Electronic Supplementary Material

Tetrahydroxy-anthraquinone induced structural change of Zeolitic Imidazolate Framework for Asymmetric Supercapacitor Electrode Material Application

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1. Electrochemical test

The working electrode, counter electrode, and reference electrode refer to electrode material on nickel foam, platinum electrode, and saturated calomel electrode (SCE), separately. Electrochemical measurements were carried out on a CHI 660E electrochemical workstation (Chenhua, Shanghai, China) and a CT2001A-LAND cell test system (Landian, Wuhan, China). The electrode was prepared by following procedures: TZM(8.0 mg) or TM(8.0 mg), acetylene black (1.5 mg) and PTFE (0.5 mg) were mixed homogeneously with ethanol by sonication and coated on nickel foams (a mass ratio of 80:15:5, 1×1 cm^2). And the as-prepared electrode materials were dried at 55 °C in vacuum for 24 h, the nickel foams were pressed under <15 MPa for 20 s. Then the loading mass of active substance was measured to be about 2.0 mg.

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TZM and TM were studied in 3 M and 6 M KOH electrolyte. Cyclic voltammetry (CV) test was done at the scan rates of 10, 20, 30, 40, and 50 $mV\cdot s^{-1}$. Galvanostatic charge-discharge(GCD) curves were obtained at the current densities of 1.0, 2.0, 3.0, 4.0 and 5.0 $A\cdot g^{-1}$. Electrochemical impedance spectroscopy (EIS) measurement were carried out in the frequency ranging from 0.01~100 KHz. The capacitance was calculated by the following equation [33]:

$$C = \frac{I\Delta t}{m\Delta V} \quad (1)$$

TZM//ACS aqueous asymmetric capacitor was constructed by using 1 M KOH aqueous electrolyte. The weight ratio of positive and negative is decided by the following charge balance equations:

$$Q_{+} = Q_{-} \quad (2)$$

$$\frac{m_{+}}{m_{-}} = \frac{\Delta V_{-} \cdot C_{-}}{\Delta V_{+} \cdot C_{+}} \quad (3)$$

The mass of electroactive substance (The mass loading are 2.0 mg and 1.1 mg for positive and negative electrodes, respectively): acetylene black: PTFE binder = 80:15:5. The specific energy density and power density derived from GCD test can be calculated from the equations:

$$C_T = \frac{I\Delta t}{m_T\Delta V} \quad (4)$$

$$SE = \frac{C_s\Delta V^2}{2 \times 3.6} \quad (5)$$

$$SP = \frac{3600 \times SE}{\Delta t} \quad (6)$$

The C_T, I, m_T, Δt and ΔV refer to the specific capacitance ($F\cdot g^{-1}$), current density (A), charge-discharge time (s), the total mass of negative and positive electrode materials (g) and potential (V) of TZM//ACS asymmetric aqueous supercapacitor, respectively. The SE and SP refer to the specific energy density ($Wh\cdot kg^{-1}$) and specific power density ($W\cdot kg^{-1}$).

2. Preparation of PVA-KOH gel

The PVA-KOH gel was used as both the ionic electrolyte and separator of the all-solid-state asymmetric supercapacitor, which was prepared based on the reported procedure as follows: 1.5 g of KOH was dispersed into 30 mL deionized water, and then 3 g PVA was added under stirring until the solution became clear at 80 ℃[46]. The resulting gel was poured onto a watch glass and dried in room temperature after evaporation of the excess water the jelly-like gel was solidified and cut into pieces matching the size of the electrodes, and then the all-solid-state asymmetric supercapacitor was carefully built with the solidified PVA-KOH gel.

3. Related figures and tables

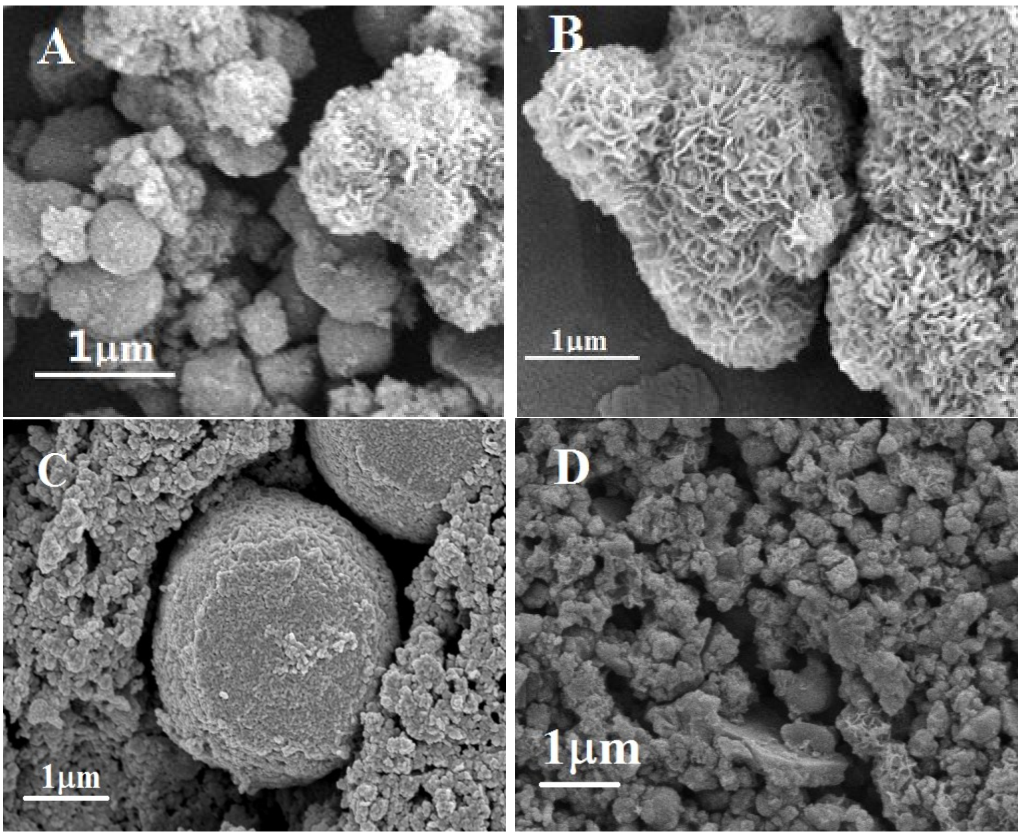

Figure S1 SEM images of the products (TZM) prepared in 20h(A) and 48h(B); SEM images of TZM(C) and TM(D) after 2000 charging and discharging cycles

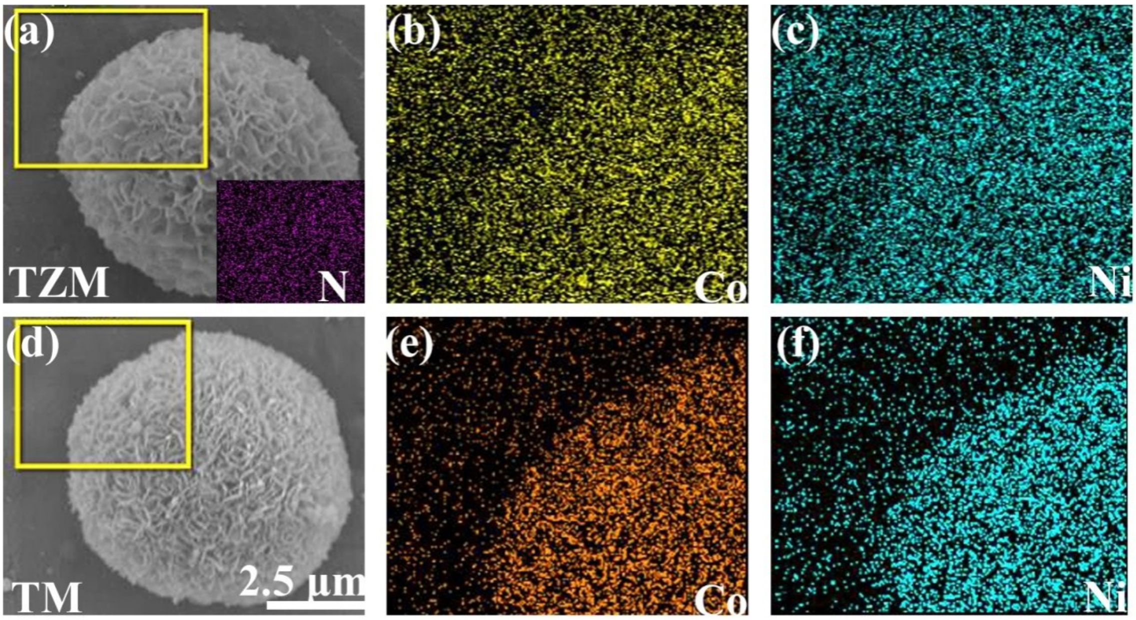

Figure S2 EDS area mapping of the TZM **(a)** and TM **(d)**, and corresponding Co **(b and e)**, and Ni **(c and f)** elements, respectively (Inset is the area mapping of N).

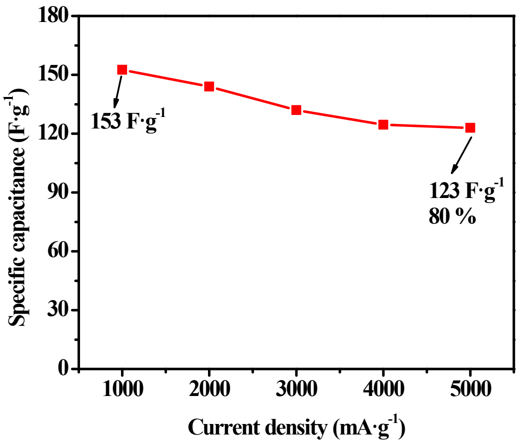

Figure S3 Comparison of the specific capacitances of TZM//ACS aqueous asymmetric supercapacitor at various current densities

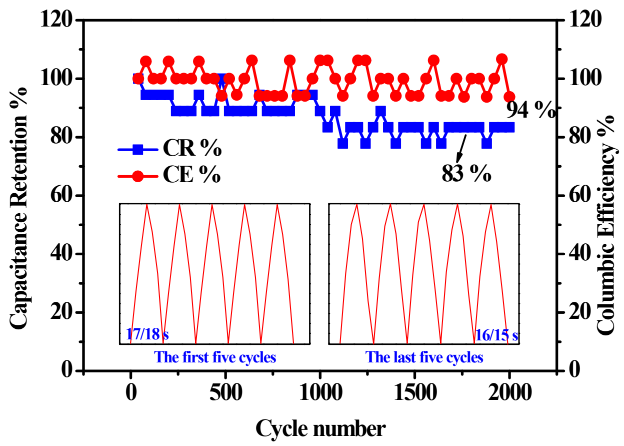

Figure S4 Cycle stability performance for TZM//ACS aqueous asymmetric supercapacitor at the current density of 10 $A \cdot g^{-1}$

Table S1 Comparison of the electrochemical performances of the reported Co/Ni-ZIF and AQ-modified materials with this work

Electrode materials	**Electrolyte**	**Current density**	**Specific capacitance**	**Cycle stability**	**Refs**
C-ZIF-8@MWCNTs	2 M KOH	1.0 $A \cdot g^{-1}$	326$F \cdot g^{-1}$	99.7% -10000	[10]
CNT@CZIF-2	6 M KOH	0.5 $A \cdot g^{-1}$	324$F \cdot g^{-1}$	93.5 % -1000	[14]
AQ/OMCs	1 M H_2SO_4	0.5 $A \cdot g^{-1}$	346$F \cdot g^{-1}$	-	[17]
Ni-CoLDH-NFA	2 M KOH	2.0 $A \cdot g^{-1}$	894$C \cdot g^{-1}$	-	[29]
THAQ/rGO	1 M H_2SO_4	1.0 $A \cdot g^{-1}$	259$F \cdot g^{-1}$	81.8% -2000	[31]
AQ/GF	1 M H_2SO_4	1.0 $A \cdot g^{-1}$	396$F \cdot g^{-1}$	97 % -2000	[35]
C_{AQ}	0.1 M H_2SO_4	10$mV \cdot s^{-1}$	195$F \cdot g^{-1}$	83 % -10000	[37]
AQ-HPCNTs	1 M H_2SO_4	1.0 $A \cdot g^{-1}$	710$F \cdot g^{-1}$	96 % -1000	[38]
AZ-SGHs	1 M H_2SO_4	1.0 $A \cdot g^{-1}$	350$F \cdot g^{-1}$	-	[39]
AQSGH	1 M H_2SO_4	0.3 $A \cdot g^{-1}$	258$F \cdot g^{-1}$	100 % -2000	[40]
ANS-rGO	1 M H_2SO_4	1.3 $A \cdot g^{-1}$	373$F \cdot g^{-1}$	97.5 % -1000	[41]
TZM	3 M KOH	1.0 $A \cdot g^{-1}$	2030$F \cdot g^{-1}$	90.7%-1000 94%-2000	This work

Table S2 Comparison of the energy density (SE) and specific power density (SP) of TZM//ACS and the results reported in other literatures

Materials	**Electrolyte**	**SE** ($Wh\cdot kg^{-1}$)	**SP** ($W\cdot kg^{-1}$)	$\mathbf{V_{max}}$ (V)	**Refs**
AQ/OMCs//OMC	1 M H_2SO_4	6.3	18000	1.2 V	[17]
AQ-C//Ru oxide	1 M H_2SO_4	12.7	17300	1.3 V	[19]
Ni-Co LDH-NFA//AC	6 M KOH	18.5	17000	1.7 V	[29]
GF//AQ/GF	1 M H_2SO_4	13.2	917.4	1.6 V	[35]
$Co(OH)_2$//AC	1 M KOH	26.4	195.1	1.6 V	[36]
AZ-SGHs//AZ-SGHs	1 M H_2SO_4	18.2	700	1.4 V	[39]
C-AQ//C-DHB	1 M H_2SO_4	1.1	6300	1.2 V	[45]
AQ@PNCNTs//PNTs	1 M H_2SO_4	32.7	700	1.4 V	[46]
rGO/$Co(OH)_2$//AC	1 M KOH	44.6	13000	1.6 V	[47]
TZM//AC	1 M KOH	47.7	750	1.5 V	This work