

A 3D structural NC/ZnO@carbon cloth matrix as potassiophilic host for dendrite-free potassium metal anode

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Experimental Section

Materials

Zinc acetate ($C_4H_6O_4Zn$, 99.0%), anhydrous ethanol (99.5%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.99%), hexamethylenetetramine ($C_6H_{12}N_4$, 99.0%), N, N-dimethylformamide (DMF, anhydrous, 99.8%) and 2-Methylimidazole ($C_4H_6N_2$, 98%) were purchased from Aladdin Co. Ltd. (China) and used as received without further purification. If it is not specified, all solutions were prepared with deionized water (DI) and used directly without further purification.

Synthesis of ZnO@CC

First, the commercial carbon cloth was ultrasonically cleaned in methanol for 1 h, rinsed more than 5 times with deionized water, and dried at 60 °C for 12 h. 1.0975 g of $(CH_3COO)_2Zn \cdot 2H_2O$ was dissolved in 100 ml of anhydrous ethanol to form a homogeneous solution A. Then the dried carbon cloth was cut into 4×4 cm pieces and completely immersed in solution A for 30 minutes, and then dried in an oven. The dried carbon cloth was put into a muffle furnace for oxidative calcination (5 °C/min, 350 °C, 20 min) to obtain carbon cloth full of ZnO seeds. Dissolve 0.41215 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.24535 g of hexamethylenetetramine in 70 ml deionized water, then add 4 ml of ammonia dropwise and stir for 30 minutes to obtain a homogeneous solution B. Transfer solution B to 90 ml of PTFE liner, put the carbon cloth filled with ZnO seeds vertically into it, cover with a sealing lid, put on a stainless steel shell, and put it into an oven at 95 °C for 8h. Finally, wait for the autoclave to come down to room temperature and then remove the carbon cloth, wash it with deionized water 2~3 times, and finally put it into the oven for 8 hours at 60 °C to obtain ZnO@CC.

Synthesis of ZnO/ZIF-8@CC

0.164 g of 2-methylimidazole (2-MIM) was weighed and dissolved into a mixture of N, N-dimethylformamide (DMF) and DI (12 ml for DMF and 4 ml for DI). A uniform solution was obtained by ultrasonic shock for 5 minutes. Transfer the above uniform solution to the PTFE liner, then immerse ZnO@CC in the solution, seal the cover, put the lining into the stainless-steel shell, and put it in the oven at 70 °C for 24 h to get ZIF-8/ZnO@CC.

Synthesis of ZnO/NC@CC

Finally, ZIF-8/ZnO@CC was placed in a tubular furnace under the protection of N₂ at a heating rate of 5 °C/min to 650 °C and held for 2 h. After cooling to room temperature, ZnO/NC@CC is obtained.

Synthesis of KPB

First, 0.5406 g of ferric chloride hexahydrate was dissolved in 20 ml of DI to form solution A, and then 0.4224 g of potassium ferrocyanide was dissolved in 80 ml of DI to form solution B. Pour solution A into solution B during stirring, and then the solution will produce precipitate immediately. After the dark blue solution was sealed and settled for 24 hours, the supernatant was poured out and the bottom precipitate was collected. After vacuum drying at 80 °C for 12 h, KPB cathode was obtained.

Materials characterization

XRD patterns were acquired with an X-ray diffractometer (Bruker, AXS D8 ADVANCE) in the 2θ range of 5-80° (Cu Kα, λ = 1.5418 Å). Thermo VG ESCALAB250 was used for X-ray photoelectron spectroscopy (XPS) examination. The

morphology of the prepared samples was observed by a field emission scanning electron microscope (FEI, Nova Nano SEM 450). The microstructure was observed by a transmission electron microscope (FEI, Tecnai G220).

Electrochemical Characterization

Half, symmetric, and full cells were assembled with standard CR-2032 coin type cells in an argon-filled glove box (O_2 and H_2O less than 0.1ppm). 0.8 M KFSI in EC/DEC (1: 1, v/v) was selected as electrolyte. Cut the glass fiber membrane (Whatman GF/D) into 19 mm diameter round pieces to serve as the separator.

For the half-cells, the cells were assembled with CC and NC/ZnO@CC as working electrodes and K metal as counter electrode. To test the plating/stripping behavior of K, the metal anodes were initially plated on different substrates at a current density of 1 mA cm^{-2} with a area capacity of 1 mAh cm^{-2} and then stripped to 1 V. To further explore the plating/stripping behavior of K at high current densities, the current density was further increased to 2 mA cm^{-2} with the same area capacity. Coulombic efficiency was calculated by the ratio of the amount of K stripped to the amount of K deposited in each cycle. For symmetric cells, 10 mAh cm^{-2} of K was first pre-deposited on CC and NC/ZnO@CC using a half-cell at a current density of 1 mA cm^{-2} , and then two identical K@CC or K@NC/ZnO@CC were assembled as symmetric cells. Cycling performance was investigated by galvanostatic cycling measurements at a current density of 0.5 mA cm^{-2} with an area capacity of 0.5 mAh cm^{-2} and a current density of 1 mA cm^{-2} with an area capacity of 1 mAh cm^{-2} . For the rate performance, the testing protocol was the following: 0.5 mA cm^{-2} from 1 to 10 cycle, 1 mA cm^{-2} from 11 to 20 cycle, 2 mA cm^{-2}

from 21 to 30 cycle, 3 mA cm⁻² from 31 to 40 cycle, 4 mA cm⁻² from 41 to 50 cycle, 5 mA cm⁻² from 51 to 60 cycle, and then back to 0.5 mA cm⁻². The electrochemical impedance spectroscopy (EIS) was tested by an electrochemical workstation (Zahner Ennium pro) in a frequency range from 100 KHz to 0.01 Hz. For the full cell, the cathode is consists of 80% KPB, 10% carbon black and 10% polyvinylidene fluoride (PVDF), and the anode is bare K metal and K@NC/ZnO@CC. The full cells were tested in the voltage range of 2-4 V. CV tests were performed at a sweep rate of 0.1 mV s⁻¹ and the long cycle tests were at a current density of 100 mA g⁻¹. Rate tests were performed at current densities ranging from 50 mA g⁻¹ to 2000 mA g⁻¹.

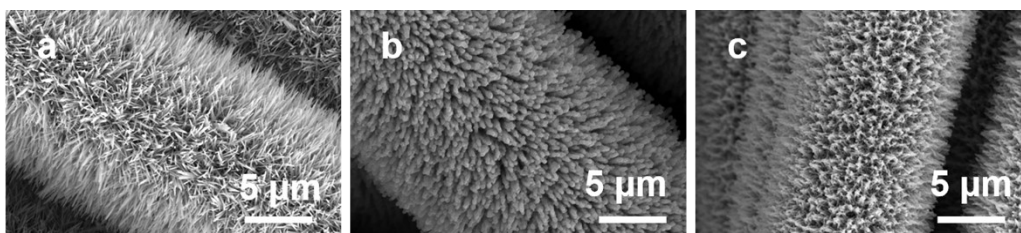


Fig. S1. Enlarged SEM images of (a) ZnO@CC; (b) ZIF-8/ZnO@CC; (c) NC/ZnO@CC.

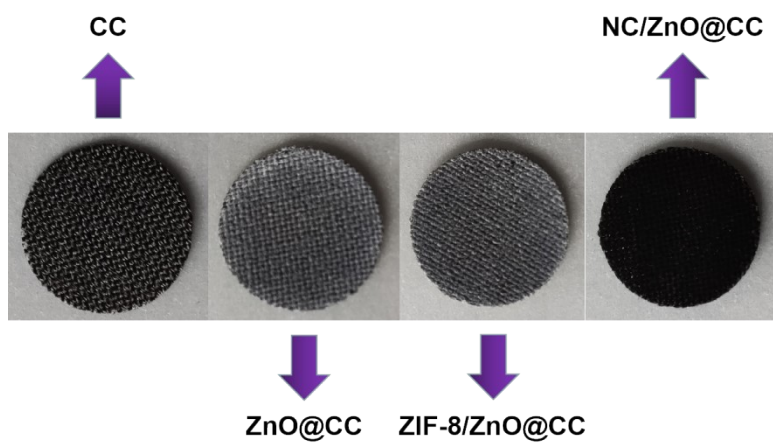


Fig. S2. Color change of carbon cloth at various stages of the preparation process.

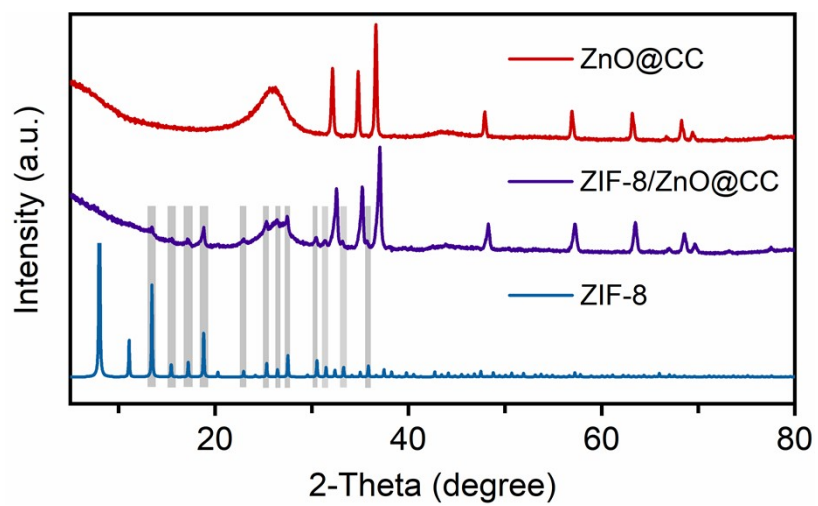


Fig. S3. XRD patterns of ZnO@CC, ZIF-8/ZnO@CC and ZIF-8.

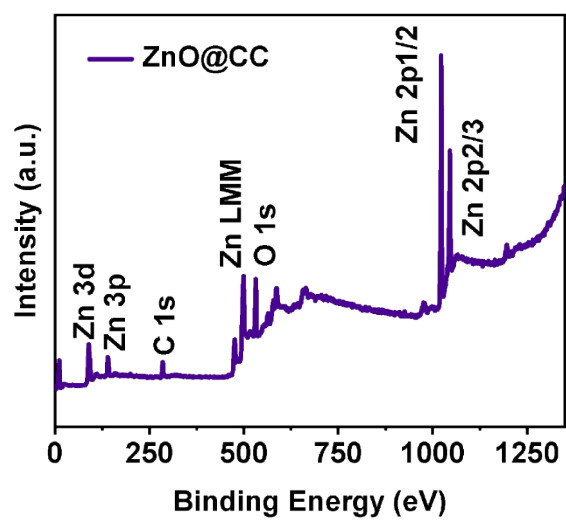


Fig. S4. XPS spectrum of ZnO@CC.

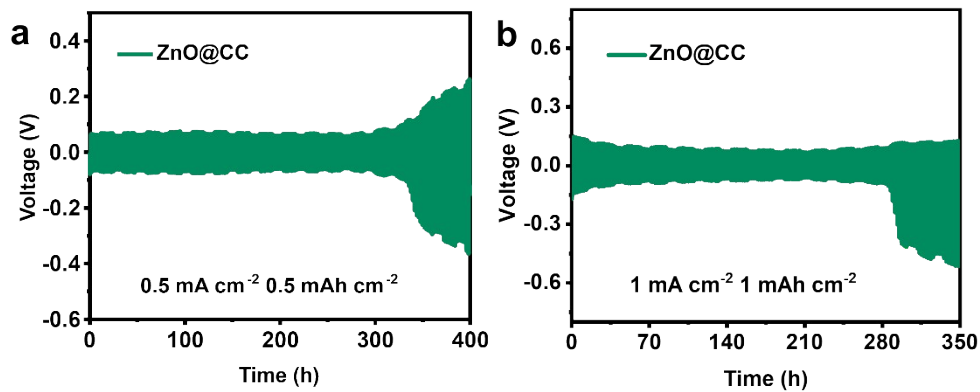


Fig. S5. $\text{K}@\text{ZnO}@\text{CC}||\text{K}@\text{ZnO}@\text{CC}$ stripping/plating cycling performance at (a) 0.5 mA cm^{-2} , 0.5 mAh cm^{-2} ; (b) 1 mA cm^{-2} , 1 mAh cm^{-2} .

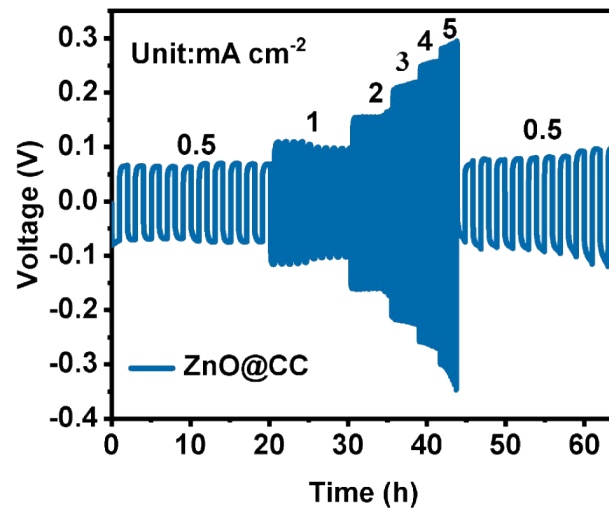


Fig. S6. Rate performance of K@ZnO@CC symmetric cells at different current densities.

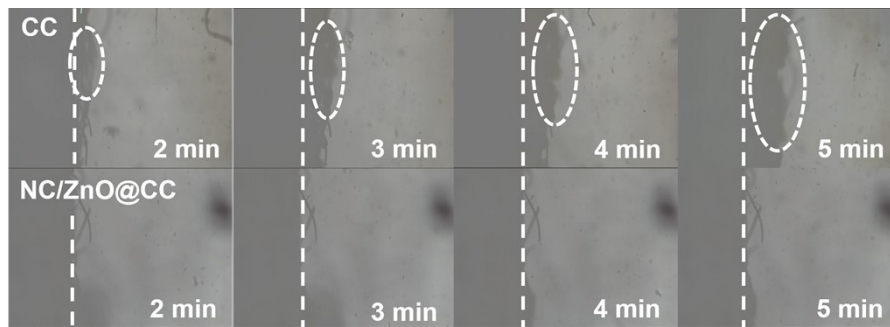


Fig. S7. In situ optical microscopy visualization of K plating on the bare CC and NC/ZnO@CC.

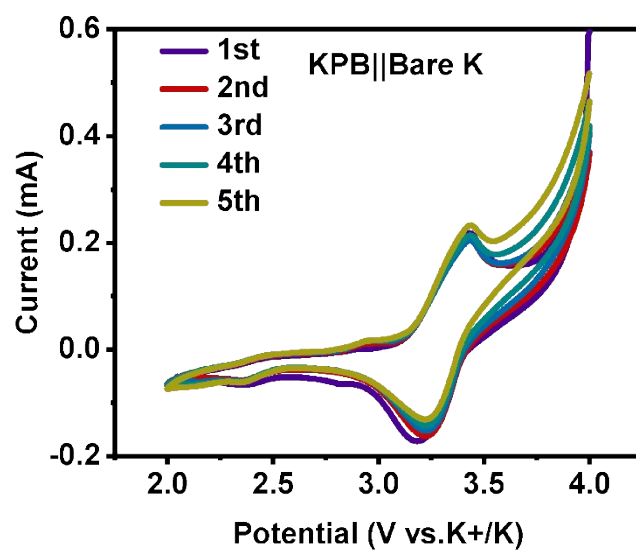


Fig. S8. CV curves of K||KPB full cell.

Table S1 Performance Comparison of K@NC/ZnO@CC||KPB full cells with reported potassium metal batteries.

Full cell	Capacity/Current density	Cycling life	Ref.
K@NC/ZnO@CC KPB	53 mAh g ⁻¹ /100 mA g ⁻¹	200 cycles	This work
K PB (DEE)	38 mAh g ⁻¹ /50 mA g ⁻¹	240 cycles	[1]
SC-Al ₂ O ₃ @K PB	52 mAh g ⁻¹ /100 mA g ⁻¹	100 cycles	[2]
SnS ₂ @CP-K KPB	51 mAh g ⁻¹ /50 mA g ⁻¹	150 cycles	[3]
K K ₂ VOP ₂ O ₇	51 mAh g ⁻¹ /50 mA g ⁻¹	100 cycles	[4]
K NCM622	45 mAh g ⁻¹ /0.2C	100 cycles	[5]
K K ₃ V ₂ (PO ₄) ₃	35 mAh g ⁻¹ /200 mA g ⁻¹	100 cycles	[6]
K K _{0.8} V ₂ O ₅	51 mAh g ⁻¹ /0.1C	180 cycles	[7]
K e-ADN	40 mAh g ⁻¹ /4 mA cm ⁻²	200 cycles	[8]

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