

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

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Sandwiched Porous C/ZnO/Porous C Nanosheet Battery Anodes with Stable Solid-Electrolyte Interphase for Fast and Long Cycling

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Supplementary Information S1:

Preparation of porous organic template: A degradable polyurethane foam template was prepared by crosslinking poly-(propylene oxide) (PPO) and poly-(propylene oxide)-block-poly lactide (PPO-*b*-PLA) copolymers using isocyanate (*J. Appl. Polym. Sci.*, 2010, **118**, 2304-2313.). PPO-*b*-PLA copolymers was synthesized by ring-opening polymerization of L-lactide (LLA) or D,L-lactid (DLLA) using low unsaturated PPO. The mixture containing polyol (PPO triols mixed with PPO-*b*-PLA, 86.2%), water (blowing agent, 4.2%), A-33 (catalyst, 0.2%), Sn(Oct)₂ (catalyst, 0.2%) and B8110 (surfactant, 1.2%) were charged into a stainless steel container and stirred for 60 s at 1300 rpm. Then, a predetermined amount of isocyanate was rapidly poured into the container and the reactants were mixed thoroughly for 7 s with a high-speed stirrer at 2000 rpm. The reactants were rapidly poured into a mold with dimensions of 250*250*250 mm³. The mold was kept at room temperature for 10 min, and polyurethane foam was formed by blowing and gelling reactions. The foam was allowed to fully develop with an additional 1 h cure at 100 °C.

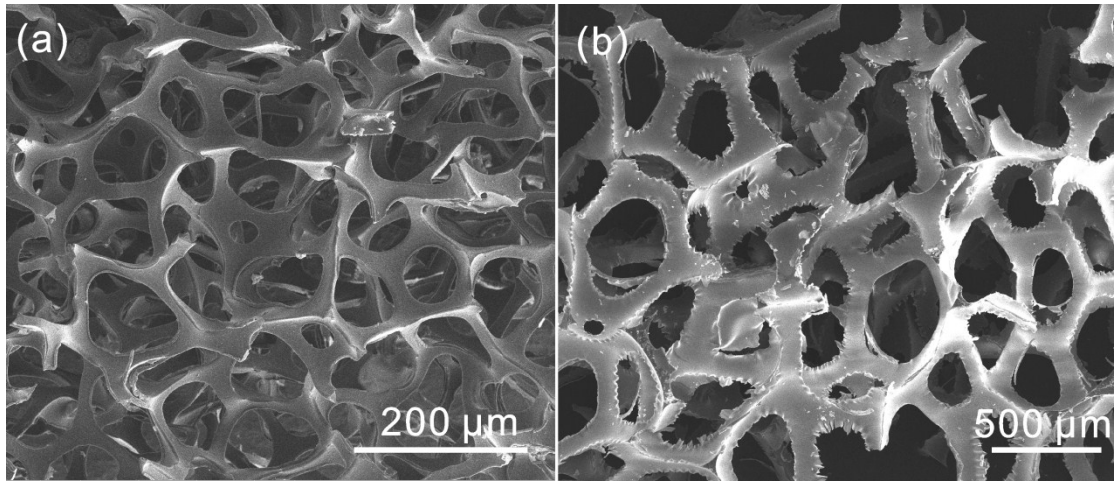


Fig. S2 SEM images of (a) the self-made porous template and (b) the template coated by ZnO nanomembrane (200 ALD cycles).

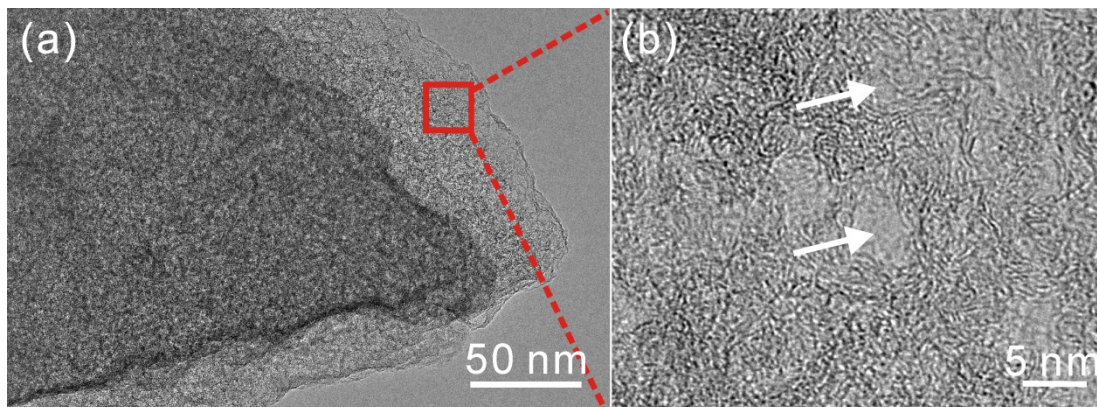


Fig. S3 (a) and (b) TEM images of CZC nanosheet with voids/pores on carbon coating surface.

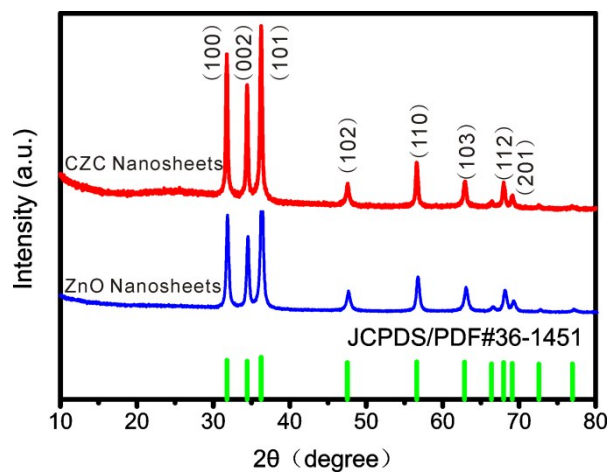


Fig. S4 XRD patterns of CZC nanosheets and ZnO nanosheets.

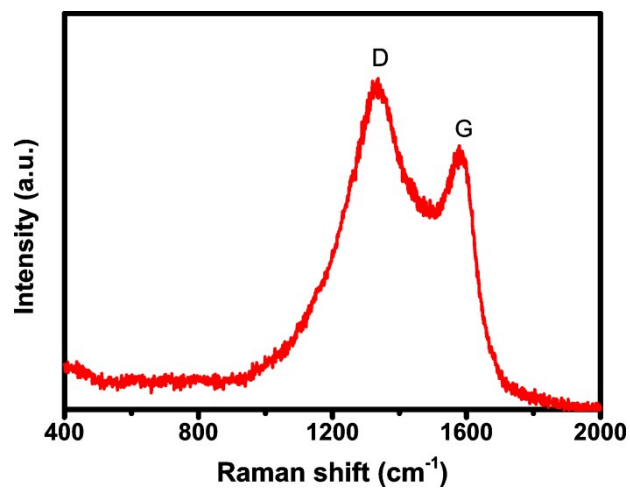


Fig. S5 Raman spectrum of carbon sheets with pyrolysis temperatures of 700 °C. The intensity of the D band is stronger than that of G band, indicating an overall amorphous nature.

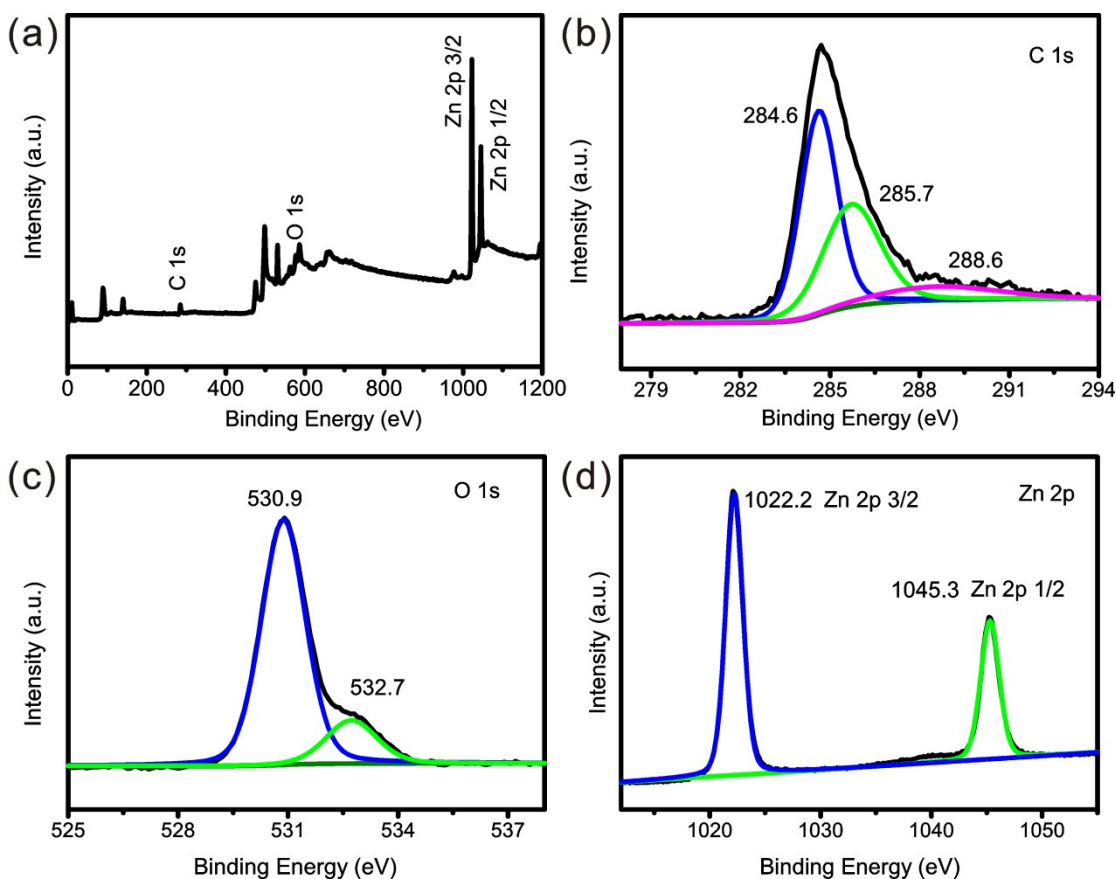


Fig. S6 XPS spectra of CZC nanosheets: survey spectrum (a) and high-resolution spectra with peak fitting of C 1s (b), O 1s (c), and Zn 2p (d). The black line is the experimental data while the red, blue, and green lines are the fitting results.

The presence of C, O, and Zn elements can be confirmed by the characteristic spectra of C 1s, O 1s, and Zn 2p in the full wide-scan spectrum (Fig. S6a). Fig. S6b shows the high resolution C 1s spectrum. The strongest peak at 284.6 eV is ascribed to nonoxygenated C-C bond^[1,2] and the peaks at 285.7 and 288.6 eV are related to C-OH^[2] and carbonyl C=O^[3] respectively. The peak at 284.5 eV also suggested the presence of C-O-Zn^[4]. Fig. S6c is the high resolution O 1s spectrum, which consists a strong peak at 530.9 eV and a shoulder peak at 532.7 eV, corresponding to O²⁻ in the crystal ZnO structure^[5] and oxygen functional group^[2] respectively. Meanwhile, two strong peaks at 1022.2 and 1045.3 eV respectively assigned to Zn 2p_{3/2} and Zn 2p_{1/2} are detected in Zn 2p spectrum (Fig. S6d), indicating the Zn²⁺ state in the CZC nanosheets.^[3]

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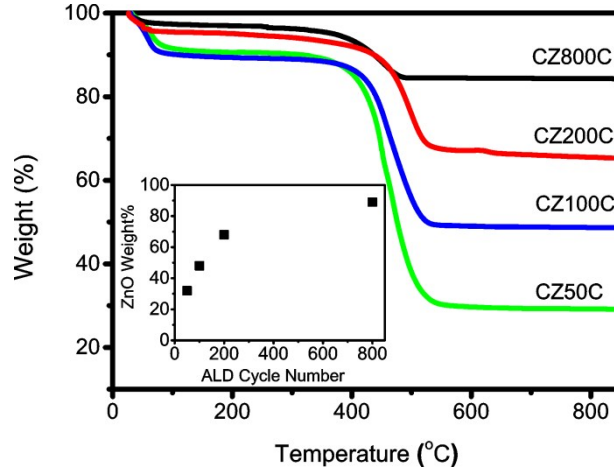


Fig. S7 TGA of CZC nanosheets samples. The ZnO% is 32%, 51%, 68%, and 89% in CZ50C, CZ100C, CZ200, and CZ800C respectively (inset), showing a gradually increase of ZnO% with ALD cycles.

We assume that the weight of porous carbon layer is M . Thus, the ZnO concentration in the composites can be expressed as:

$$ZnO\% = \frac{m * n}{M + n * m} = 1 - \frac{1}{1 + \frac{m}{M} * n}$$

where n is the number of ALD cycles and m is mass of ZnO deposited in each ALD cycle, which should be constant. We calculated the m/M values for all the samples from the TGA results and find the values vary around 0.0101 with less than 7% fluctuation ($m/M= 0.0094, 0.0104, 0.0106, \text{ and } 0.0101$ for CZ50C, CZ100C, CZ200C, and CZ800C, respectively). Therefore, the values of M are constant in all the samples. Correspondingly, the thicknesses of the carbon layers should also be constant. Considering the fabrication process, we think that the carbon layers with almost the same thicknesses (~ 34 nm, see Fig. 1e) in all the samples are reasonable.

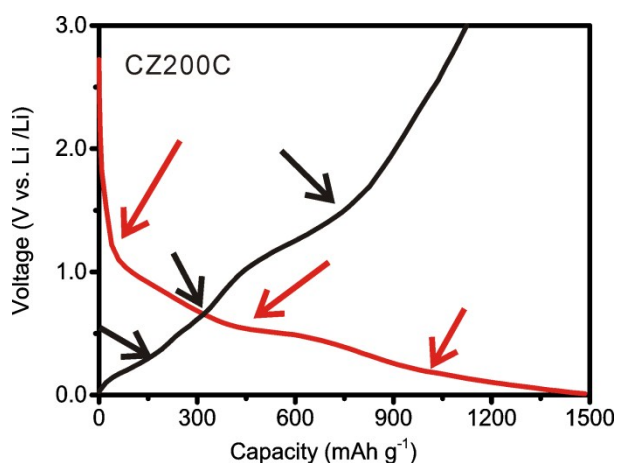


Fig. S8 The first charge-discharge profile of CZ200C at 80 mA g⁻¹.

For the discharge curve, three plateaus can be distinguished at around 1.2~0.8 V, 0.6~0.4 V, and 0.2~0.1 V. The plateau at 1.2~0.8 V corresponds to two peaks in CV cathodic scan (red line in Fig. 2a): the peak at 1.7 V of SEI layer formation and 0.9 V of conversion reaction between ZnO and Li⁺ to form Zn and Li₂O.¹ The plateau at 0.6~0.4 V corresponds to peak at 0.6 V for multi-step alloying process between Zn and Li⁺ to generate Li_xZn (red line in Fig. 2a).² The plateau at 0.2~0.1 V corresponds to the sharp peak near 0.1 V (red line in Fig. 2a) for the Li⁺ lithiation into amorphous carbon.³ After the first cycles, a stable SEI is gradually formed. Thus the first plateau in discharge profiles stables at around 0.9 V (Fig. 2b) and wild peak at ~0.8 V can also be observed in CV cathodic scan (black and green lines in Fig. 2a). For the charge profile, there are also three plateaus can be discerned: 0.2~0.3 V, 0.5~0.7 V, and 1.3~2.1 V (see the black arrows in Fig. S8). The plateaus at 0.2~0.3 V and 0.5~0.7 V may correspond to the peaks at 0.2 and 0.5 V (red line in Fig. 2a) for the multi-step dealloying process of Li_xZn alloy to form Zn.^{1,4} While the wide plateau at 1.3~2.1 V can be ascribed to the oxidation of ZnO (peaks at ~1.7 and ~2.2 V in CV anodic scan).^{1,3,5} Therefore, the CV curve in Fig. 2a are consistent with the charge-discharge profiles.

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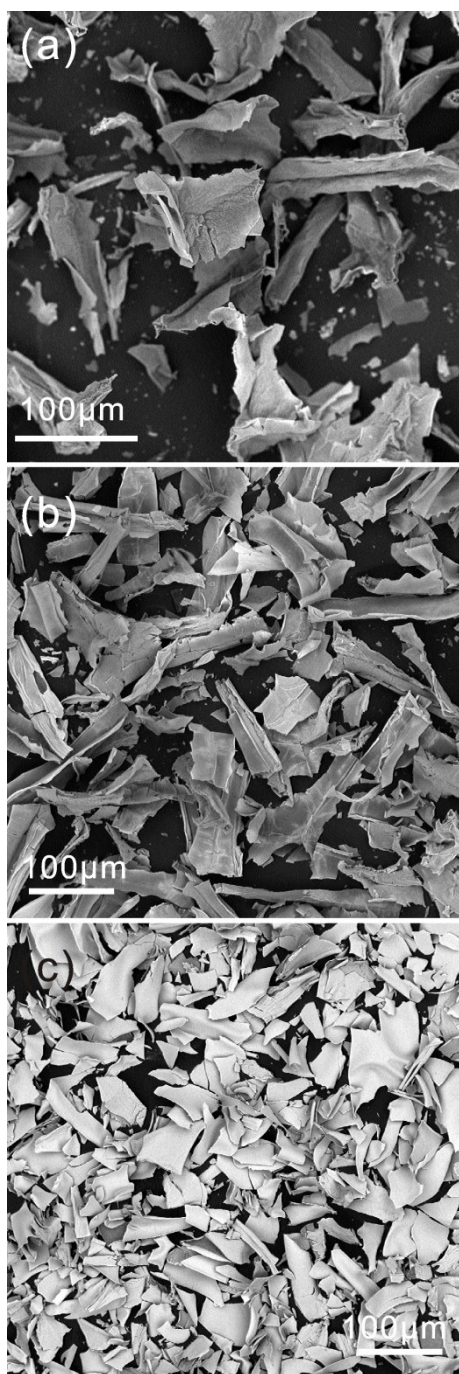


Fig. S9 SEM images of CZC nanosheets with different ALD cycles: (a) 50 ALD cycles, CZ50C nanosheets, (b) 100 ALD cycles, CZ100C nanosheets, and (c) 800 ALD cycles, CZ8000C nanosheets.

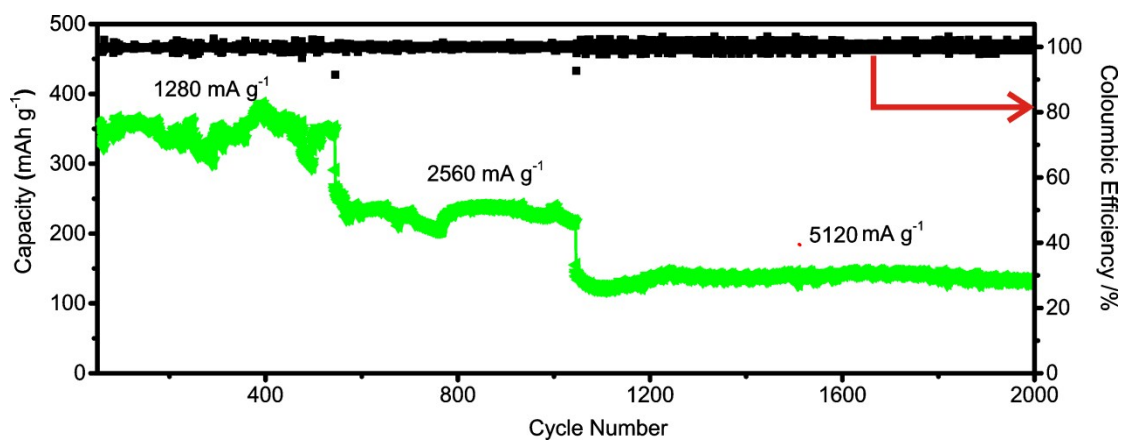


Fig. S10 Cycling performance of CZ100C nanosheets anode at 1280 mA g⁻¹ for 500 cycles, 2560 mA g⁻¹ for 500 cycles, and 5120 mA g⁻¹ for 1000 cycles.

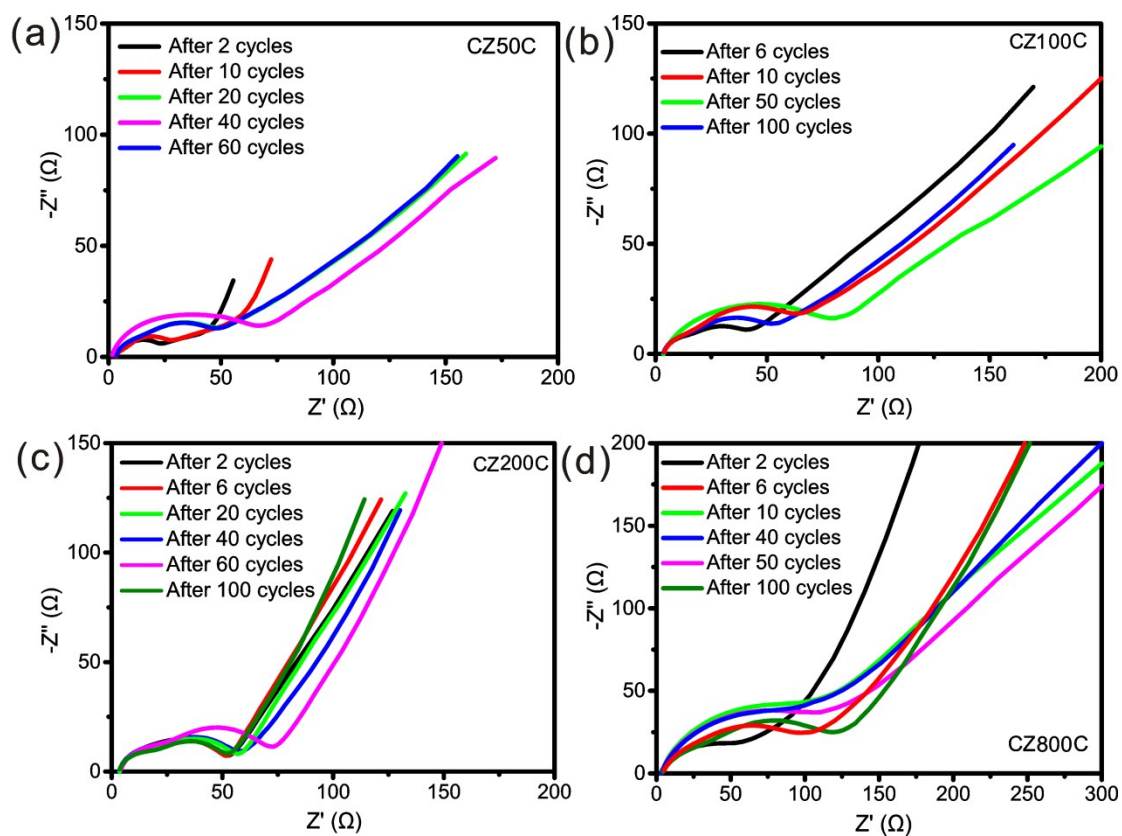


Fig. S11 EIS spectra of CZC nanosheets with (a) 50, (b) 100, (c) 200, and (d) 800 ALD cycles after various galvanostatic discharge/charge cycles.

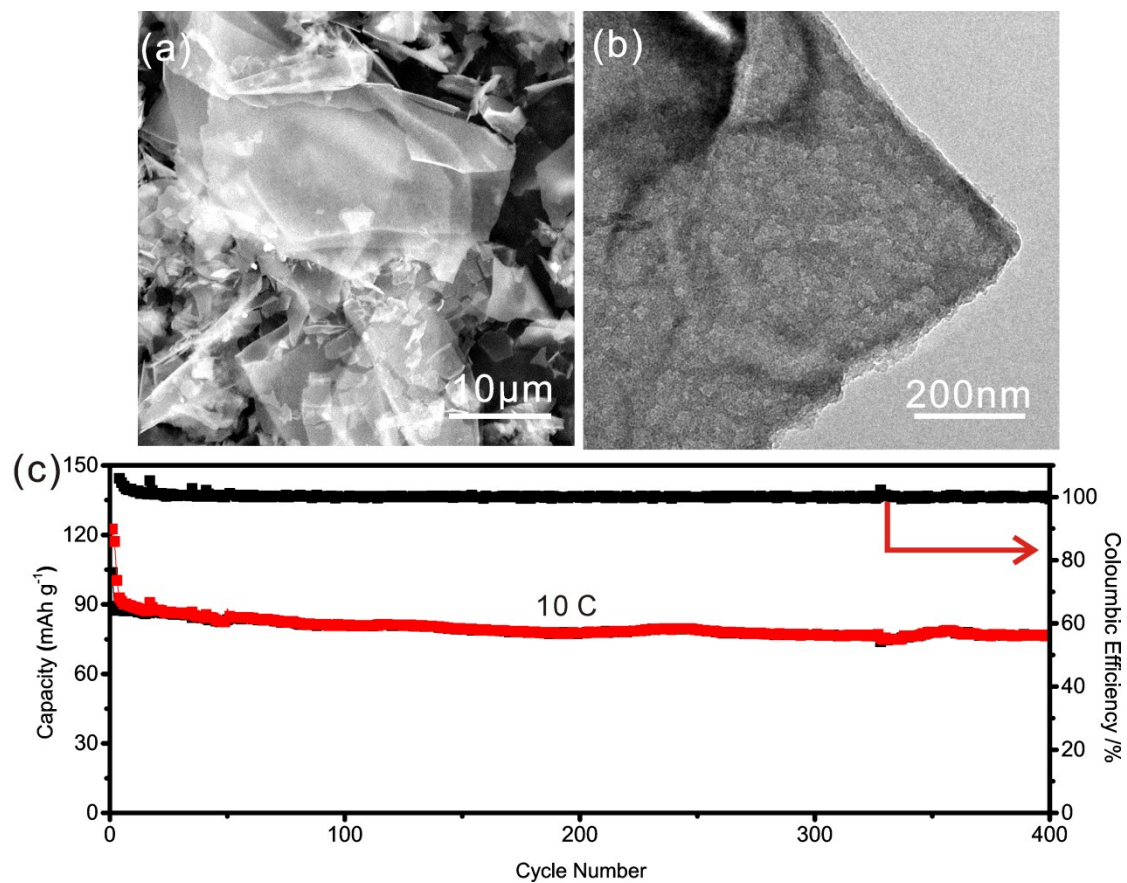


Fig. S12 (a) SEM and (b) TEM images of CTC nanosheets. (c) Cycling performance of CT200C nanosheets anode at 10 C for 400 cycles. The capacity is calculated based on the mass of the composite.