Constructing robust solid electrolyte interface *via* ZrO_2 coating layer for hard carbon anode in sodium-ion batteries

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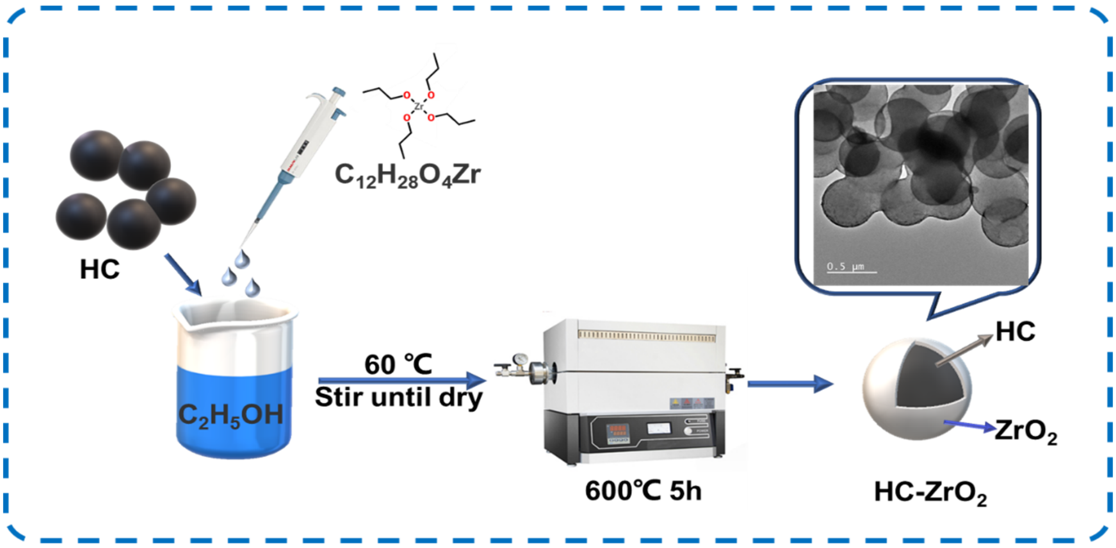
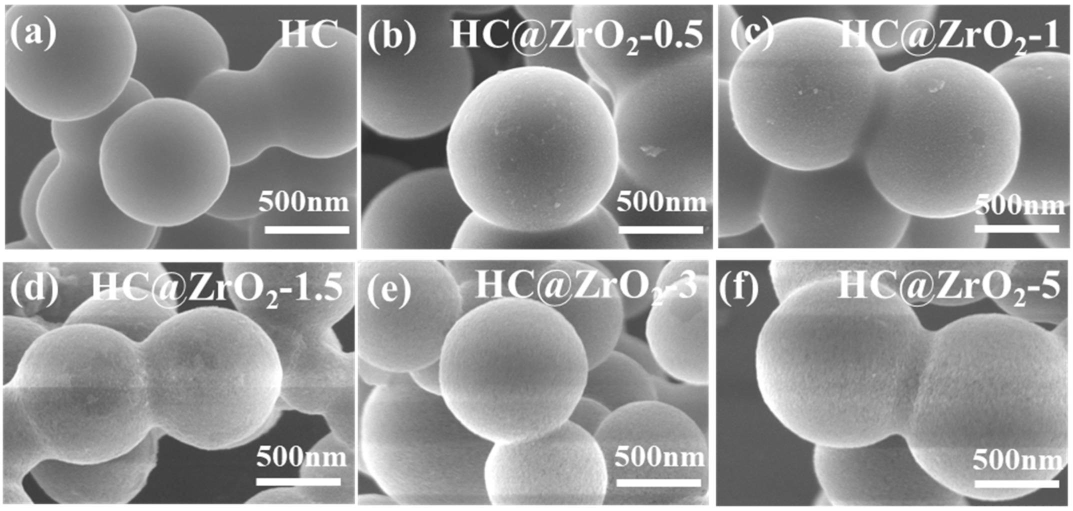
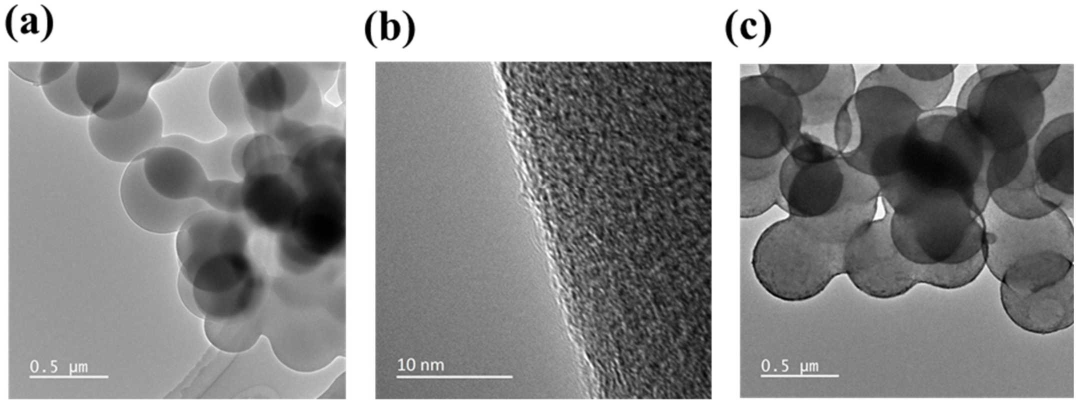
Supplementary information



Supplementary Figure S1. Schematic diagram of experimental process.



Supplementary Figure S2. SEM images of HC and HC@ZrO_2.



Supplementary Figure S3. TEM images of HC (a, b) and HC@ZrO_2-1 (c).

Supplementary Table S1. The layer spacing and corresponding crystal information of ZrO_2 (PDF #49-1642)

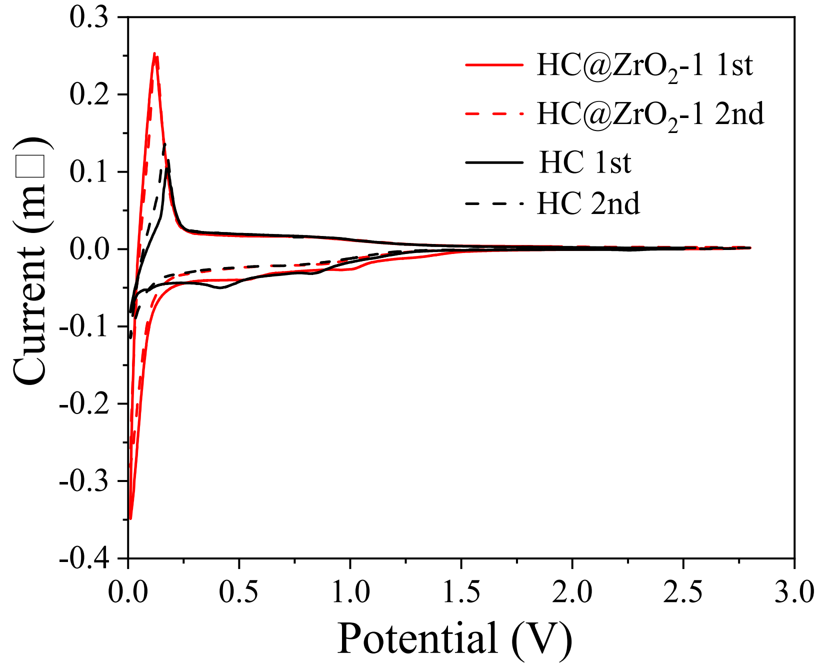
2-Theta	d (Å)	(h k l)
30.1	2.9646	(1 1 1)
34.9	2.5645	(2 0 0)
50.2	1.8152	(2 2 0)
59.7	1.5467	(3 1 1)
62.7	1.481	(2 2 2)
73.9	1.2809	(4 0 0)

Supplementary Table S2. BET results of HC and $HC@ZrO_2$-1

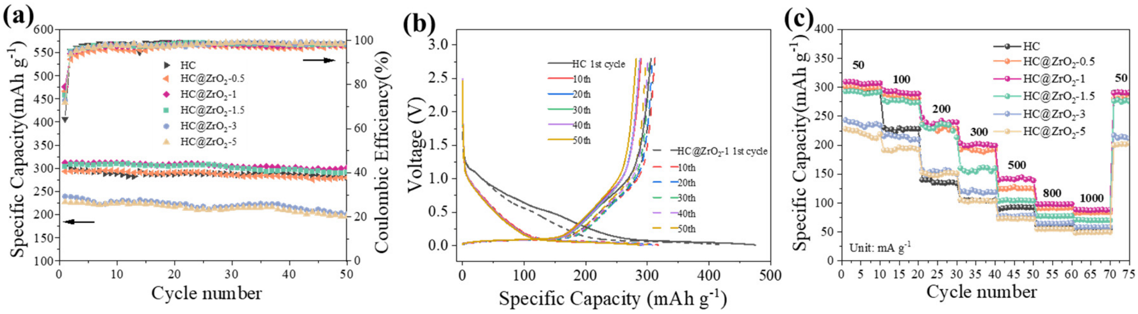
Samples	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
HC	17.84	0.014365	1.4745
$HC@ZrO_2$-1	22.35	0.021644	3.873

Supplementary Table S3. The electrochemical properties of HC and HC@ZrO_2

Samples	Charge specific capacity (m□h·g^{-1})	Discharge specific capacity (m□h·g^{-1})	ICE (%)
HC	305.8	475.1	64.4
HC@ZrO_2-0.5	305.3	395.2	77.3
HC@ZrO_2-1	313.2	395.3	79.2
HC@ZrO_2-1.5	304.4	404.6	75.2
HC@ZrO_2-3	239.5	329.1	72.8
HC@ZrO_2-5	227.5	317	71.8



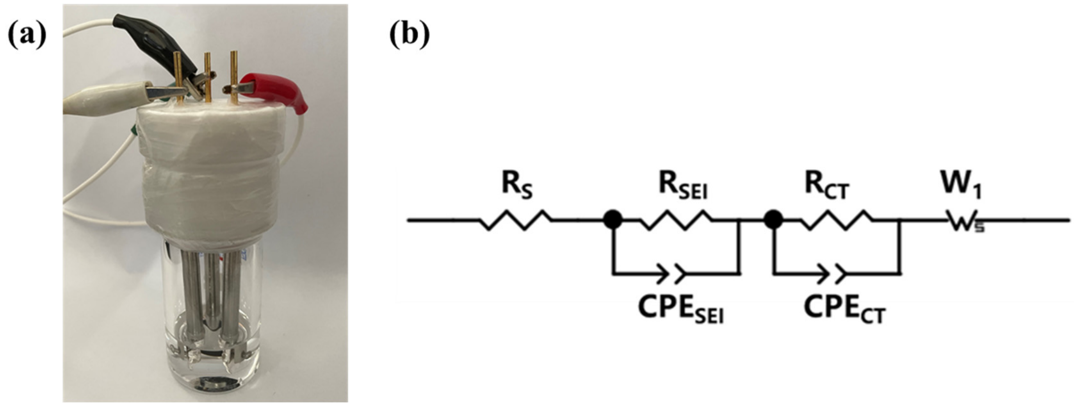
Supplementary Figure S4. The CV curves for the first two cycles for HC and HC@ZrO_2-1.



Supplementary Figure S5. (a) Cycling performance of the HC and HC@ZrO_2 electrodes at 50 m□ g^{-1}. (b) Charge-discharge profiles of the HC and HC@ZrO_2-1 electrodes at different cycles. (c) Rate performance of the HC and HC@ZrO_2 electrodes.

Supplementary Table S4. ICE literature comparison of improving HC anode of SIBs by surface engineering.

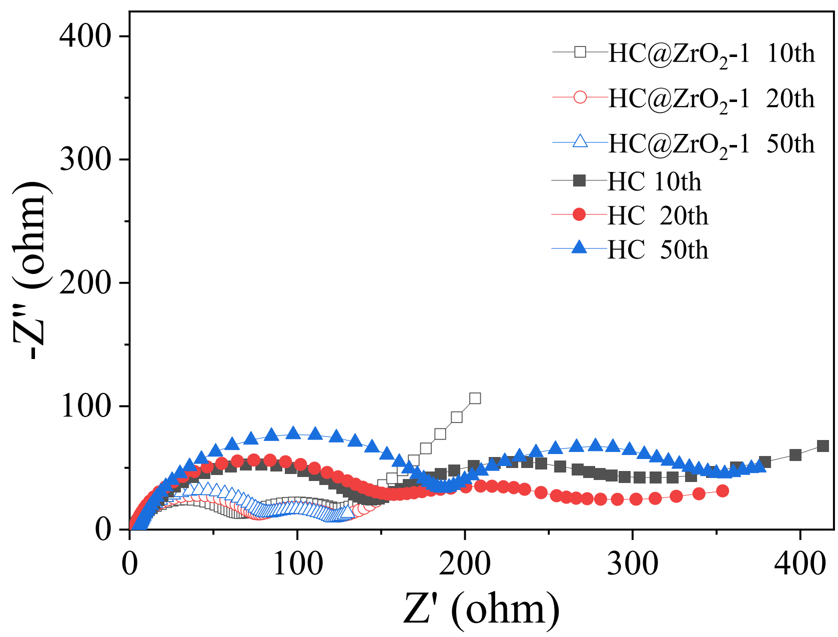
Materials	Preparation method	Electrolyte	Current density	ICE untreated	ICE after modification	Ref.
HC-$\square l_2O_3$	$\square l_2O_3$ coating in aqueous phase	1 M $NaPF_6$ in EC/DEC	50 m□ g^{-1}	64.7%	81.1%	[1]
HC-DEB□	DEB□ coating in aqueous phase	1 M $NaPF_6$ in EC/DEC	50 m□ g^{-1}	65.2%	77.2%	[2]
$\square l_2O_3$-coated HC	□tomic layer deposition	1 M $NaClO_4$ in EC/DEC	20 m□ g^{-1}	67%	75%	[3]
Hydrophilic HC	Oxygen plasma treatment	1 M $NaClO_4$ in EC/PC	50 m□ g^{-1}	51.4%	65.9%	[4]
Monodispersed HC spherules	Soft carbon coating by pyrolysis of toluene	1 M $NaClO_4$ in EC/DEC	30 m□ g^{-1}	53%	83%	[5]
HC@ZrO_2	ZrO_2 coating in aqueous phase	1 M $NaPF_6$ in EC/DEC	50 m□ g^{-1}	64.4%	79.2%	This work



Supplementary Figure S6. (a) Digital photo of three-electrode system. (b) The equivalent circuit of EIS curve.

Supplementary Table S5. The fitted results of the EIS plots using the equivalent circuit in Figure S5b.

Samples	R_s (Ω)	R_{SEI} (Ω)	R_{CT} (Ω)
HC	2.324	113.3	61.7
HC@ZrO_2-1	3.303	79.2	58.2



Supplementary Figure S7. EIS plots of HC and HC@ZrO$_2$-1 electrodes after different cycles.

Reference

[1] Yu, C.; Li, Y.; Ren, H.; Qian, J.; Wang, S.; Feng, X.; Liu, M.; Bai, Y.; Wu, C. Engineering homotype heterojunctions in hard carbon to induce stable solid electrolyte interfaces for sodium-ion batteries. *Carbon Energy*, **2022**, DOI: 10.1002/cey2.220.

[2] Yu, C.; Li, Y.; Wang, Z.; Wang, X.; Bai, Y.; Wu, C. Surface engineering based on in situ electro-polymerization to boost the initial Coulombic efficiency of hard carbon anode for sodium-ion battery. *Rare Met*. **2022**, *41*, 1616-1625.

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