

Supporting Information

Introducing nanodiamond in TiO₂-based anode for improving the performance of lithium-ion batteries

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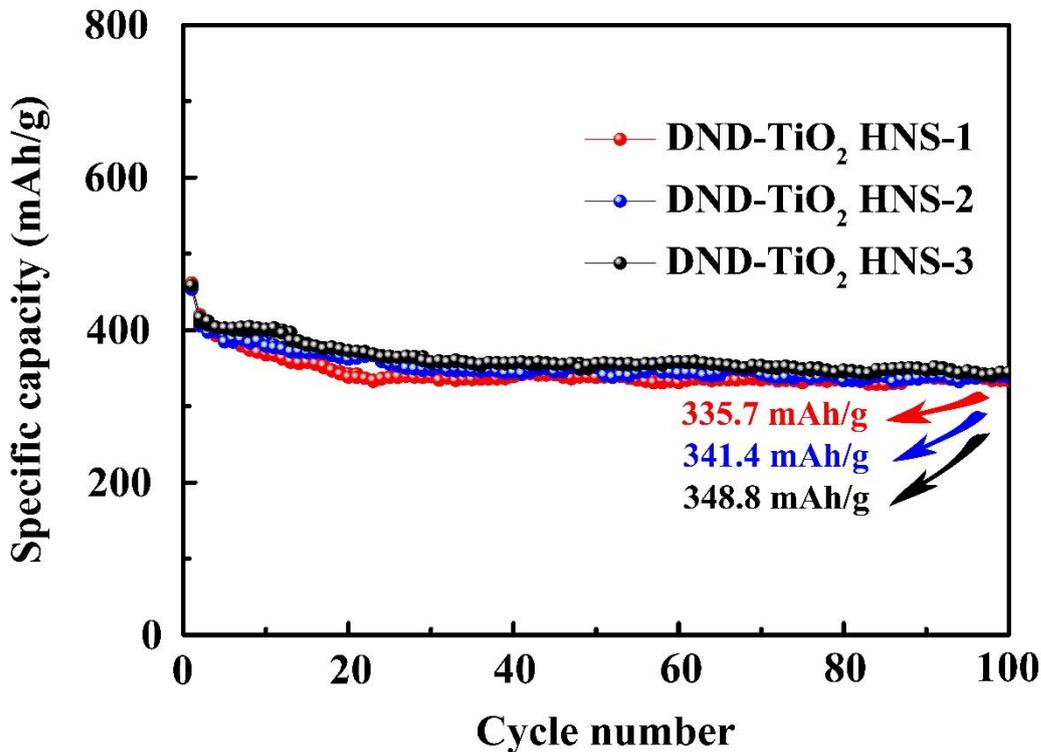


Fig. S1 Repetitive experiments of DND-TiO₂ HNS at a constant rate of 0.5 C.

We perform repetitive experiments using three sets of samples fabricated under the same condition as discussed in the text (DND-TiO₂ HNS-1 and DND-TiO₂ HNS-2 as the control group, DND-TiO₂ HNS-3 used in the manuscript). It can be seen that the first discharge specific capacity of DND-TiO₂ HNS-1 and DND-TiO₂ HNS-2 are 461.6 mAh/g and 453.6 mAh/g, respectively, which is similar with that for DND-TiO₂ HNS-3 (458.2 mAh/g). In addition, the initial Coulombic efficiencies for DND-TiO₂ HNS-1, DND-TiO₂ HNS-2 and DND-TiO₂ HNS-3 are 91.2%, 89.4% and 92.8%, respectively. Moreover, the specific capacity of the control group are 341.4 mAh/g and 335.7 mAh/g after 100 cycles at a rate of 0.5 C, which are similar to the data of DND-TiO₂ HNS-3 (348.8 mAh/g). Consequently, it is demonstrated that the DND-TiO₂ HNS anodes reported in the paper has good reproducibility.

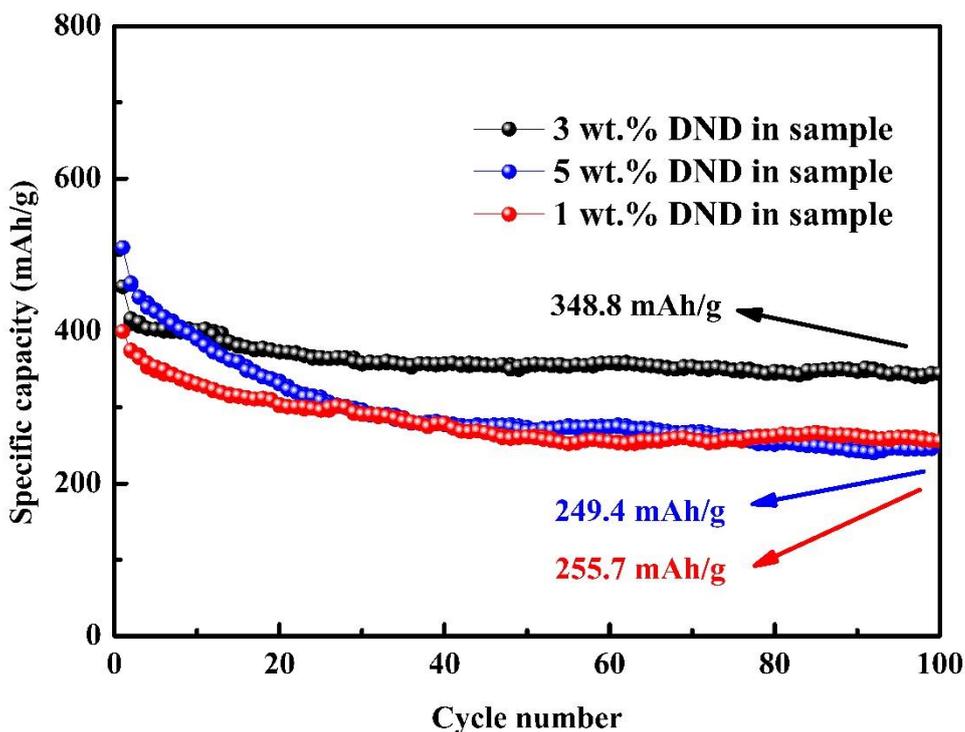


Fig. S2 The cyclic performance profiles of different DND content in samples of DND-TiO₂ HNS at a constant rate of 0.5 C.

In order to determine the effect of DND amount on the rate cycling performance of the samples, 1 wt.%, 3 wt.% and 5 wt.% (compared to tetrabutyl titanate) of DND content are investigated as comparative tests. The specific capacity of the three anodes of DND-TiO₂ are 249.4 mAh/g, 348.8 mAh/g and 255.7 mAh/g, respectively, after 100 cycles at a rate of 0.5 C. It reveals that the optimized DND content in the DND-TiO₂ HNS anodes is ~3 wt%.

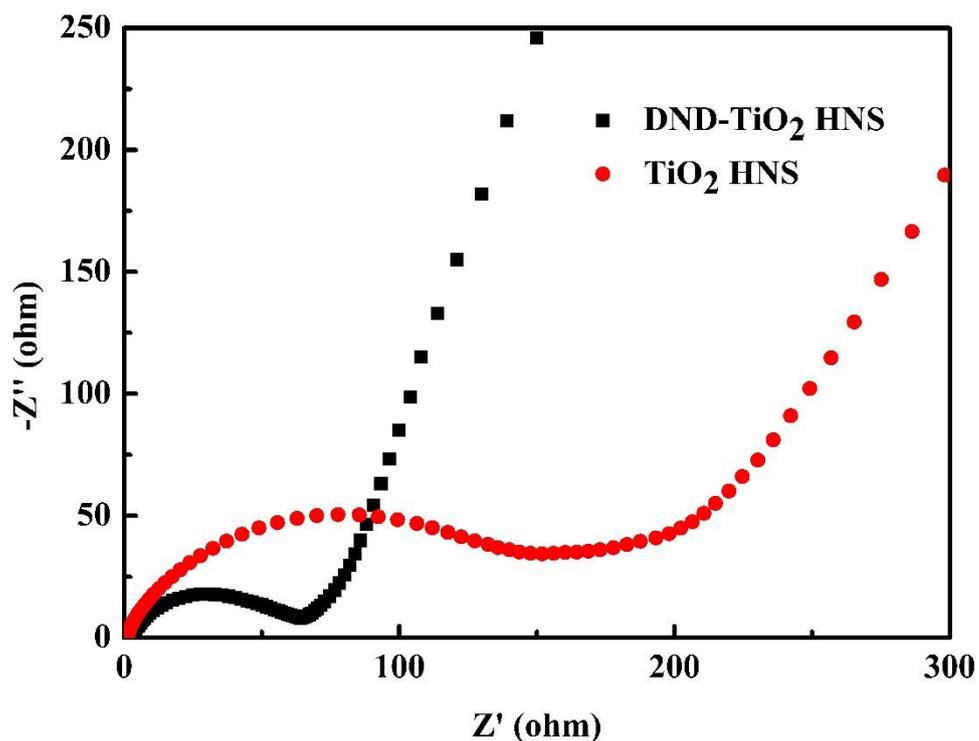


Fig. S3 Nyquist plots for the EIS of DND-TiO₂ and pure TiO₂ HNS anodes before cycling.

The Nyquist plots for both electrodes show oblique lines in the low frequency range, while there is only one semicircle in the high frequency range. The oblique line and the high frequency oblate correspond to the diffusion process and charge transfer impedance of Li⁺ at the electrode/electrolyte interface, respectively. Compared with the resistance of the pure TiO₂ HNS anode (151.9 Ω), DND-TiO₂ HNS anode has smaller resistance value (64.1 Ω), indicating the introduction of DND can effectively improve the electron transport.

Table S1.Comparison of electrochemical performances of the TiO₂-carbon based anodes for lithium-ion batteries.

Electrode Material	Electrochemical Performance	Ref.
TiO ₂ /C	140.2 mAh/g at 500 mA/g after 1000 cycles	1
Carbon-coated TiO ₂ (B)/anatase nanosheets	158.6 mAh/g at 800 mA/g after 500 cycles	2
Mesoporous H-TiO ₂ /GC hollow spheres	137 mAh/g at 5 C after 1000 cycles	3
TiO ₂ -RGO nanocomposite	154 mAh/g at 1200 mA/g after 300 cycles	4
C-TiO ₂	159.8 mAh/g at 1C after 960 cycles	5
Hierarchical nanosheet constructed C/TiO ₂ hollow composites	204 mAh/g (1 C), 135.2 mAh/g (10 C)	6
Porous TiO ₂ /C nanocomposite shells	168.8 mAh/g (5 C), 139.9 mAh/g (10 C)	7
Porous core/shell TiO ₂ spheres	158 mAh/g (5 C), 136 mAh/g (10 C)	8
TiO ₂ with soft carbon	122.8 mAh/g at 500 mA/g after 1000 cycles	9
C-TiO ₂ composite	140 mAh/g at 5.88 C after 1000 cycles	10
C@TiO ₂ composite aerogel	133 mAh/g at 10 C after 3000 cycles	11
DND-TiO ₂ hollow nanosphere	246.3 mAh/g at 5 C after 800 cycles	This work

References:

1. Wang, L.-Y.; Bai, X.; Wu, Y.; Lun, N.; Qi, Y.-X.; Bai, Y.-J., Improving the Li-ion storage performance of commercial TiO₂ by coating with soft carbon derived from pitch. *Electrochim. Acta*, 2016, **212**, 155-161.
2. Jiang, S.; Wang, R.; Pang, M.; Wang, H.; Zeng, S.; Yue, X.; Ni, L.; Yu, Y.; Dai, J.; Qiu, S.; Zhang, Z., Assembling porous carbon-coated TiO₂(B)/anatase nanosheets on reduced graphene oxide for high performance lithium-ion batteries. *Electrochim. Acta* 2015, **182**, 406-415.
3. Liu, H.; Li, W.; Shen, D.; Zhao, D.; Wang, G., Graphitic Carbon Conformal Coating of Mesoporous TiO₂ Hollow Spheres for High-Performance Lithium Ion Battery Anodes. *J. Am. Chem. Soc.*, 2015, **137** (40), 13161-13166.
4. Li, W.; Wang, F.; Feng, S.; Wang, J.; Sun, Z.; Li, B.; Li, Y.; Yang, J.; Elzatahry, A. A.; Xia, Y.; Zhao, D., Sol-Gel Design Strategy for Ultradispersed TiO₂ Nanoparticles on Graphene for High-Performance Lithium Ion Batteries. *J. Am. Chem. Soc.*, 2013, **135** (49), 18300-18303.
5. Chen, Y.; Ma, X.; Cui, X.; Jiang, Z., In situ synthesis of carbon incorporated TiO₂ with long-term performance as anode for lithium-ion batteries. *J. Power Sources*, 2016, **302**, 233-239.
6. Jin, Z.; Yang, M.; Wang, J.; Gao, H.; Lu, Y.; Wang, G., One-Pot Fabrication of Hierarchical Nanosheet-Based TiO₂-Carbon Hollow Microspheres for Anode Materials of High-Rate Lithium-Ion Batteries. *Chem.-Eur. J.*, 2016, **22** (17), 6031-6036.
7. Wang, W.; Sa, Q.; Chen, J.; Wang, Y.; Jung, H.; Yin, Y., Porous TiO₂/C Nanocomposite

- Shells As a High-Performance Anode Material for Lithium-Ion Batteries. *ACS Appl. Mater. Inter.*, 2013, **5** (14), 6478-6483.
8. Cai, Y.; Wang, H.-E.; Zhao, X.; Huang, F.; Wang, C.; Deng, Z.; Li, Y.; Cao, G.; Su, B.-L., Walnut-like Porous Core/Shell TiO₂ with Hybridized Phases Enabling Fast and Stable Lithium Storage. *ACS Appl. Mater. Inter.*, 2017, **9** (12), 10652-10663.
 9. Bai, X.; Li, T.; Qi, Y.-X.; Gao, X.-P.; Yin, L.-W.; Li, H.; Zhu, H.-L.; Lun, N.; Bai, Y.-J., Simple fabrication of TiO₂/C nanocomposite with enhanced electrochemical performance for lithium-ion batteries. *Electrochim. Acta*, 2015, **169**, 241-247.
 10. Zheng, W.; Yan, Z.; Dai, Y.; Du, N.; Jiang, X.; Dai, H.; Li, X.; He, G., Interpenetrated Networks between Graphitic Carbon Infilling and Ultrafine TiO₂ Nanocrystals with Patterned Macroporous Structure for High-Performance Lithium Ion Batteries. *ACS Appl. Mater. Inter.*, 2017, **9** (24), 20491-20500.
 11. Zhang, C.; Liu, S.; Qi, Y.; Cui, F.; Yang, X., Conformal carbon coated TiO₂ aerogel as superior anode for lithium-ion batteries. *Chem. Eng. J.*, 2018, **351**, 825-831.