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Titanicone-derived TiO_2 quantum dots@carbon encapsulated ZnO nanorods anodes for stable lithium storage

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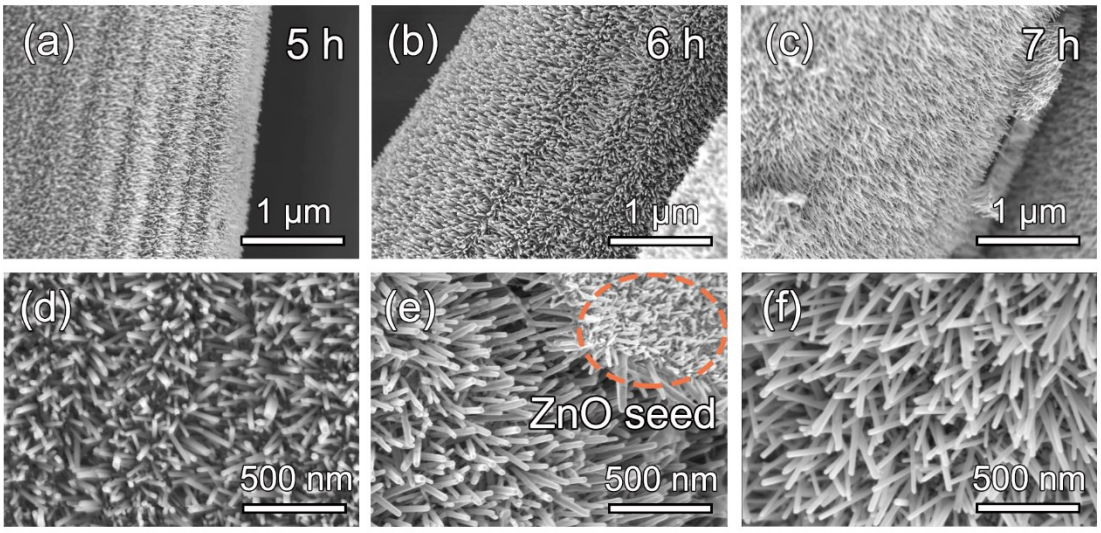

Fig. S1 FESEM images of the ZnO products obtained with different hydrothermal reaction times of (a, d) 5 h, (b, e) 6 h, and (c, f) 7 h.

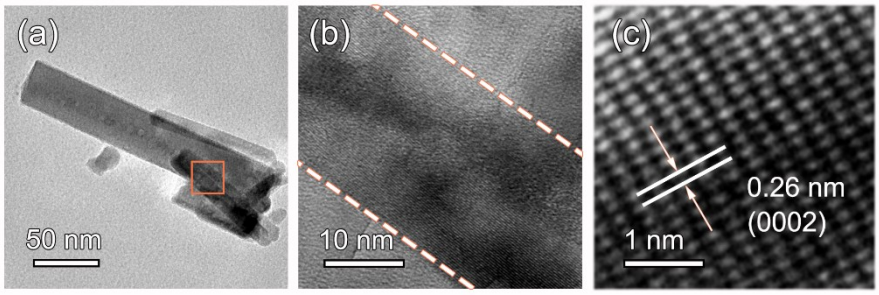

Fig. S2 (a) Low-magnification, (b) high-magnification, and (c) high resolution TEM images of ZnO NRs

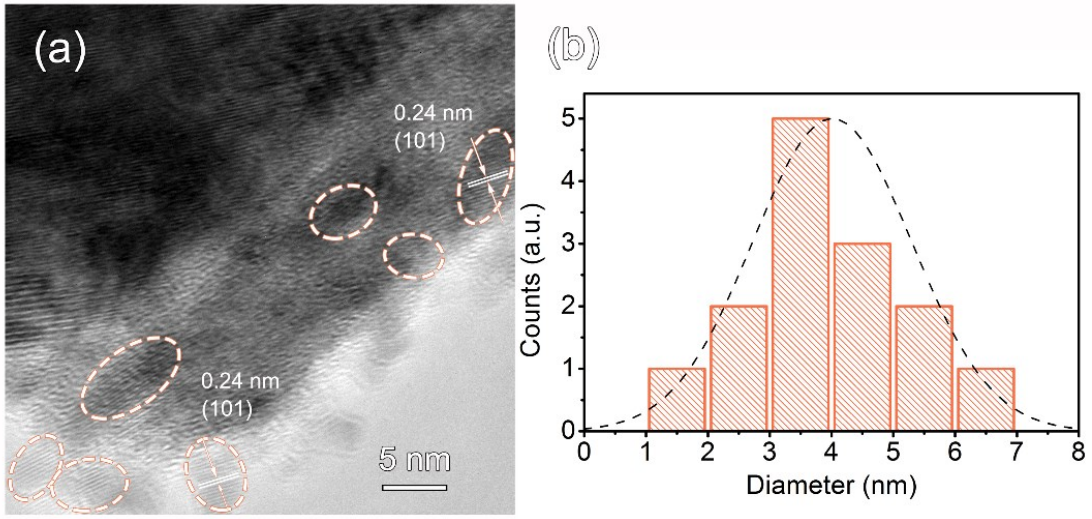

Fig. S3 (a) HRTEM image of TiO_2 QDs@carbon@ZnO NRs and (b) the corresponding diameter dispersion of the TiO_2 QDs.

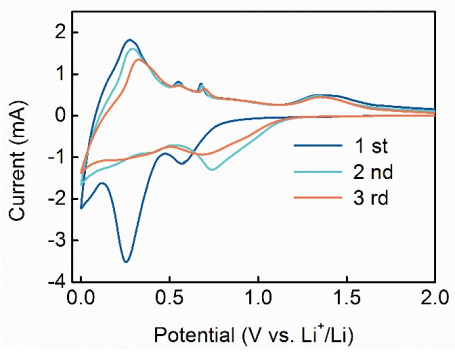

Fig. S4 The first three CV curves of the control sample of ZnO NRs anode.

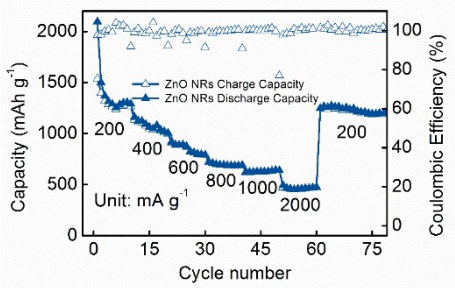

Fig. S5 Rate capacity at different current densities of ZnO nanorods sample.

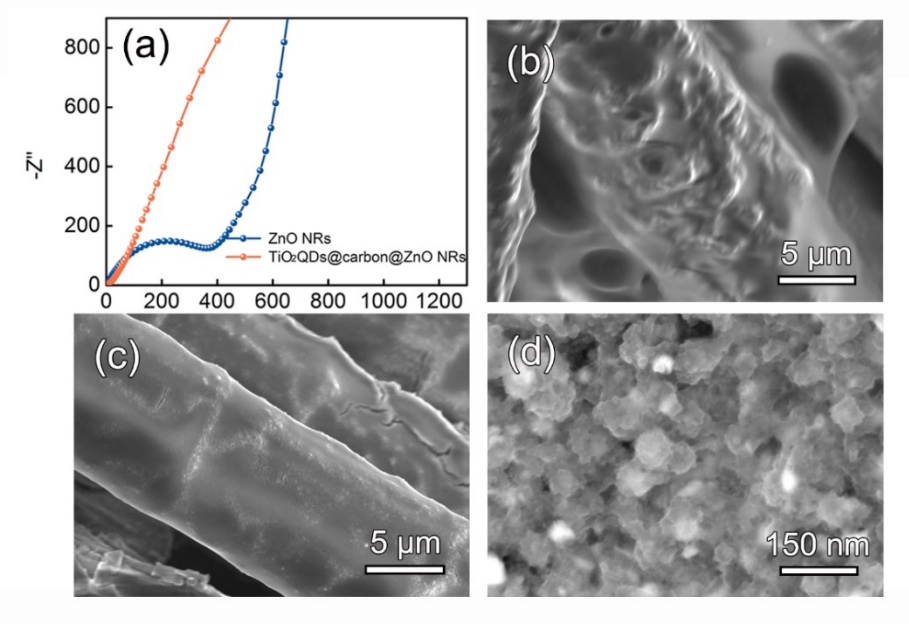

Fig. S6 (a) Nyquist plots of the TiO_2 QDs@carbon@ZnO NRs composite and the ZnO NRs electrodes before cycling. SEM images of (b) ZnO NRs and (c, d) TiO_2 QDs@carbon@ZnO NRs electrodes after 500 cycles at a current density of 2 A g^{-1}.

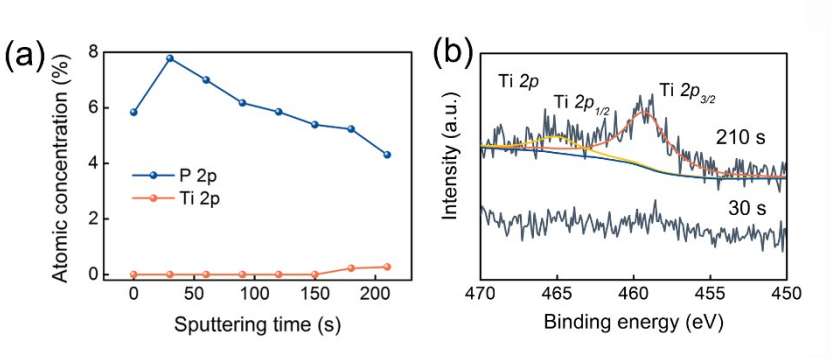

Fig. S7 XPS depth profile of TiO_2 QDs@carbon@ZnO NRs electrodes after 500 cycles. (a) Atomic concentration distribution of P and Ti elements with sputtering time. (b) Ti 2p spectra after etch time of 30 s and 210 s.

To further study the TiO_2 QDs effect on carbon matrix, we calculated the migration barriers for Li^+ transported within the pure carbon and the TiO_2 QDs@carbon layer interior using the density functional theory (DFT) as implemented in the CASTEP code. The atomic structures were fully relaxed in all calculations in both pure carbon and TiO_2 QDs@carbon. A vacuum distance in the z axis was set to 8.5 Å, which led to negligible interactions between successive slabs. The energy cut-off was set to 500 eV, and Brillouin zone integration was represented using the K-point sampling scheme of a 3×3×1 Monkhorst-Pack grid. The energy barrier (ΔE) was defined as $\Delta E=E_{TS}-E_{IS}$, where E_{TS} and E_{IS} represent the energy of the transition state and the initial state, respectively.

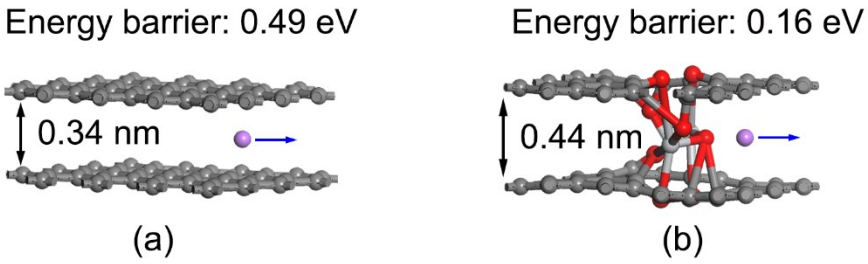

Fig. S8 Lattice spacing and Li^+ migration energy barrier of (a) the graphite and (b) TiO_2 QDs@carbon layer.

Table S1 XPS compositional ratio of TiO_2 QDs@carbon@ZnO NRs.

Sample	Atomic ratio (at %)			
	Ti	C	O	Zn
TiO_2 QDs@carbon@ZnO	7.42	46.34	33.54	12.70

Table S2 Main synthesis methods and electrochemical performance for the ZnO-based electrodes with different morphologies.

Morphology	Synthetic method	Current density ($A\ g^{-1}$)	Cycle number	Specific capacity ($mA\ h\ g^{-1}$)	Ref.
ZnO on carbon black	ALD	0.1	500	1026	[1]
ZnO/NiO microspheres	Solvothermal	0.1	200	1008.6	[2]
ZnO@$ZnSnO_3$ QDs NR	CBD	0.2	110	1073	[3]
ZnO@C nanoflower	Hydrothermal	0.1	80	1200	[4]
		5	500	420	
ZnO@TiO_2 heterostructure	ALD	1	250	1000	[5]
ZnO QDs/graphene	ALD	0.1	50	960	[6]
ZnO@ZnO QDs/C	Hydrothermal	0.5	100	699	[7]
CNT@ZnO composites	Liquid-phase method	0.1	50	709.2	[8]
ZnO@CF	Hydrothermal	0.1	200	850	[9]
TiO_2 QDs@carbon@ZnO composite	MLD	0.2	100	1154	**This work**
		2	500	470	

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