Supporting Information

A Core–Shell-Structured TiO$_2$ (B)@RuO$_2$ as a Carbon-Free Cathode Catalyst for High Performance Li–O$_2$ Battery

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1. Material Preparation

**Synthesis of TiO$_2$ (B) nanofibers** The TiO$_2$ (B) nanofibers were synthesized at a concentrated alkaline condition via a hydrothermal route. Briefly, the TiO$_2$-B material was synthesized by adding 6 g of anatase to 28 ml of a 15 M solution of NaOH in distilled water. The mixture was transferred to a 45 ml Teflon-lined stainless steel autoclave, sealed and maintained at 150°C for 72 h in an electric oven. The white product of the hydrothermal reaction was directly dispersed in 200 mL acid solution (1 M HCl) under stirring condition. Then, the resulting solution was kept at rest for 24 hours. Next, the white product was washed and filtrated with a large amount of distilled water, dried in air and then heated to 400°C for 5 h.

**Synthesis of RuO$_2$ nanoparticles** RuO$_2$ nanoparticles were prepared following a similar sol-gel process for preparation of TiO$_2$ (B)@ RuO$_2$-75. Specifically, a 0.3 M NaHCO$_3$ aqueous solution was added slowly to 0.1 M RuCl$_3$ in the absence of TiO$_2$ (B) until the pH of the solution reached 7. After stirring, the sediments were washed with distilled water, and then dried in air flow at room temperature. The black powder was also annealed at 150°C for 19 h in air.

2. Detection of Li$_2$O$_2$ via XPS

Firstly, a Li-O$_2$ battery with TiO$_2$ (B)@ RuO$_2$-75 cathode was discharged at a current density of 0.25 mA cm$^{-2}$ with a fixed capacity of 500 mAh g$^{-1}$. After that, the cell was disassembled in a glove box filled with Ar to obtain the discharged electrode. Then, the discharged electrode was washed with DMC and was dried under vacuum at room temperature for 3 hours. Next, the discharged electrode was detected by XPS. The O$_2$
catalytic electrode before discharge (or after recharge) was detected with the same method.

**Fig. S1** Characteristic of the as-prepared TiO\(_2\) (B) nanofibers: (a, b) SEM images, and (c, d) TEM images with different magnifications.
**Fig. S2** SEM images of the as-prepared RuO$_2$ nanoparticles with different magnifications.

**Fig. S3** SEM images of the as-prepared TiO$_2$ (B)@ RuO$_2$-50 with different magnifications.
Fig. S4 Discharge/charge curves of Li–O₂ cells using different cathodes for initial 10 cycles at a current density of 0.125 mA cm⁻²: (a) TiO₂(B) nanofibers cathode, (b) TiO₂(B)@ RuO₂-50 cathode and (c) RuO₂ nanoparticles cathode. As shown in Fig. S4, the TiO₂ (B) nanofibers cathode, TiO₂ (B)@ RuO₂-50 cathode and RuO₂ nanoparticles cathode display poor cycle performance, compared with TiO₂(B)@ RuO₂-75 cathode.
Fig. S5 The discharge/charge curves of Li–O₂ batteries using different cathodes at different applied current densities: (a) TiO₂ (B) nanofibers cathodes, (b) TiO₂ (B)@RuO₂-50 cathodes and (c) RuO₂ nanoparticles cathodes. As shown in Fig. S5, the TiO₂ (B) nanofibers cathodes, TiO₂ (B)@RuO₂-50 cathodes and RuO₂ nanoparticles cathodes display inferior rate performance, compared with TiO₂ (B)@RuO₂-75.
Fig. S6 Discharge/charge curves of Li–O₂ cells using different cathodes at a current density of 0.25 mA cm⁻² with a fixed capacity of 300 mAh g⁻¹: (a) TiO₂ (B) nanofibers cathode, (b) TiO₂ (B)@ RuO₂-50 cathode and (c) RuO₂ nanoparticles cathode. As shown in Fig. S6, the cycle performance of the TiO₂ (B) nanofibers cathode, TiO₂ (B)@ RuO₂-50 cathode and RuO₂ nanoparticles cathode with limited discharge/charge depth is still inferior to that of TiO₂ (B)@ RuO₂-75 cathode.
Fig. S7 Comparison of discharge/charge curves of Li–O₂ batteries using TiO₂ (B)@ RuO₂-75 cathode, TiO₂ (B)@ RuO₂-50, TiO₂ (B) nanofibers cathode and KB cathode. These cells were tested with a fixed capacity of 300 mAh g⁻¹ at current density of 0.25 mA cm⁻². As shown in Fig. S7, the round-trip efficiency (the ratio of discharge to charge voltage) of the TiO₂ (B)@ RuO₂-75 cathode is much higher than these of the TiO₂ (B) nanofibers cathode, TiO₂ (B)@ RuO₂-50 cathode and KB cathode, indicating that the discharge and charge voltage of the Li–O₂ cell can be significantly improved with the help of the uniform RuO₂ coating layer.
**Fig. S8** SEM images of TiO$_2$ (B)@ RuO$_2$-75 cathodes at different states: (a) before discharge, (b) after discharge and (c) after recharge. At the end of discharge, the surface of the TiO$_2$ (B)@ RuO$_2$-75 cathode is almost fully covered by the Li$_2$O$_2$ nanosheets; and even some flower structure of discharge product is also formed, which consists of Li$_2$O$_2$ nanosheets (**Fig. S8b**). During the subsequent recharge process, all of the discharge products have been decomposed (**Fig. S8b**), indicating the reversible conversion from Li$_2$O$_2$ to O$_2$. 
Fig. S9 The analyses for TiO$_2$ (B)@ RuO$_2$-75 cathodes: (a) ex-situ XRD patterns at different discharge-charge stages: before discharge, after discharge and after recharge; (b) ex-situ FTIR spectra before discharge, after discharge and at the end of charge at 1st cycle. As compared with the XRD pattern of the fresh electrode, new diffraction peaks were observed for the discharged electrode. Although these peaks were very weak, they can be reasonably assigned as the diffraction peaks of Li$_2$O$_2$ (as highlighted in Fig. S9a). Furthermore, the diffraction peaks of Li$_2$O$_2$ disappeared when the battery was completely recharged, which suggests that the discharge product Li$_2$O$_2$ is decomposed at the end of the charging process. This was further confirmed by the FT-IR spectra data in Fig. S9b, where the weak characteristic peak for Li$_2$O$_2$, observed at the end of discharge, is absent from the spectrum at the end of charge. These results also demonstrate the reversibility of the O$_2$/Li$_2$O$_2$ conversion over the cycles for the Li–O$_2$ batteries.
Fig. S10 Picture of a cell for the DEMS analysis. The DEMS system was built in-house and guided by the requirement to detect the gases evolved during the charge. A quadrupole mass spectrometer (NETZSCH QMS 403 C) with leak inlet is connected to a customized Swagelok cell assembly (Fig. S10). The cathode current collector is integrated with two tubes as purge gas inlet and outlet (Fig. S10). Each tested cell was discharged with a fixed capacitance of 500 mAh g⁻¹ in the sealed assembly, and then online gas analysis was performed during the recharge process with a purge Ar stream at a current density of 0.25 mA cm⁻². Before the charge test and online gas analysis, the system was purged with pure Ar stream for 12 hours, and the background for O₂ and CO₂ was calibrated. Purge gas flows were typically 10 mL/min.