Supporting Information

Biotemplated fabrication of hierarchically porous NiO/C composite from lotus pollen grains for lithium-ion batteries

Yang Xia¹, Wenkui Zhang¹*, Zhen Xiao², Hui Huang¹, Huijuan Zeng¹, Xiaorong Chen¹, Feng Chen¹, Yongping Gan¹, and Xinyong Tao¹*

¹College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou, 310014, P. R. China. ²Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P.R. China.

Preparation of pure NiO particles

The pure NiO particles were prepared as follows: the reaction solution was obtained by mixing 40 ml of 1M nickel sulfate, 30 ml of 0.25 M potassium persulfate. Then 10 ml of aqueous ammonia (25-28%) was added into the above reaction solution. After continuing stirring for 20 min room temperature, the obtained black sample was filtered, washed and dried at 80 °C for 12h. Finally, the as-prepared sample was annealed in a tube furnace at 500 °C for 2 h in flowing nitrogen atmosphere.

a 0

10.0

Characterization of pure NiO particles

5.0kV 11.1mm x3.50k SE(M

Fig. S1 SEM images of pure NiO particles. (a) a low-magnification SEM image; (b) a high-magnification SEM image taken from (a).

15.0kV 11.1mm x20.0k SE(M)

Fig. S1 presents SEM images of the prepared pure NiO particles. The obtained NiO particles are seen to be flower-like and densely assembled from many nanosized NiO petals. These pure NiO particles also have a porous structure, which is similar to the surface morphology of pollen-templated NiO/C microspheres.



Fig. S2 (a) Nitrogen adsorption-desorption isotherm loop; (b) Pore-size distribution curve.

Fig. S2 displays the Nitrogen adsorption-desorption and pore-size distribution curve of pure NiO sample. As seen in **Fig. S2a**, a distinct hysteresis loop in the range of 0.4-0.9 P/P_0 indicates the dominance of mesopores in pure NiO particles. The absence of a distinct hysteresis loop in the range of 0.9-1.0 P/P_0 implies that the lack of macropores in pure NiO particles. These results also can be confirmed by the pore-size distribution curves of pure NiO (**Fig. S2b**) and pollen-templated NiO/C (**Fig. 5b**). Therefore, it is easy to conclude that the wide peak at 70 nm (see **Fig. 5b**) is ascribed the template of pollen. In addition, the BET specific surface area of the pure NiO sample is 104.39 m²g⁻¹, which is much smaller than that of pollen-templated NiO/C sample (171.58 m²g⁻¹).



Electrochemical performances of pure NiO and pollen-templated NiO/C

Fig. S3 The Nyquist plots of pollen-templated NiO/C and pure NiO at room temperature with the frequency range of 10^{-2} to 10^{6} Hz.

The Nyquist plots of the AC impedance for the pollen-templated NiO/C sample and pure NiO sample, which were measured at about 2.7 V (*vs.* Li/Li⁺) after three discharge/charge cycles, are shown in **Fig. S3**. Both profiles exhibit a straight line and a semicircle in low- and high-frequency regions. The straight line in the low-frequency is attributed to the diffusion of the lithium ions into the active anode materials, which is the typical Warburg behavior. The semicircle in the high-frequency region represents charge-transfer resistance. The value of the diameter of the semicircle on Z_{re} axis implies an approximate indication of the charge transfer resistance (R_{ct}). As seen in **Fig. S3**, it clearly shows that the charge transfer resistance of pollen-templated NiO/C is smaller than that of the pure NiO. Usually, if the charge transfer resistance is small, it means the facile charge transfer at the active material/electrolyte interface. The low charge transfer resistance is benefit to enhance the electron kinetics in the electrode material and improve the electrochemical performance of the electrode material. So, the pollen-templated NiO/C with multiple pore size distribution can allow better penetration of electrolyte to enhance the electrochemical performance.



Fig. S4 (a) Charge-discharge profiles of pure NiO sample at different cycles in the potential range from 0.05 to 3.0 V with the current density of 0.1 A g⁻¹. (b) The comparison of cycling performance of pure NiO and pollen-templated NiO/C.

Fig. S4a demonstrates the charge-discharge properties of pure NiO sample. As seen in **Fig. S4a**, the charge-discharge curves of pure NiO are similar to pollen-templated NiO/C. However, there are a large specific discharge capacity of 1095 mAh g^{-1} and an irreversible capacity of 381 mAh g^{-1} for pure NiO at a current density of 0.1 A g^{-1} . The initial coulombic efficiency is 65.2%, which is much lower than that of pollen-templated NiO/C (74.5%). In the second cycle, the discharge capacity and charge capacity reduce to 682 and 633 mAh g^{-1} , whereas the coulombic

efficiency increases to 92.8%. However, the discharge capacity of pure NiO decreased sharply and only delivered a discharge capacity of 348 mAh g⁻¹ after 10 cycles at a current density of 0.1 A g⁻¹ (**Fig. S4b**). In contrast, the pollen-templated NiO/C sample could maintain a stable discharge capacity of 700 mAh g⁻¹ from the fifth cycle, exhibiting a good capacity retention property.

Based on the above electrochemical performance comparison of pure NiO and pollen-templated NiO/C, it could be known that although the pure NiO sample has a porous structure and a high specific surface area, the cycling performance of the pure NiO still is very poor. The superior cycling performance of pollen-templated NiO/C can be caused by the following two factors. On the one hand, pollen-templated NiO/C with the multiple porous structures can provide larger surface area and induce the intimate contact between electrolyte and NiO to maximize the contact area. Consequently, the high contact area of electrolyte/electrode is favorable to provide more reaction sites for lithium ions intercalation/de-intercalation. While, as seen in Fig. S1, there is an obvious aggregation in the pure NiO particles. Nevertheless the surface area of pure NiO particles is large; the electrolyte could not flow into the inner of NiO particles. On the other hand, NiO nanowalls grow directly on the surface of support (carbonized pollen). It can form a good adhesion and better electrical contact between NiO and C (carbonized pollen), which is beneficial to enhance the kinetics of NiO during cycling with different rates. In contrast, due to the pure NiO particles have no supports, the NiO nanowalls will flake off continuously from the particles because of the large volume expansion/constriction. Therefore, the solid electrolyte interface (SEI) film of pure NiO will be repeated destroyed and not formed well, which will cause the continuous capacity fade.