Supporting information

Self-Assembly of Ultrathin Porous NiO Nanosheets/Graphene Hierarchical Structure for High-Capacity and High-Rate Lithium Storage

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Chemicals and Materials

Nickel nitrate [Ni(NO₃)₂·6H₂O, Aladdin Reagent, AR], Urea (CH₄N₂O, Aladdin Reagent, AR), Ethylene glycol (C₂H₆O₂, Aladdin Reagent, AR), Graphite powders (325 mesh, Alfa Aesar, 99.8%, AR), Potassium permanganate (KMnO₄, Aldrich Reagent, AR), Sulfuric acid (H₂SO₄, \geq 98%, Beijing Chemical Work, AR), Phosphoric acid (H₃PO₄, \geq 85%, Beijing Chemical Work, AR), Hydrogen peroxide (H₂O₂, 30%, Aladdin Reagent, AR), Hydrochloric acid (HCl, 36%-38%, Beijing Chemical Work, AR), Acetylene black (Hong-xin Chemical Works), Polyvinylidenefluoride (PVDF, DuPont Company, 99.9%), N-methyl-2-pyrrolidinone (NMP, Aladdin Reagent, AR), Separator (polypropylene film, Celgard 2400), Electrolyte (1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with the weight ratio of 1:1, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd).

Experimental details

Graphite oxide was synthesized by an improved Hummers method.¹ Briefly, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (45:5 mL) was added to a mixture of graphite flakes (0.375 g) and KMnO₄ (2.25 g). The reaction was then heated to 50 °C and stirred for 24 h. The reaction was cooled to room temperature and poured onto ice (200 mL) with 30% H_2O_2 (3 mL). After that, the mixture was centrifuged (8000 rpm for 5 min). The remaining solid material was then washed in succession with 200 mL of 30% HCl for two times, and 200 mL of water for three times. For each wash, the mixture was centrifuged (13000 rpm for 20 min) and obtains the remaining material. The final resulting material was freeze-dried for 24 hours to obtain graphene oxide. Graphite oxide was further diluted in deionized water, ultrasonication for 60 min to

obtain graphene oxide.

In a typical synthesis of self-assembled ultrathin porous NiO nanostructure, 150 mg of Ni(NO₃)₂·6H₂O and 150 mg of urea were dissolved in a mixture of 15 mL ethylene glycol and 15 mL deionized water. After the Ni(NO₃)₂·6H₂O and urea totally dissolved under stirring, the solution was transferred to a 50 mL Teflon lined stainless steel autoclave for a hydrothermal reaction at 120 °C for 4 h. NiO precursor powders were collected after centrifuging, washing with copious de-ionized water and drying. NiO nanosheets were obtained by further sintering in air at 500 °C for 2 h at a heating rate of 5 °C min⁻¹.

Nickel oxide nanosheets/graphene sheets (NiO/GNS) hierarchical Structure was fabricated via the electrostatic interaction between positively charged NiO and negatively charged graphene oxide in aqueous solutions. In a typical process, graphene oxide aqueous solution (0.5 mg mL⁻¹) was dropped into 20 mL NiO dispersion (1.5 mg mL⁻¹) under mild magnetic stirring until forming the largest amounts of aggregation. The NiO/GNS hierarchical Structure is obtained by centrifugation, dried in air and further heated in Ar at 400 °C for 2 h (reduction of GO).

Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku-Dmax 2500 diffractometer with Cu K α radiation (λ = 1.5405 Å). Scanning electron microscopy (SEM) was performed on a field emission Hitachi S-4800 instrument, operating at an accelerating voltage of 10 kV. Samples for SEM were prepared by dispersing the as-prepared product in ethanol, and then depositing it onto a silicon wafer, attached to SEM brass stub. Transmission electron microscope (TEM)

was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Samples dispersed in ethanol were applied onto the Cu grid with carbon coated on Lacey support film and dried in air before TEM imaging. Zeta potential (ζ , effective surface charge) was measured by dynamic light scattering N₂ adsorption/desorption was (Malvern Nano-ZS, UK). determined by Brunauer-Emmett-Teller (BET) measurements using an NOVA 1000 Surface Area Analyzers. Thermogravimetric analysis was performed on a SDT 2960 Simultaneous DSC-TGA Operator's Manual. Atomic Force Microscope measurements were performed using a Multimode-V instrument (Veeco Metrology, Inc). XPS spectra were obtained with an ESCALABMKLL X-ray photoelectron spectrometer using an Al K α source. The electrical conductivities were measured by four-point probe method (Keithely 2400).

Electrochemical measurement

The electrochemical experiments were performed *via* CR2025 coin-type test cells assembled in a dry argon-filled glove box with both moisture and oxygen contents below 1 ppm. The test cell consisted of a working electrode and lithium foil which were separated by a Celgard 2400 membrane. The electrolyte solution was prepared by dissolving 1 M LiPF₆ in EC-DMC (1:1 w/w). The working electrodes were prepared by casting slurry containing 70% active material, 20% acetylene black and 10% polyvinylidene fluoride (PVDF) onto a copper foil. After vacuum drying at 80 °C for about 12 hours, the electrode disks (d = 12 mm) were punched and weighed. Each electrode has approximately 1-3 mg of active material. Galvanostatic

charge-discharge cycling tests were performed using an LAND CT2001A multi-channel battery testing system in the voltage range between 0.01 and 3 V at room temperature. Impedance and Cyclic voltammogram (CV) tests were carried out with a BioLogic VMP3 Electrochemical workstation.



Fig. S1 Zeta potentials of NiO and graphene oxide in aqueous solutions with various pH values.

To direct the assembly by adopting the appropriate pH values, we examined the surface charges of NiO nanosheets and graphene oxide by zeta potential measurements. As shown in Fig. S1, the surface of graphene oxide was negatively charged (zeta potential = -40~-53 mV) over the investigated pH range (2-12). The surface charge of NiO nanosheets switched from positive (zeta potential = +38 mV) to negative (zeta potential = -7 mV) with an increase of the pH value from 2 to 12. It is obviously that the mutual assembly can be easiest triggered when NiO nanosheets and graphene oxide were oppositely charged and with biggest charge difference. In pH = 4, the electrostatic interaction of NiO nanosheets and graphene oxide is almost the most intimate, so we choose pH = 4 as the interaction condition.



Fig. S2 XPS Ni 2p spectra of NiO and NiO/GNS.

As we can see, the Ni 2p spectra of NiO comprise two regions representing the Ni $2p_{3/2}$ (850-865 eV) and Ni $2p_{1/2}$ (870-885 eV) spin orbit levels. The Ni $2p_{3/2}$ region consists of a main peak at 853.5 eV with a shoulder peak at 855.6 eV and a satellite peak at 860.6 eV; similar features are observed for the Ni $2p_{1/2}$ region with a main peak at 871.5 eV and a satellite peak at 878.3 eV. The binding energies of the main and satellite peaks in the Ni 2p core level are consistent with the previous report on NiO.²

Interestingly, after combined with GNS, no obviously shift can be found in the Ni 2p core level, which indicates that there is no obviously chemical bond between NiO and GNS. So the driving force for the stability of the hierarchical structure might be the inter-molecule force.



Fig. S3 Atomic Force Microscope (AFM) images of NiO precursor (a), ultrathin porous NiO nanosheets (b), and graphene oxide (c).

We deposited NiO precursor, NiO and graphene oxide suspension on mica substrate via drop casting and examined them with an atomic-force microscope to confirm that the structure had the correct dimensions. The apparent thicknesses of NiO precursor and NiO nanosheets are less than 6 nm, indicating the excellent ultrathin structure maintained after sintering.

The graphene oxide is mostly single-layer structure with thicknesses of 0.6-1.1nm and sizes from nanoscale to microscale. Nanoscaled graphene oxide could enter into the macropore of the self-assembly ultrathin porous NiO structure and adsorb on NiO nanosheets. Meanwhile, the whole of the self-assembly structure might load on microscaled graphene oxide to form a 3D network structure.

It should be noted that the size of the employed graphene oxide should covers the range from nanoscale to microscale, which is of critical importance for our strategy to ensure that both the self-assembled NiO and its each nanosheet can be effectively covered or supported by graphene oxide. Importantly, almost all the NiO and graphene oxide are fully assembled to leave a almost transparent aqueous solution.



Fig. S4 Photographs of the co-assembly process of graphene oxide and NiO nanosheets in the aqueous solutions with pH = 4.

A: Graphene oxide (GO) aqueous solution. Graphene oxide was uniformly dispersed in deionized water and forming brown solution;

B: NiO nanosheets aqueous solution. NiO nanosheets could uniformly disperse in deionized water for hours.

C: NiO/GO aqueous solution. Graphene oxide aqueous solution (A) was dropped in NiO nanosheets aqueous solution (B) and stirred for seconds. It can be found aggregation of NiO nanosheets and GO in this photograph, indicating the successful assembly between Graphene oxide and NiO nanosheets.

D: NiO/GO aqueous solution after standing for a few minutes. A gray black precipitate was accumulating in the bottom and supernatant solution is completely colorless and transparent, concluding that almost all the graphene oxide sheets are homogeneously dispersed onto the surface of NiO nanosheets.



Fig. S5 TG/DSC curves of NiO/GNS hierarchical structure measured from 30 to 850 °C at a heating rate of 10 °C min⁻¹ in air.

Thermogravimetric analysis was performed in order to determine the mass ratio of graphene nanosheets (GNS) in the composites. For the NiO/GNS hierarchical structure, large weigh loss occurred at \sim 350-580 °C, which is ascribed to the decomposition of GNS. The remaining materials are quite stable and with only a little weight loss above 580 °C. Therefore the weight percentage of GNS in the NiO/GNS hierarchical Structure could be determined to be \sim 13 wt%.



Fig. S6 TEM image of NiO/GNS hierarchical structure, from which we can find a large number of hexagonal holes in the NiO nanosheets (yellow hexagons in the pattern).

The image suggests that most of the holes in NiO nanosheets are hexagonal. As can be seen from the image, hexagonal holes were stacked with each other, indicating the formation of 3D network structure of porous NiO nanosheets and graphene sheets.



Fig. S7 BET images of the self-assembled ultrathin porous NiO nanosheets structure (a) and NiO/GNS hierarchical Structure (b).

The products are characterized by nitrogen adsorption and desorption isotherm at 77 K to determine the BET surface area of NiO nanosheets. The samples show a BET surface area of 59.2 $\text{m}^2 \text{ g}^{-1}$ for NiO nanosheets and 43 $\text{m}^2 \text{ g}^{-1}$ for NiO/GNS hierarchical Structure. It is concluded that the porous structure of self-assembled ultrathin porous NiO nanosheets has not been destroyed because of self-assembly with graphene oxide and sintering.



Fig. S8 SEM images of NiO/GO (a), and NiO/GNS (b).

Continues 3D flake structure could be observed from the images, it is difficult to distinguish NiO nanosheets from graphene oxide or graphene nanosheets, which could indicate the intimate coexistence of graphene and NiO. In the other hand, there is no obviously difference between NiO/GO and NiO/GNS, suggesting the structure remained after sintering.



Fig. S9 Energy dispersive spectroscopic (EDS) characterization of NiO/GNS hierarchical Structure: (a) SEM image of NiO/GNS hierarchical Structure; (b) EDS mapping of the whole region shown in (a); (c) EDS carbon mapping of region (b); (d) EDS nickel mapping of region (b).

To further confirm element distribution of NiO/GNS hierarchical Structure, energy dispersive spectroscopic (EDS) mapping is employed (Fig. S9). As expected, the existence and distribution of carbon (Fig. S9c), and nickel (Fig. S9d) unanimously confirm the intimate coexistence of graphene and NiO.



Fig. S10 Galvanostatic charge/discharge profile of bare graphene sheets (GNS).

Galvanostatic charge–discharge profile of bare GNS is carried out in the potential window of 0.01-3.0 V versus Li. Fig.S10 shows the first charge–discharge profile of the GNS electrode at a current density of 100 mA g⁻¹.

It is found that a specific discharge capacity of 960 mAh g^{-1} and a charge capacity of 585 mAh g^{-1} is achieved for bare GNS, which is much lower than the first discharge/charge capacity of NiO (discharge: 1500 mAh g^{-1} ; charge: 998 mAh g^{-1}). So the combination of NiO and GNS would sacrifice the capacity of NiO, which is reason why the capacity of NiO is higher than NiO/GNS in the first cycle (figure 4c in main text). Electronic Supplementary Material (ESI) for Journal of Materials Chemistry This journal is $\ensuremath{\mathbb{O}}$ The Royal Society of Chemistry 2012



Fig. S11 Cyclic voltammograms of NiO (a) and NiO/GNS (b) at a scan rate of 0.1 mV s^{-1} . (c) Nyquist plots for the cells made of NiO and NiO/GNS composites in the

frequency range between 100k and 10m Hz at room temperature.

The cyclic voltammetric (CV) curves were tested over a voltage range from 0.01 to 3.0 V at a scan rate of 0.1 mV s⁻¹. There is a characteristic cathodic peak around 0.43 V for bare NiO, which is shifted to ~ 0.41 V for the NiO/GNS composite. Those correspond to the initial reduction of NiO to Ni (NiO +2Li⁺ +2e⁻ \rightarrow Ni + Li₂O) and the formation of amorphous Li₂O and solid electrolyte interface (SEI). Two anodic peaks are observed around 1.56 and 2.24 V, which corresponds to the NiO formation and Li₂O decomposition (Ni + Li₂O \rightarrow NiO + 2Li⁺+2e⁻).^{3,4} The cathodic peaks both shift to about 1.02 and the anodic peaks shift to about 1.56 and 2.29 V for the second cycles due to the drastic lithium driven, structural or textural modifications during the first lithiation process.⁴ The cathodic and anodic peaks are well matched with the discharge and charge plateaus.

The electrochemical impedance spectra of NiO and NiO/GNS composites are shown in Fig. S11c. The typical characteristics of the Nyquist plots are one semicircle in the high frequency range and a sloping straight line in the low frequency range. The radii of the semicircles of the NiO/GNS composites is smaller than NiO electrode, indicating that NiO/GNS composites electrode possesses lower contact and charge-transfer impedances. This result confirmed that the assembly with graphene and NiO largely improves the electrochemical activity of as-obtained NiO.

	Zeta potential / mV	Thickness	BET /	Electrical
	(pH = 4, aqueous	/ nm	$m^2 g^{-1}$	conductivities / S m ⁻¹
	solution)			
GO	-48	0.6-1.1		
NiO precursor		< 6		
NiO	31	< 6	59.2	2.78×10 ⁻⁶
NiO/GNS			43	1.85×10 ⁻²

Table S1 The physical and textural properties of all samples.

Reference

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