Supplementary Material: Ultrasonication-assisted fabrication of porous ZnO@C nanoplates for lithium-ion batteries

Supplementary Figure 1. TGA profiles of prepared ZnO-BTC nanosheets and H$_3$BTC in N$_2$ atmosphere in the temperature region of 40-700 °C at a heating rate of 10 °C min$^{-1}$.

The thermal behaviour of the ZnO-BTC intermediate was investigated via thermo gravimetric analysis (TGA) at a heating rate of 10 °C min$^{-1}$ in N$_2$ atmosphere. The recorded TGA curves (Supplementary Figure 1) indicated that there were mainly 3 steps of mass loss for ZnO-BTC within the temperature region from 40-700 °C. From 40-200 °C, a weight loss of 11.2 % was detected, corresponding to the loss of physically adsorbed water and or ethanol on the intermediates.[1] In the following region of 200-420 °C, a 4.8% weight loss was observed, which can be ascribed to the release of chemically adsorbed water or lattice water.[2-3] The structure collapse and combustion of ZnO-BTC started from around 420 °C and 12.5% weight loss was measured until 500 °C.[4-5] After 500 °C, the mass of sample remained relatively stable, implying the completely conversion of intermediates. According to the TGA analysis, 500 °C was selected as the optimal pyrolysis temperature in the subsequent experiment. For comparison, thermal behaviour of H$_3$BTC was measured at same condition and it started to decompose at around 280 °C, implying the successful reaction between ZnO and H$_3$BTC under ultrasonication at room temperature.

Supplementary Figure 2. FT-IR spectra of H$_3$BTC (black line) and ZnO-BTC (red line).

The surface composition and functional groups of H$_3$BTC and prepared ZnO-BTC were characterized by Fourier transform infrared spectra (FT-IR), conducted through BRUKER Tensor 27 on a KBr pellet in the wavenumber
range of 500-4000 cm\(^{-1}\). Both spectra (Supplementary Figure 2) presented broad adsorption bands in the range of 3500-3000 cm\(^{-1}\), corresponding to physically adsorbed water molecules and/or acid OH of carboxylic groups.\(^6\) The adsorption bands located around 3000-2500, 1760, 1420, 1300-1200, 920 cm\(^{-1}\) were assigned to -COOH groups in trimesic acid.\(^7\) However, no adsorption bands related to -COOH group were observed in the spectrum of ZnO-BTC. Instead, four adsorption peaks appeared between 1550-1645 cm\(^{-1}\) and 1440-1360 cm\(^{-1}\), which were attributed to asymmetric vibration and symmetric vibration of -COO\(^-\).\(^8\) The above analysis suggested H\(_3\)BTC were completed deprotonated during ultrasonication process.

**Supplementary Figure 3.** XPS spectra of ZnO-BTC: (A) survey spectrum and high-resolution spectrum of (B) Zn 2p, (C) C 1s and (D) O 1s.

XPS (X-ray photoelectron spectroscopy) analysis was conducted to investigate the surface characteristics and chemical state of the sonication synthesized ZnO-BTC nanoplates (Supplementary Figure 3). In the full spectrum, the binding energies around 1046 eV, 1022 eV, 285 eV and 531 eV can be ascribed to Zn 2p\(_{3/2}\), Zn 2p\(_{1/2}\), C 1s and O 1s, respectively. The curve fitting of C 1s spectrum showed two characteristic reflections at 284.4 eV and 288.5 eV, which correspond to sp\(^2\) carbon and O-C=O.\(^9\) The high resolution XPS spectrum of Zn 2p showed low energy Zn 2p\(_{3/2}\) (1021.8 eV) and high energy Zn 2p\(_{1/2}\) (1044.8 eV) reflections with an energy separation of 23 eV, which implied valence state of zinc is +2.\(^10\) The fitting of O1s resulted in two peaks that were assigned to the oxygen bonded to Zn metal (531.7 eV) and O=C=O (532.6 eV).\(^11\)\(^12\)

**Supplementary Figure 4.** XPS survey spectrum (A) and O 1s high resolution spectrum (B) of ZnO@C.
Supplementary Figure 5. BET analysis of ZnO-BTC nanosheets. (A) N$_2$ adsorption/desorption isothermal plots and (B) pore diameter distribution.

To illuminate the pore structures of intermediates nanoplates, BET analysis was performed on Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The BET specific surface area and pore volume of ZnO-BTC were 30.55 m$^2$ g$^{-1}$ and 0.07 cm$^3$ g$^{-1}$, respectively (Supplementary Figure 5A). The pore size distribution of ZnO-BTC sample was depicted in Supplementary Figure 5B, calculated with The Barrett-Joyner-Halenda (BJH) model. It can be deduced that ZnO-BTC nanoplates were mainly composed of micropores and mesopores with a sharp peak located at around 1-3 nm.

Supplementary Figure 6. SEM images of (A) commercial ZnO and (B-D) ZnO-BTC intermediate. EDS mapping area (E), spectrum (F), and element mapping images for C(C), O(D), Zn(E) of the ZnO-BTC.

The morphologies of ZnO-BTC were observed by SEM. Clearly, ZnO-BTC was nanoplates with size of several micrometres (Supplementary Figure 6B-D), while the ZnO precursors were aggregation of nanoparticles (Supplementary Figure 6A). The EDS spectrum (Supplementary Figure 6F) confirmed that the prepared nanoplates were constituted of Zn, C, O. As depicted in Supplementary Figure 6G-I, the homogenous distribution of C, O, Zn elements in ZnO-BTC nanoplates sample was observed. In addition, Zn content in ZnO-BTC was estimated to be 46 wt.% via Inductively coupled plasma mass spectrometry (ICP-OES, SPECTRO-BLUE).
Supplementary Figure 7. Rate capability of ZnO@C composites obtained by annealing ZnO-BTC at 500℃ for different time 2H, 4H, 6H.

To assess the influence of the annealing time on the electrochemical performance of ZnO@C composites, the obtained ZnO@C materials prepared by sintering ZnO-BTC for 2H, 4H and 6H were tested by galvanostatic charge/discharge at different current density (Supplementary Figure 7). The ZnO@C-2H and ZnO@C-6H exhibited similar specific capacities at all rates. However, ZnO@C-4H delivered obviously higher specific capacity. Consequently, four-hour annealing of ZnO-BTC under nitrogen atmosphere was determined to be the optimal preparation condition of ZnO@C.

Supplementary Figure 8. Differential capacity vs. voltage (dQ/dV) plots of ZnO composites for 2nd to 5th cycles.
at a current density of 0.1 C

Supplementary Figure 9. The first and 100th Charge-discharge curves of ZnO and ZnO@C materials at a current density of 0.5C.

Supplementary Figure 10. (A) Cyclic voltammetry curves of ZnO@C anode at different scan rates; (B) calculations of b value by log (peak current) vs log (scan rate) plots; (C) Diffusion contribution and capacitive contribution at 0.8 mV/s; (D) percentage of capacitive contribution at different scan rates.

Supplementary Figure 11. Equivalent circuit applied to fit the Nyquist plots.
Supplementary Figure 12. (A) Relationship between real impedance with the low frequencies $\omega^{-0.5}$ and (B) comparison of Warburg impedance coefficient $\sigma_w$ before and after cycle of ZnO and ZnO@C electrodes. 

EIS spectra were also applied to calculate the lithium diffusion coefficient $D$ in electrode using the following equation $S1$:[13-14]

$$D = \frac{R^2T^2}{2A^2n^2F^4C^2\sigma^2}$$  

in which, $R$ is the gas constant, $T$ represents the absolute temperature, $A$ refers to the surface area of electrode, $n$ is the number of $e^-$ per molecule attending the electronic transfer reaction, $F$ for the Faraday constant, $C$ denotes the concentration of lithium ion in electrode, and $\sigma$ represents the Warburg factors. $\sigma$ can be determined through the EIS spectra in the low frequency region using the equation as follows $S2$:[15]

$$Z_{re} = R_s + R_p + R_{ct} + \sigma\omega^{-1/2}$$  

Therefore, the curves of $Z_{re}$ against $\omega^{-0.5}$ should be a straight line with a slope of $\sigma$. The relationship between $Z_{re}$ and $\omega^{-0.5}$ was plotted in Supplementary Figure 12A, and calculated $\sigma$ values for both electrode before and after cycle were plotted in Supplementary Figure 12B. Before cycling, ZnO electrode exhibited a slightly smaller $\sigma$ values than the ZnO@C electrode, indicating higher lithium-ion diffusion coefficient. After 100 cycles, the lithium-ion diffusion in the ZnO@C was greatly enhanced deduced from reduced $\sigma$ values, while the lithium-ion transportation in ZnO electrode was distinctly more sluggish. And according to the much higher $\sigma$ value of ZnO electrode than ZnO@C after cycle, the lithium-ion diffusion was obviously faster and easier in the ZnO@C composite electrode than its counterpart.

Supplementary Figure 13. (A)XRD patterns of ZnO@C, rGO and ZnO@C@rGO. (B) Raman spectra of rGO and ZnO@C@rGO.

ZnO@C@rGO composites were fabricated by annealing the ZnO-BTC/rGO composites at 500 °C for 4 hours. ZnO-BTC/rGO composites were prepared via stirring and sonication of the mixture of GO and ZnO-BTC, followed by freeze-drying. GO was prepared by modified Hummer’s method. [16-17] The phase identification and crystallinity prepared ZnO/C and ZnO@C@rGO composites were acquired by XRD (Supplementary Figure 12A).
XRD patterns of ZnO@C and ZnO@C@rGO were well matched with zincite structure ZnO (PDF #36-1451). While the peak appeared at around 26° for RGO and ZnO@C@rGO can be assigned to graphite. The electronic structure of carbonaceous materials is usually characterized by Raman scattering (Supplementary Figure 12B). The Raman spectra of RGO and ZnO@C@rGO were exhibited in Supplementary Figure 11B. Both of them presented two prominent peaks located at around 1354 and 1593 cm⁻¹, which can be ascribed to the D and G bands of carbon, respectively. The D-band is related to carbon disorder coordination, while the G band is associated with the E₂g stretching vibrations in the basal plane of the ordered crystalline graphite. I_D/I_G, the intensity ratio between D band and G band peak, can be a powerful index to evaluate the carbon materials’ degree of crystallinity. The I_D/I_G ratios of rGO and ZnO@C@rGO were calculated to be 0.32 and 0.42, respectively. The increase of the I_D/I_G ratio in the ZnO@C@rGO composites implies decrease of the sp² domains average size and defects creation, as well as the possible interaction between ZnO@C nanocomposites and graphene sheets.

**Supplementary Figure 14.** Morphologies observation of ZnO@C@rGO. (A) SEM image, (B) TEM image, (C) high resolution TEM image and (D) SAED.

ZnO@C composites were well distributed and wrapped intimately by reduced graphene oxide sheets with wrinkles (Supplementary Figure 14A and B), which will facilitate the electronic interactions between ZnO@C and reduced graphene oxide and endows ZnO@C@rGO excellent electrochemical properties. HRTEM images (Supplementary Figure 14C) displayed clear lattice fringe with crystalline interplanar spacing value (d) of 0.26 nm, corresponding to the (002) crystal face of ZnO. SAED images, depicted in Supplementary Figure 14D, indicated the polycrystal nature of the composites. And the well-defined diffraction rings in Supplementary Figure 13D were corresponded to the (102), (002), (110) and (100) planes, which were consisted with the result of XRD. The introduction of reduced graphene oxide would endow good electrochemical properties of ZnO@C@rGO composites benefiting from rGO’s intrinsic high electronic conductivity and stress cushioning ability.

**Reference**


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