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Supporting information

ZnO quantum dots@ covalent organic frameworks for high-performance alkaline zinc-based batteries

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Experimental Section

Chemicals

All solvents and reagents obtained from commercial sources were used without further purification. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, 99%, CAS 5970-45-6), lithium hydroxide monohydrate ($LiOH·H_2O$, 99.95%, CAS 1310-66-3), ethanol (CH_3CH_2OH, 99.7%, CAS 64-17-5), 3-aminopropyltriethoxysilane (APTES, 99%, CAS 919-30-2), 2,4,6-trihydroxy-1,3,5-benzenetricarboxaldehyde (Tp, 97%, CAS 34374-88-4), p-Phenylenediamine (Pa-1, 99%, CAS 106-50-3), mesitylene (C_9H_{12}, 97%, CAS 108-67-8), acetic acid (CH_3COOH, 36%, CAS 64-19-7), N-N dimethylacetamide (C_3H_7NO, AR, CAS 127-19-5), acetone (CH_3COCH_3, 99.5%,67-64-1) were obtained from Sinopharm Chemical Reagent.

Computational details

The DFT calculation were carried out using the $DMol_3$ in Material Studio programs. The Perdew-Burke-Enzzhof (PBE) function in the generalized gradient approximation (GGA) method was used for the calculation. The Monkhorst-Pack network method is used to sample the Brillouin k-point in the reciprocal space, and the network size is 3 × 3 × 1. The energy tolerance accuracy, the maximum force, and the displacement are set to 1×10^{-5} Ha, 2×10^{-3} Ha / Å, and 5×10^{-3} Å, respectively. The binding energies of $Zn(OH)_4^{2-}$ ions absorbed on TpPa-1 COF calculated by the equation (1):

$E(Zn(OH)_4^{2-}$ on TpPa-1 COF) = E ($Zn(OH)_4^{2-}$ andTpPa-1 COF) – E($Zn(OH)_4^{2-}$) – E(TpPa-1 COF) (1)

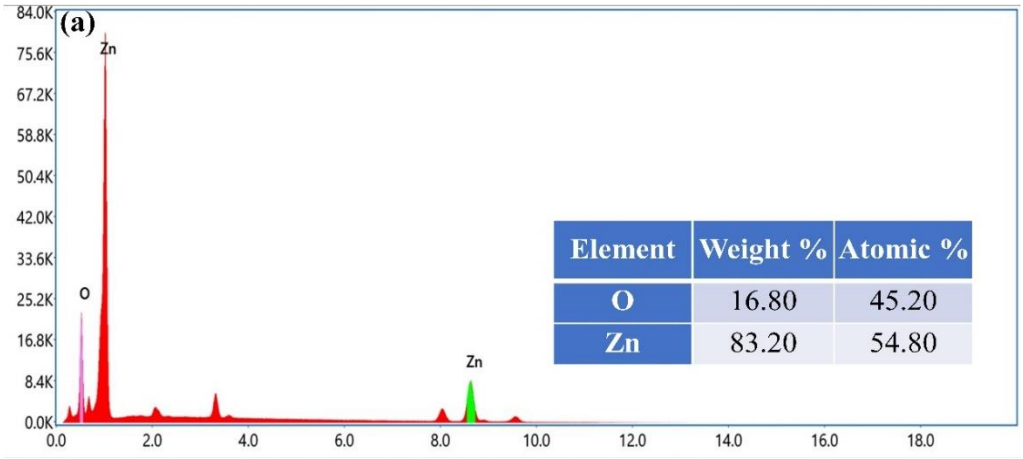
where the E($Zn(OH)_4^{2-}$ on TpPa-1 COF) represented the total energies of $Zn(OH)_4^{2-}$ ions adsorption on TpPa-1 COF.

And E($Zn(OH)_4^{2-}$), E(TpPa-1 COF)were the energies of $Zn(OH)_4^{2-}$ ion and TpPa-1COF alone, respectively.

Charge density difference distribution of $Zn(OH)_4^{2-}$ on TpPa-1 COF was calculated by the equation (2):

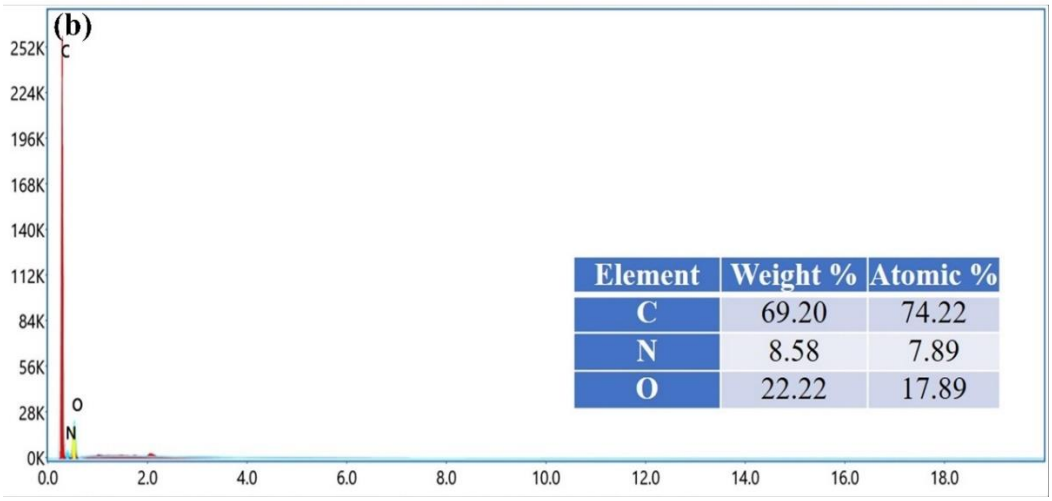
$\Delta\rho = \rho(Zn(OH)_4^{2-}$ @TpPa-1 COF) – $\rho(Zn(OH)_4^{2-})$ – ρ(TpPa-1 COF) (2)

where $\rho(Zn(OH)_4^{2-}$ @TpPa-1 COF), $\rho(Zn(OH)_4^{2-})$, and ρ(TpPa-1 COF) was the charge density distribution of $Zn(OH)_4^{2-}$@TpPa-1 COF , $Zn(OH)_4^{2-}$, and TpPa-1 COF alone, respectively.



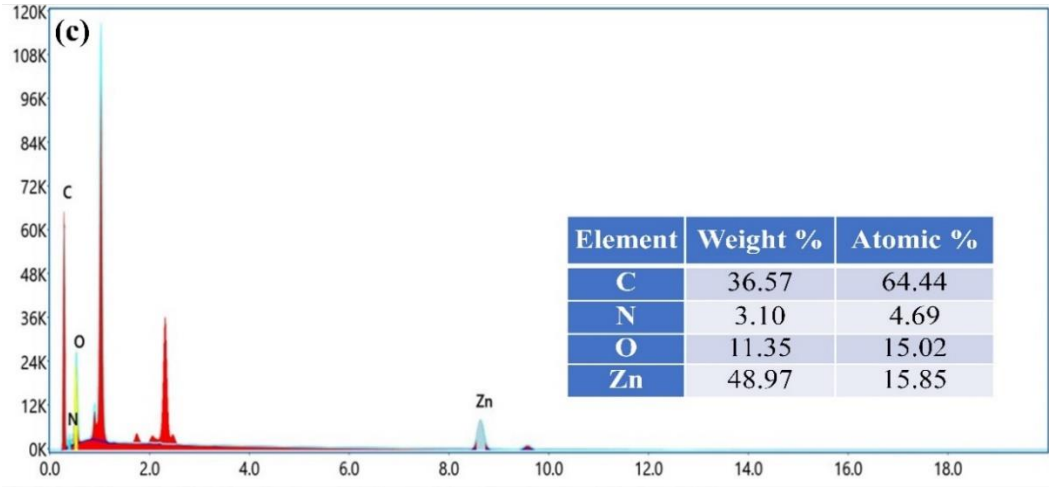
Element	Weight %	Atomic %
O	16.80	45.20
Zn	83.20	54.80

Fig. S1 The content of Zn and O in ZnO QDs.



Element	Weight %	Atomic %
C	69.20	74.22
N	8.58	7.89
O	22.22	17.89

Fig. S2 The content of C, N and O in TpPa-1 COF.



Element	Weight %	Atomic %
C	36.57	64.44
N	3.10	4.69
O	11.35	15.02
Zn	48.97	15.85

Fig. S3 The content of Zn, C, N and O in ZnO QDs@TpPa-1 COF.

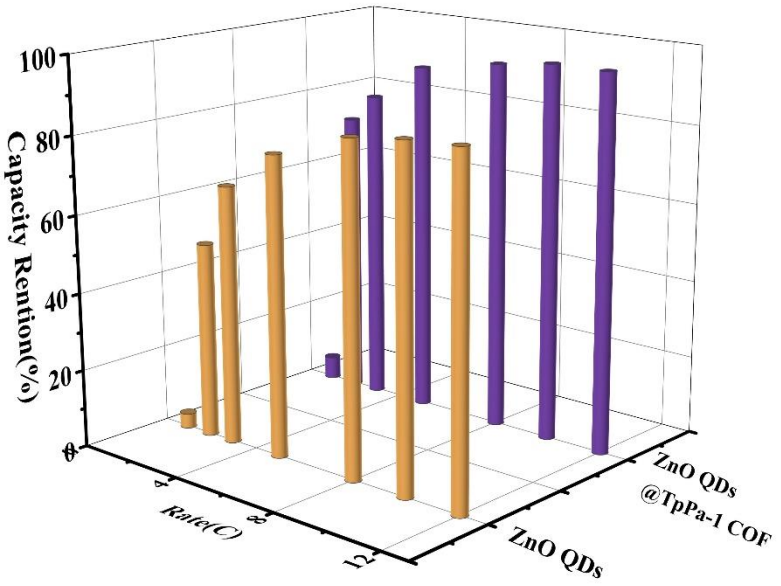


Fig. S4 Discharge capacity retention at different rates.

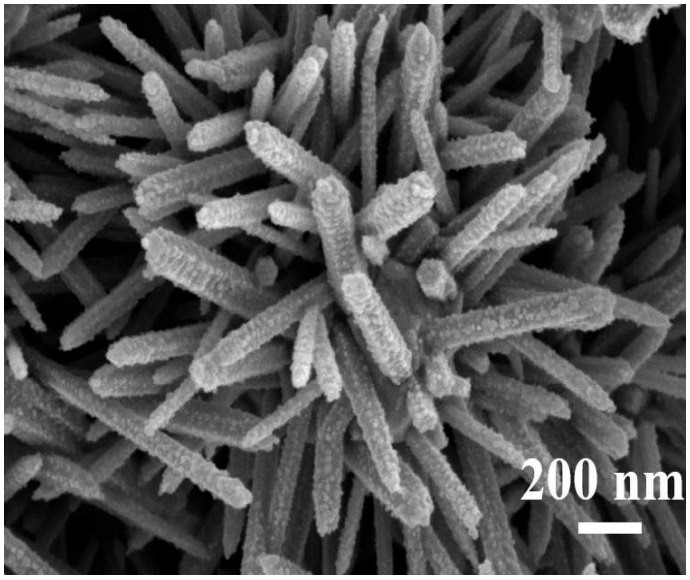


Fig. S5 SEM image of commercial ZnO electrodes after 600 cycles.

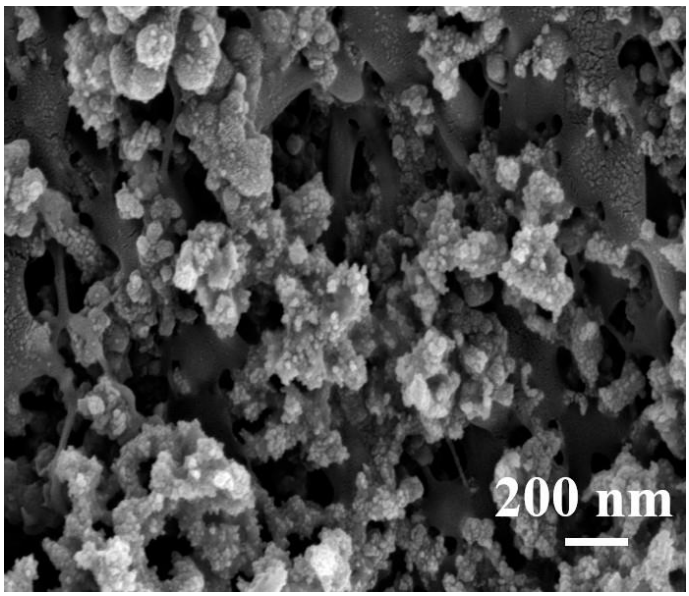


Fig. S6 SEM image of ZnO QDs electrodes after 600 cycles.

Table S1. The peak and peak difference of oxidation and reduction peaks of commercial ZnO, ZnO QDs and ZnO QDs@TpPa-1COF at 10 mV s^{-1}.

Samples	Oxidation peak(V)	Reduction peak (V)	peak difference（V）
Commercial ZnO	-1.165	-1.542	0.377
ZnO QDs	-1.156	-1.529	0.373
ZnO QDs@TpPa-1COF	-1.19	-1.536	0.346

Table S2. Corrosion current corrosion voltage parameters of in ZnO, ZnO QDs and ZnO QDs@TpPa-1COF Talfe test.

Samples	Commercial ZnO	ZnO QDs	ZnO QDs@TpPa-1COF
Ecorr/(V vs. Hg/HgO)	-1.395	-1.382	-1.339
Icorr/(mA·cm^{-2})	6.699× 10^{-2}	2.058× 10^{-2}	1.126× 10^{-2}

Table S3. Parameters of in ZnO, ZnO QDs and ZnO QDs@TpPa-1COF EIS test.

	Initial		After 200 th	
Samples	[a]Rs /(Ω)	[b]Rct/(Ω)	[a]Rs /(Ω)	[b]Rct/(Ω)
Commercial ZnO	0.61936	6.988	0.62577	22.13
ZnO QDs	0.55218	1.914	0.59274	3.112
ZnO QDs@TpPa-1COF	0.33931	0.2225	0.53925	0.81752

[a]Rs, internal resistance or equivalent series resistance.

[b]Rct, charger-transfer resistance.

Related equivalent circuit.

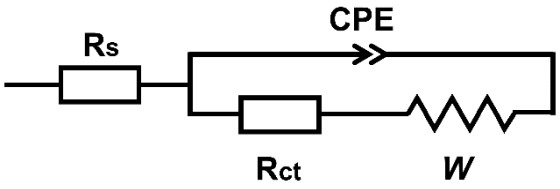


Table S4. The comparison for performances of the zinc–nickel battery based on ZnO QDs@TpPa-1COF electrode in this work with that in previous research

Anode material	**Cycle life**	**Specific capacity (mAh g^{-1})**	**Rate(C)**	**Ref.**
ZnO@MXene	1500	625	10 C	[1]
ZnO@SnO_2	1000	584	10 C	[2]
ZnO@rGO	1700	550	10 C	[3]
ZnO_{1-x}	2000	612	10 C	[4]
ZnSe @ZnO	1460	577.5	10 C	[5]
CeO_2 @ZnO	50	543	5 C	[6]
ZnO@CaC_2O_4	2100	570.7	10 C	[7]
This work	4000	576	12 C	

References

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