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Supporting Information

Fabrication of hierarchical NiO/C composite hollow sphere and its enhanced supercapacitor performance

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1. Experimental section

1.1 Preparation of SiO₂/C sphere

The SiO₂/C sphere was fabricated via a facile approach according to a previous report ¹. In a typical synthesis, the mixture containing ethanol (24 mL), deionized water (80 mL) and ammonium hydroxide (1.0 mL, 25 wt%) was vigorously stirred for 0.5 h. Then 1.0 mL of tetraethoxysilane (TEOS) was dropwise added into the above solution and stirred for another 15 min. 0.4 g of dopamine hydrochloride (DA) dissolved in 9 mL of H₂O was transferred to the above solution. The SiO₂/polydopamine (SiO₂/PDA) spheres were obtained after reaction at room temperature (RT) for 36 h. Followed by calcination at 800 °C for 2 h under N₂ atmosphere, SiO₂/PDA spheres were converted to SiO₂/C spheres. C-HS was prepared after etching the SiO₂ core with hydrofluoric acid (10 wt%).

1.2 Synthesis of NiO/C-HS

SiO₂/C spheres (20mg) were ultrasonicated in 35 mL of deionized water for 30 min. After adding 200 mg of urea and 60 mg of Ni(NO₃)₂·6H₂O under mild stirring, the mixture was sealed into a 50 mL Teflon-lined stainless steel autoclave and kept at 120 °C for 16 h. After cooling down naturally, Ni(OH)₂/C-HS was harvested after washing and centrifugation three times. Finally, NiO/C-HS was obtained by the calcination of Ni(OH)₂/C-HS at 350 °C for 2 h under N₂ atmosphere. For comparison, NiO hollow sphere (NiO-HS) was prepared using the same procedure except that SiO₂ sphere was adopted as the template rather than SiO₂/C sphere.

1.3 Materials characterization

The morphologies were evaluated by field-emission electron microscopy (FESEM, JSM-7500) and transmission electron microscopy (TEM, Titan G2). The structure and component analysis were obtained by Powder X-ray diffraction (XRD, Rigaku X-ray diffractometer, Cu K α , $\lambda = 0.15418$ nm), X-ray photoelectron spectroscopy (XPS, Thermo ESCALA 250) and Raman spectrum (Renishaw Raman microscope, λ exc = 633 nm). The specific surface area and the pore size distribution were conducted on Micromeritics ASAP 2020 nitrogen adsorption apparatus. Zeta potential measurement was carried out on a Malvern Zetasizer Naono ZS.

1.4 Electrochemical measurement

Each working electrode was fabricated by brushing the slurry of active material, acetylene black and polyvinylidene fluoride (mass ratio 8:1:1) on a piece of nickel foam and drying at 80 °C for 12 h. The mass loading of NiO/C-HS was around 1.0 mg cm⁻². Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were conducted on a CHI 760E electrochemical workstation in 2 M KOH aqueous solution with a three-electrode configuration, where platinum foil and Ag/AgCl (4 M KCl) electrode served as counter and reference electrodes, respectively. ASC was assembled by using NiO/C-HS as the positive electrode and activated carbon (AC) as the negative electrode with a glassy fibrous separator in a 2032 button cell. And the mass loadings of both electrodes were optimized to be 1.2 and 1.44 mg, respectively. To reveal the difference, analogously, another ASC was assembled by using NiO as the positive electrode. Similarly, the mass loadings of positive and negative electrodes were

optimized to be 1.5 and 0.46 mg, respectively.

2. Calculation equations

For the three-electrode system, the specific capacitance, C_s (F g⁻¹), of the working electrode can be obtained from the GCD curves based on the following equations:

$$C_{s-CD} = \frac{I \times \Delta t}{m \times \Delta V} \tag{1}$$

Where *I* is the charge-discharge current (A), ΔV is the width of potential window (V), Δt is the time of discharge (s), and *m* is the loading mass of active material (g).

For asymmetric supercapacitors (ASCs), charge balance is required to optimize the capacitive performance. Generally, the charge balance $(q^+=q^-)$ is decided based on the capacitive performance of each electrode. The mass balancing is valuated from Equation 3 according to the specific capacitance (C_s) and potential range (ΔV).

$$q = m \times C_s \times \Delta V \tag{2}$$

$$\frac{m_{+}}{m_{-}} = \frac{C_{s-} \times \Delta V_{-}}{C_{s+} \times \Delta V_{+}}$$
(3)

Where m_+ is the anode active-material mass and m_- is the cathode active-material mass. Total capacitance, *C* (F g⁻¹), energy density, *E* (Wh kg⁻¹), and power density, *P* (W kg⁻¹), of ASCs are determined by the following equations:

$$C = \frac{I \times \Delta t}{M \times V} \tag{4}$$

$$E = \frac{1}{2} \times \frac{1}{3.6} \times C \times V^2$$
 (5)

$$P = 3600 \times \frac{E}{\Delta t} \tag{6}$$

Where V is the operating voltage window (V), Δt is the time of discharge (s), and M is the total active material mass of these two electrodes (g).



Fig. S1 FESEM images of (a) SiO_2/PDA , (b) SiO_2/C spheres and (c) SiO_2 .



Fig. S2. The distribution of zeta potentials of SiO_2/C spheres.



Fig. S3 (a) XPS survey scan and (b) Si 2p high-resolution XPS spectra of SiO₂/C, $Ni(OH)_2$ /C-HS and NiO/C-HS.



Fig. S4 EDX spectra of SiO₂/C and Ni(OH)₂/C-HS.



Fig. S5 HAADF images and elemental mapping for SiO₂/C, Ni(OH)₂/C-HS and NiO/C-HS.



Fig. S6 TEM images of (a and b) Ni(OH)₂/C-HS and (c and d) NiO/C-HS.



Fig. S7 FESEM images of (a and b) $Ni(OH)_2/C$ -HS and (c and d) $Ni(OH)_2$ -HS.



Fig. S8 FESEM images of (a and b) NiO/C-HS and (c and d) NiO-HS.

FESEM images (Fig. S7a and b, ESI[†]) showed that Ni(OH)2 nanosheets entwined each other, forming 3D interconnected network on the surface of C-HS, displaying the hierarchical structure of the composite. Likewise, Ni(OH)2-HS (Fig. S7c and d, ESI[†]) possessed similar morphology. However, rather than the complete intact spheres, some broken hollow spheres appeared, induced by the absence of C-HS as backbone. After the calcination process, NiO/C-HS (Fig. S8a and b, ESI[†]) and NiO-HS (Fig. S8c and d, ESI[†]) inherited the morphologies perfectly from their precursors.



Fig. S9 (a) CV and (b) GCD curves of NiO/C-HS, (c) CV and (d) GCD curves of NiO $\,$

HS. These properties were tested in the three-electrode system.



Fig. S10 (a) CV and (b) GCD curves for bare nickel foam and NiO/C-HS electrodes with different loading mass (1 and 5 mg cm⁻²).



Fig. S11 (a) CV and (b) GCD curves of NiO/C-HS with the active material loading mass of 5 mg cm⁻², (c) specific capacitance for NiO/C-HS with different loading mass.

Types of materials	Specific capacitance	Capacitance retention	Ref.
Hierarchically porous NiO film	309 F g ⁻¹ at 1 A g ⁻¹	89% after 4000 cycles at 1 A g^{-1}	2
NiO nanosheet assembles	81.6 F g^{-1} at 0.5 A g^{-1}	79% after 3000 cycles at 0.5 A g^{-1}	3
Multishelled NiO hollow spheres	612.5 F g ⁻¹ at 0.5 A g ⁻¹	90% after 1000 cycles at 3A $\rm g^{-1}$	4
Porous NiO hollow spheres	560 F g ⁻¹ at 10 A g ⁻¹	107% after 1000 cycles at 10 A $\rm g^{-1}$	5
Microtubular carbonized kapok fiber/NiO composites	575.7 F g ⁻¹ at 0.5 A g ⁻¹	130% after 4000 cycles at 1mV $\rm s^{-1}$	6
Hollow core-shell NiO microspheres	455 F g ⁻¹ at 0.5 A g ⁻¹	120% after 500 cycles at 2 A g^{-1}	7
NiO nanostructure on nickel foam	250 F g ⁻¹ at 0.5 A g ⁻¹	70% after 2000 cycles at 0.5 A g^{-1}	8
Flower-like NiO	364 F g ⁻¹ at 1 A g ⁻¹	100% after 1200 cycles at 1A g^{-1}	9
Hierarchically porous NiO hollow spheres	287 F g ⁻¹ at 1 A g ⁻¹	105% after 2000 cycles at 1A g $^{-1}$	10
NiO/graphene with 3D hierarchical structure	555.0 F g ⁻¹ at 1 A g ⁻¹	90% after 2000 cycles at 1A $\rm g^{-1}$	11
3D NiO @ Carbon Hollow Hybrid Networks	572.5 F g ⁻¹ at 1 A g ⁻¹	113% after 2000 cycles at 100 mV $\rm s^{-1}$	12
Double-shelled C@NiO hollow microspheres	211.0 F g ⁻¹ at 1 A g ⁻¹	96% after 1000 cycles at 5A $\rm g^{-1}$	13
NiO/graphene aerogel nanocomposite	587.3 F g ⁻¹ at 1 A g ⁻¹	98.5 after 1000 cycles at 1A g ⁻¹	14
NiO/reduced graphene oxide composites	590 F g ⁻¹ at 1 A g ⁻¹	100% after 1000 cycles at 1A g ^{-1}	15
NiO nanoparticles	752 F g ⁻¹ at 2 A g ⁻¹	100% after 1000 cycles at 10A g ⁻¹	16
NiO/carbon nanofibers	526 F g ⁻¹ at 1 A g ⁻¹	80% after 1000 cycles at 5A $\rm g^{-1}$	17
NiO nanoparticles in mesoporous carbon	406 F g ⁻¹ at 1 A g ⁻¹	91% after 10000 cycles at 3A g^{-1}	18
nanospheres			
NiO nanotube	245 F g ⁻¹ at 2 mV s ⁻¹		19
Hierarchical flower-like C/NiO composite hollow microspheres	585 F g ⁻¹ at 1 A g ⁻¹	100% after 6000 cycles at 5A g^{-1}	20
NiO/C-HS with core-shell architecture	686 F g ⁻¹ at 1 A g ⁻¹	100% after 5000 cycles at 1A g^{-1}	Present

Table S1. Capacitive performance of different NiO-based electrodes.



Fig. S12 (a) Configuration of ASC based on NiO/C-HS and AC in 2 M KOH electrolyte; (b) CV curves of NiO/C-HS AC and electrodes measured in a three-electrode system; (c) CV and (d) GCD curves for NiO/C-HS||AC device; (e) CV and (f) GCD curves for NiO-HS||AC device.



Fig. S13 The specific capacitances at various current densities of NiO/C-HS||AC and NiO-HS||AC.



Fig. S14 N₂ adsorption/desorption isotherm for NiO/C-HS and NiO HS.

The specific surface area and pore volume of NiO/C-HS were 227 m² g⁻¹ and 0.41 cm³ g⁻¹, respectively, which were much larger than those of NiO-HS (176 m² g⁻¹ and 0.34 cm cm³ g⁻¹) (Fig. S10). Such a hierarchically porous structure with a large specific surface area, contributed by the coexistence of porous C-HS and plentiful mesoporous NiO nanosheets, could accelerate charge transfer and provide sufficient space for charge storage, which is vital for electrochemical performance upgrade.

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