

Electronic Supplementary Information (ESI) for

Improved Performances of β -Ni(OH)₂ @ Reduced-Graphene-Oxide in Ni-MH and Li-ion Batteries

Baojun Li,^a Huaqiang Cao,^{*a} Jin Shao,^b He Zheng,^a Yuexiang Lu,^a Jiefu Yin,^a and Meizhen Qu^b

^a Department of Chemistry, Tsinghua University, Beijing 100084, P R China

^b Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, P R China

*Corresponding author. E-mail: hqcao@mail.tsinghua.edu.cn

Experimental Section

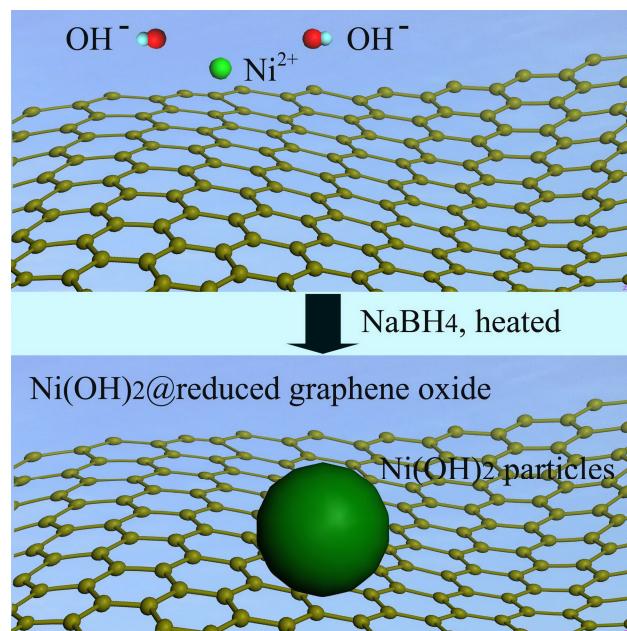
Materials Synthesis: Graphene oxide (GO) was prepared from purified natural graphite according to Hummers method reported in Ref. [S1]. GO (200 mg) and water (200 mL) was ultrasonicated for 2 h. A aqueous solution (20 mL) of Ni(NO₃)₂·6H₂O were added to the aqueous suspension. The mixture was stirred for 2 h to complete ion exchange. Aqueous solution (20 mL) of NaOH (1 equivalent) was added dropwise to the above mixture. The mixture was kept stirring for a further 1 h. The solid was obtained by centrifuge and washed thoroughly with water, dried at room temperature and then heated in air at 150 °C for 2 h. The powder was loaded into water (25 mL) to form a suspension. After stirring and ultrasonication for 30 min, NaBH₄ (0.248 g, 64.0 mmol) was added to above suspension and the mixture was transferred to an autoclave and then heated to 80 °C for 4 h. The resulted solid products were washed with deionized water (3×10 mL) and ethanol (3×10 mL) and β -Ni(OH)₂@reduced graphene oxide composites (NGC) were obtained. The weight ratio of β -Ni(OH)₂ and reduced graphene oxide (RGO) is 9:1. In the absence of GO, pure β -Ni(OH)₂ was obtained via similar process. RGO was obtained from GO by reduction with NaBH₄ via similar process.

Materials Characterization: The morphology of as-prepared products was studied by using transmission electron microscope (TEM, JEOL JEM-2100, operating at 100 kV) and scanning electron microscope (SEM, Hitachi S4800, operating at 10.0 kV). For atom force microscopy (AFM) measurement, the samples were coated on Si surface and AFM studies were performed using a Digital Instruments Dimension 3100 microscope in the tapping mode. Fourier transform infrared (FTIR) spectra measurements were carried out on a NICOLET 560 Fourier transform infrared spectrophotometer. Raman spectrum was recorded on a Renishaw RM-1000 with excitation from the 514 nm line of an Ar-ion laser with a power of about 5 mW. The phase structure of as-prepared products were characterized with X-ray diffraction (XRD, Bruker D8 advance) with Cu K α λ =1.5418 Å. X-ray photoelectron spectrum (XPS) were recorded on a PHI quantera SXM spectrometer with an Al K α = 280.00 eV excitation source, where binding energies were calibrated by referencing the C1s peak (284.8 eV) to reduce the sample charge effect. The current-voltage (I-V) curves were obtained at the Shanghai Chenhua CHI660B type electrochemical working station using the compressed pellets with a diameter of 12.5 mm, which were produced in a stainless steel mould with 12 MPa pressure from 115 mg of NGC, RGO, and β -Ni(OH)₂ samples, respectively.

Electrochemical Measurement: The NGC dispersions were prepared by mixing 0.5 mg of designed catalyst in aqueous solution (0.5 mL) containing of iso-propanol (0.1 mL) and Nafion® solution (5wt%, 25 μ L) ($V_{\text{water}}:V_{\text{iso-propanol}}:V_{5\% \text{Nafion}}=0.8:0.2:0.005$), followed by ultrasonication for 10 min. A designed amount (30 μ L) of dispersion was drop-cast onto the glassy carbon electrode (1.5 mm in diameter) and dried for 2 h. the cyclic voltammogram (C-V) measurements were conducted on Shanghai Chenhua CHI660B electrochemical workstation. Three-electrode system (Ag/AgCl electrode was as reference electrode, Pt electrode was the counter electrode, and NGC was the active material of working electrode.) was adapted and the electrolyte was aqueous solution of KOH (6 M). The scanning range was 0–0.45 V, and the scanning rate was 2–100 mV S⁻¹.

Nickel–MH battery performance was determined on the LAND battery testing system (Shenzhen Liuwei Technology Co., Ltd.). NGC sample (20 mg) and nickel powder (80 mg) was pressed at a pressure of 10 MPa for 30 s to an active plate of 13 mm in diameter. NGC electrodes were prepared via inserting the active paste into a nickel foam substrate. NGC electrode was immersed into solution of KOH (6 M) for 5 h and then used as the working electrode. Hydrogen storage alloy metal was used as the counter electrode. The electrolyte was solution of KOH (6 M). The nickel hydroxide electrodes were charged at a current density of 60 mA g^{-1} for 6 h and discharged at the same rate (current rate of 0.2 C) to 1.0 V and the cycle number was 50 times. The weight of NGC in the working electrode was used to estimate the specific discharge capacity of the battery, which was expressed in mA hg^{-1} of NGC. The corresponding Coulombic efficiency were calculated from the discharge capacity/charge capacity.

Lithium ion batteries (LIBs) performance was determined using CR 2032 type coin cells assembled in an argon–filled glove box (MBRAUN). The working electrodes prepared by mixing the NGC and CMC (3%) at a weight ratio of 90:10 were pasted on pure Cu foil (15 μm). Celgard 2400 was used as a separator. Lithium foil was used as the counter electrode. The electrolyte consisted of a solution of LiPF₆ (1 M) containing vinylene carbonate (2%) in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, volume ratio). A galvanostatic cycling test of the assembled cells was carried out on a BS–9300K system in the voltage range of 0.001–3.0 V (vs. Li⁺/Li) at current density of 200 mA g^{-1} . The corresponding Coulombic efficiency were calculated from the discharge capacity/charge capacity.



Scheme S1. The synthesis of NGC from GO.

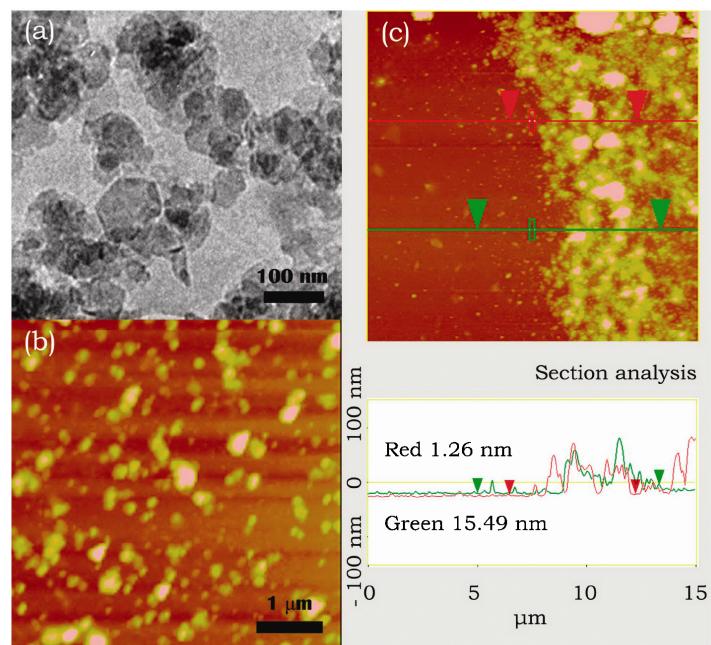


Figure S1 (a) Typical TEM image, and (b, c) AFM images of NGC.

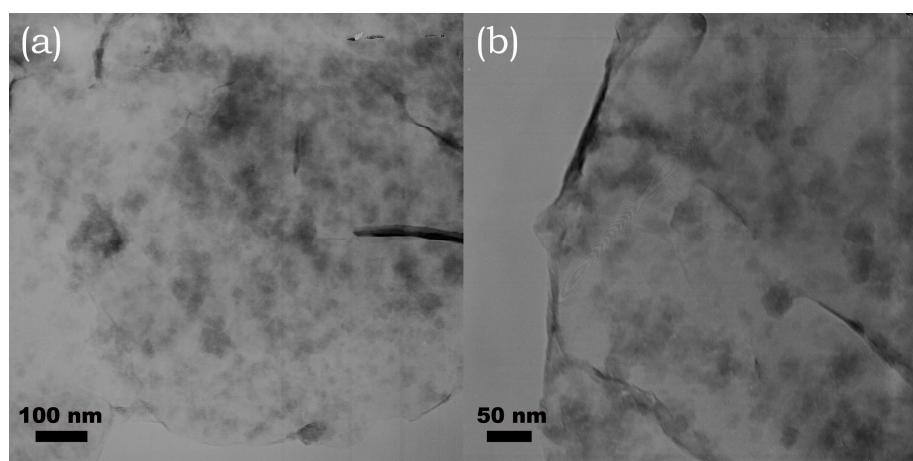


Figure S2. TEM images of NGC.

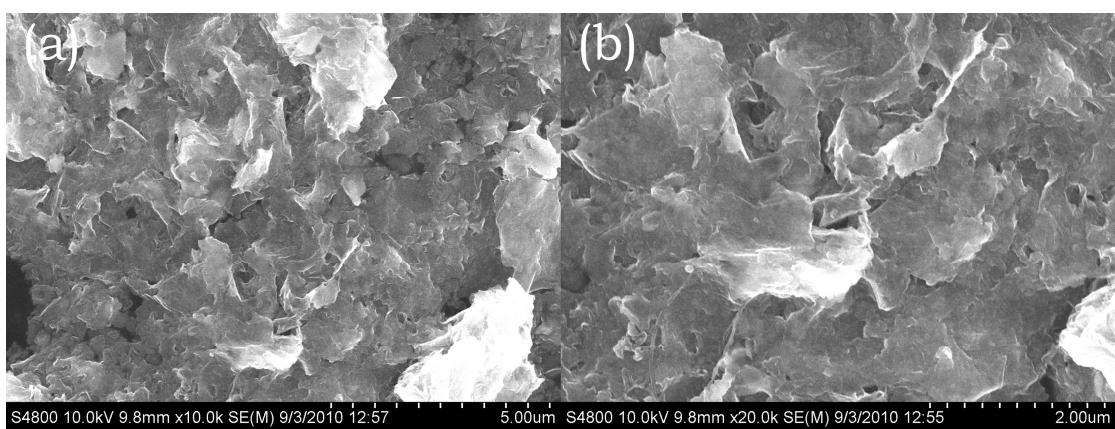


Figure S3. SEM images of NGC.

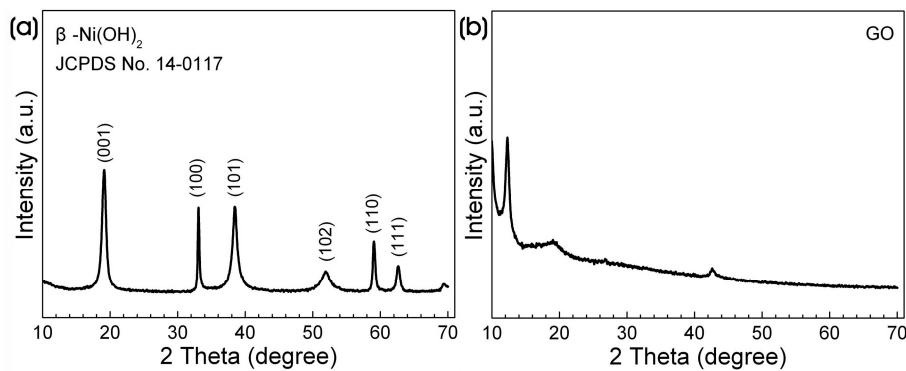


Figure S4. XRD patterns of (a) commercial β -Ni(OH)₂, and (b) GO.

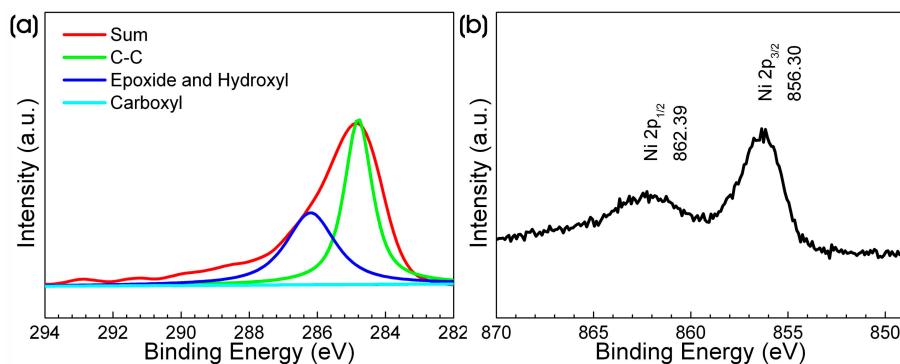


Figure S5. XPS spectra of NGC (a) C 1s, and (b) Ni 2p.

Table S1. The specific discharge capacities of electrodes fabricated with NGC, microflowers, microtubes, mesoporous β -Ni(OH)₂, nanotubes, and theoretical value.

β -Ni(OH) ₂ material	Current density/mA g ⁻¹	Specific capacity/mA hg ⁻¹	Reference (Ref.)
Theoretical value	~	289.1	Ref. S2
NGC	60	282.5, 313.8 ^a	This work
Microflowers	60	244.3	Ref. S3
Microtubes	80	232.4	Ref. S4
Mesoporous	70	241.5	Ref. S5
Nanotubes	50	315.0 ^b	Ref. S6
Ni(OH) ₂ on graphene sheets ^c	2800	1335, 935 F g ⁻¹	Ref. S7

a: calculated considering the weight ratio (90%) of β -Ni(OH)₂ in NGC. b: larger than the theoretical value. c: as supercapacitor.

References

- [S1] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339–1339.
- [S2] D. Linden and T. B. Reddy, (eds., third edition) *Handbook of Batteries*, The McGraw-Hill Companies, Inc. **2002**.
- [S3] H. Q. Cao, H. Zheng, K. Y. Liu and J. H. Warner, *ChemPhysChem*, 2010, **11**, 489–494.
- [S4] F. F. Tao, M. Y. Guan, Y. M. Zhou, L. Zhang, Z. Xu and J. Chen, *Cryst. Growth & Design*, 2008, **8**, 2157–2162.
- [S5] B. J. Li, M. Ai and Z. Xu, *Chem. Comm.*, 2010, **46**, 6267–6269.
- [S6] F. S. Cai, G. Y. Zhang, J. Chen, X. L. Gou, H. K. Liu and S. X. Dou, *Angew. Chem., Int. Ed.*, 2004, **43**, 4212–4216.
- [S7] H. L. Wang, H. S. Casalongue, Y. Y. Liang and H. J. Dai, *J. Am. Chem. Soc.*, 2010, **132**, 7472–7477.