Supporting Information

Reversible Intercalation and Exfoliation of layered Covalent Triazine-Based Frameworks for Enhanced Lithium Ion Batteries

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Experimental methods

Materials

CTF-1 was synthesized according to the literature.\textsuperscript{1} In brief, 1,4-dicyanobenzene monomer (1 g) and ZnCl\textsubscript{2} (1.06 g) were transferred into a glass ampoule (2 cm × 15 cm) under Ar atmosphere. The ampoule was evacuated, sealed, heated at 400 °C for 40 h (3 °C min\textsuperscript{-1} ramping). The product was grounded into fine powders and washed with 0.1 M HCl, water, acetone and chloroform. The obtained CTF-1 powder was vacuum dried overnight at 80 °C.

Synthesis of CTF-1 intercalated compounds

CTF-1 (200 mg) was mixed with 10 mL acid (H\textsubscript{2}SO\textsubscript{4} or H\textsubscript{3}PO\textsubscript{4}) and stirred at room temperature for 5 min. The mixture was filtered through a 0.45 μm PTFE membrane to obtain the CTF-1 intercalated compounds.

Exfoliation of CTF-1 into f-CTF-1

200 mg of CTF-1 intercalated compounds (intercalation reaction was extended to 6 hours by using H\textsubscript{2}SO\textsubscript{4}) was mixed with the mixture of H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3} (9:1 volume ratio) in a round-bottom flask equipped with a reflux condenser. The reaction system was heated by using microwave oven at 85 °C for 10 min with magnetic stirring and an output power of 300 W. The product was washed with
deionized water until neutral pH by filtration. The obtained f-CTF-1 was dispersed into 25 mL water, cooled by liquid nitrogen and freeze-dried. The yield of f-CTF-1 was measured to be ~42%.

**Evaluation of layer number of f-CTF-1 by atomic force microscope (AFM)**

According to previous studies, the theoretical thickness of single-layered CTF-1 is identical with that of the graphene (~0.34 nm). Therefore, an apparent AFM height of ~0.8 nm should be expected for the exfoliated single-layered CTF-1, considering the intrinsic out-of-plane deformation of 2D materials and the instrumental offset arising from different interaction forces between the AFM probe, nanosheets, and the substrate. However, the apparent AFM height of most the f-CTF-1 nanosheets are in the range of 1.2 to 1.9 nm, similar to that of the graphene oxide (apparent AFM height of ~1.2 nm), due to the introduction of functional groups on the basal plane and the possible trapping of solvents. Therefore, the layer number of most the f-CTF-1 nanosheets should be in the range of 1 to 2 layers.

**Electrochemical testing**

The electrochemical measurements were performed using CR2032 coin type cells. The CTF-1 and exfoliated f-CTF-1 were made into anode by mixing them with Super P Li carbon black and PVDF binder in NMP with a weight ratio of 7:2:1. The mixture was spread on Cu foil and dried at 120 °C for 12 h under vacuum. The mass loading density of the active materials was uniform and about 0.61 mg cm\(^{-2}\). All cells were assembled in an argon-filled glove box. Lithium foil was used as the counter electrodes. 1 M LiPF\(_6\) solution in a 1/1 (w/w) mixture of the EC and DMC was served as the electrolyte. The amount of electrolyte was fixed at 80 uL. Galvanostatic charge–discharge tests were carried out using a LAND battery tester from 0.05 V to 3.0 V. Cyclic voltammograms (CVs) were measured using a CHI760E Electrochemical Workstation (Shanghai Chenhua) at a scan rate of 0.1 mV s\(^{-1}\). Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying the AC amplitude of 10 mV over the frequency range of 100 kHz to 0.01 Hz.

In order to illustrate the advantages of the present strategy, we also tried the liquid-phase exfoliation of bulk CTF-1 in N-methyl pyrrollidone (NMP), a common way to exfoliate 2D materials, to prepare the CTF-1 nanosheets (L-CTF-1), but only got relatively poor yield and exfoliation degree, as can be seen in SEM characterization (Figure S12). We further tested the specific reversible capacities of L-CTF-1 anode under different current densities of 0.1, 0.2, 0.5, 1, 2, 5 and 10 A g\(^{-1}\), respectively (Figure S13). The specific capacities of L-CTF-1only showed moderate increases when compared with bulk CTF-1, which indicate the high degrees of exfoliation play a significant role in the enhancement in Li storage performance.

Complete exfoliation of CTF-1 may lead to the decrease in volumetric capacity. However, as shown in Figure S10, the f-CTF-1 can evenly mix with conductive black to form a close-packed structure, which not only improve the conductive, but also alleviate the negative effect on volumetric capacity. The f-CTF-1 also shows 1.4 to 2 times increase in specific capacitance, even if taking volumetric capacity as evaluation standard. Besides, the f-CTF-1 exhibits better rate performance than bulk CTF-1, which is also important for commercial anode.

The Li\(^+\) ion diffusion coefficient (\(D_{Li^+}\)) is derived from Eq. (1)

\[
D = 0.5 \left( \frac{RT}{AF^2 \sigma C} \right)^2
\]

(1)
where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (298.5 K), $F$ is the Faraday’s constant (9.65 × 10$^4$ C mol$^{-1}$), $A$ is the area of the electrode surface (1.13 cm$^2$), $C$ (mol cm$^{-3}$) is the molar concentration of Li$^+$ in the $f$-CTF-1 or CTF-1, and $\sigma$ is the Warburg coefficient.

The Warburg coefficient $\sigma$ can be obtained from Eq. (2):

$$Z_{re} = R_e + R_{ct} + \sigma \omega^{-0.5}$$  \hspace{1cm} (2)

Where $\sigma$ is the slope for the plot of $Z_{re}$ vs. the reciprocal root square of the lower angular frequencies. The obtained $\sigma$ for $f$-CTF-1 and CTF-1 are 25 and 32, respectively.

The C is evaluated from discharge profile curves at a current density of 0.1 A g$^{-1}$: 1 mAh = 3.6 C = 3.6 × 1.04 × 10$^{-5}$ mol electron or Li$^+$ ion. At full lithiation state, for $f$-CTF-1 with a specific capacity of 816 mAh g$^{-1}$, the mass concentration of Li$^+$ (M) is caculated to be 0.03 mol g$^{-1}$. The $C = M \times \rho$, where the $\rho$ is the measured density of $f$-CTF-1 and CTF-1.

**Characterization**

The samples were characterized by X-ray diffraction (XRD, Bruker D8 FOCUS, Cu-Ka radiation), Raman spectroscopy (Renishaw inVia reflex), $^{13}$C solid-state nuclear magnetic resonance spectroscopy ($^{13}$C NMR, BRUKER AvanceIII HD 500 MHz), X-ray photoelectron spectroscopy (PHI5000 Versa Probe), scanning electron microscopy (SEM, S-4800, HITACHI) and atomic force microscope (AFM, Benyuan-CSPM5500, China).

![Figure S1 X-ray diffraction patterns of the CTF-1, H$_3$PO$_4$ intercalated CTF-1 and corresponding deintercalated CTF-1.](image-url)
**Figure S2** Raman spectra of the CTF-1, H₃PO₄ intercalated CTF-1 and corresponding deintercalated CTF-1.

**Figure S3** C1s (a) and N1s (b) XPS results of the deintercalated CTF-1 (intercalated by H₃PO₄).
**Figure S4** FT-IR results of the CTF-1 control and the deintercalated CTF-1 (intercalated by H₃PO₄).

**Figure S5** XRD results of the exfoliated f-CTF-1 nanosheets.
Figure S6 C1s XPS results of the exfoliated f-CTF-1 nanosheets and the CTF-1 control.

Figure S7 Simulated $^{13}$C NMR results for the functional groups that may exist in f-CTF-1 skeleton. Considering the complexity of triazine cleavage, we gave several possible structures according to the XPS, NMR and FT-IR results.
Figure S8 SEM image of the bulk CTF-1.

Figure S9 Statistic size distribution of f-CTF-1 according to AFM characterization in Figure 3f.
Figure S10 CV curves of the (a) bulk CTF-1 and (b) exfoliated f-CTF-1 at a scan rate of 0.1 mV s\(^{-1}\). Galvanostatic charge–discharge profile curves of the (c) bulk CTF-1 and (d) f-CTF-1 at a current density of 0.1 A g\(^{-1}\).

The cyclic voltammetry (CV) curves of both the f-CTF-1 and CTF-1 show a broad irreversible reduction peak around 1.5 V in the first cycle, which is attributed to the formation of a solid electrolyte interface (SEI) film (a and b). The CV curves below 0.7 V present the typical features of carbonaceous materials, which also exist in other 2D COFs anode materials. c and d show the discharge–charge profiles of the first three cycles of the samples at a current density of 100 mA g\(^{-1}\) between 0.05 and 3.0 V. As can be seen, the discharging curve of f-CTF-1 exhibits significant differences in two distinct potential ranges, when compared with that of CTF-1. For the f-CTF-1, the slope starts at ~2.1 V and the specific capacities below 0.5 V are larger. These results imply that the expansion in the interlayer spacing after exfoliation may contribute additional sites for the accommodation of lithium, which is consistent with the Li storage behavior of graphene. The exfoliated f-CTF-1 exhibits an initial reversible species capacity of 932 mA h g\(^{-1}\), much higher than that of CTF-1 (389 mA h g\(^{-1}\)).
**Figure S11** The plan-view (a) and cross-sectional (b) SEM images for $f$-CTF-1 anode; the plan-view (c) and cross-sectional (d) SEM images for CTF-1 anode.

**Figure S12** The FT-IR spectra of $f$-CTF-1 and the $f$-CTF-1 anode after 100 charge-discharge cycles. The $f$-CTF-1 after cycles maintains the same basic characteristic peaks as pristine $f$-CTF-1, indicating its good electrochemical stability.
Figure S13 SEM image of the exfoliated CTF-1 (L-CTF-1) based on liquid-phase exfoliation of bulk CTF-1 in NMP.

Figure S14 Rate capability measurements for CTF-1 and L-CTF-1 (obtained from liquid-phase exfoliation of bulk CTF-1 in NMP).
Figure S15 Ex-situ high-resolution N 1s of f-CTF-1 electrode at different voltage steps

Figure 16 Ex-situ high-resolution C1s (a), O 1s (b), (c) Li O 1s and N 1s (d) of bulk CTF-1 electrode at different voltage steps.