 Symmetrical RuO₂ supercapacitor: (a) CV curves of the symmetrical RuO₂ supercapacitor at various scan rates; (b) average specific capacitance of the RuO₂ supercapacitor at various scan rates; (c) galvanostatic charge and discharge curves of the RuO₂ supercapacitor at various current densities; (d) average specific capacitance of the RuO₂ supercapacitor at various discharge current densities