

## Supplementary Information

### Modified preparation of Si@C@TiO<sub>2</sub> porous microspheres as anodes for high-performance lithium-ion batteries

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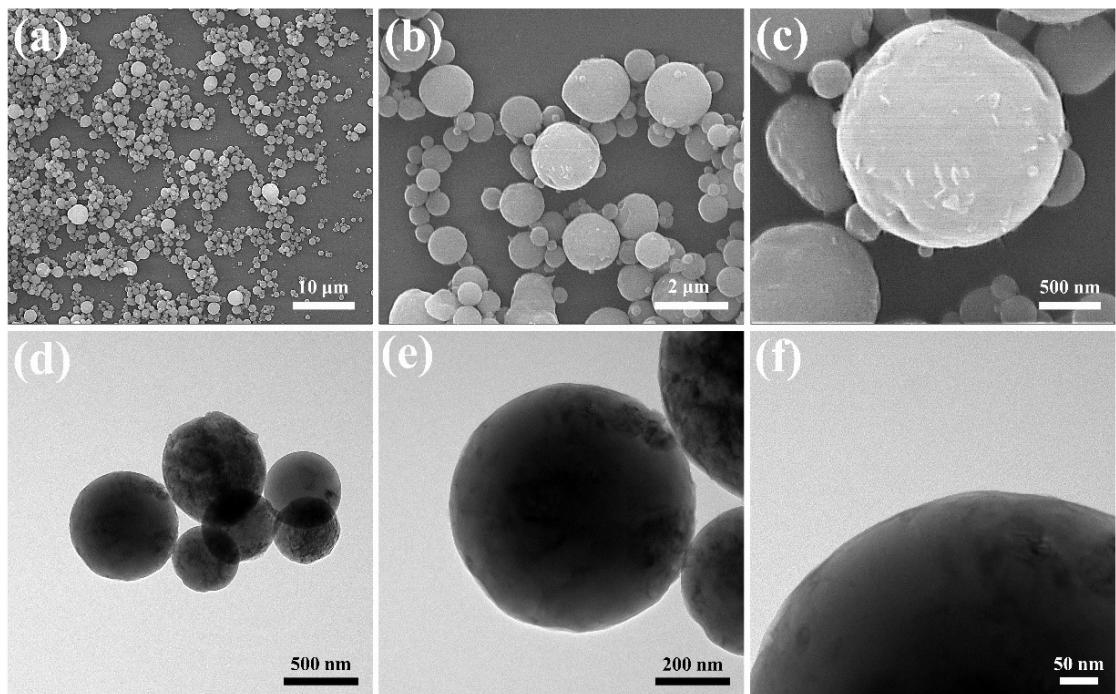
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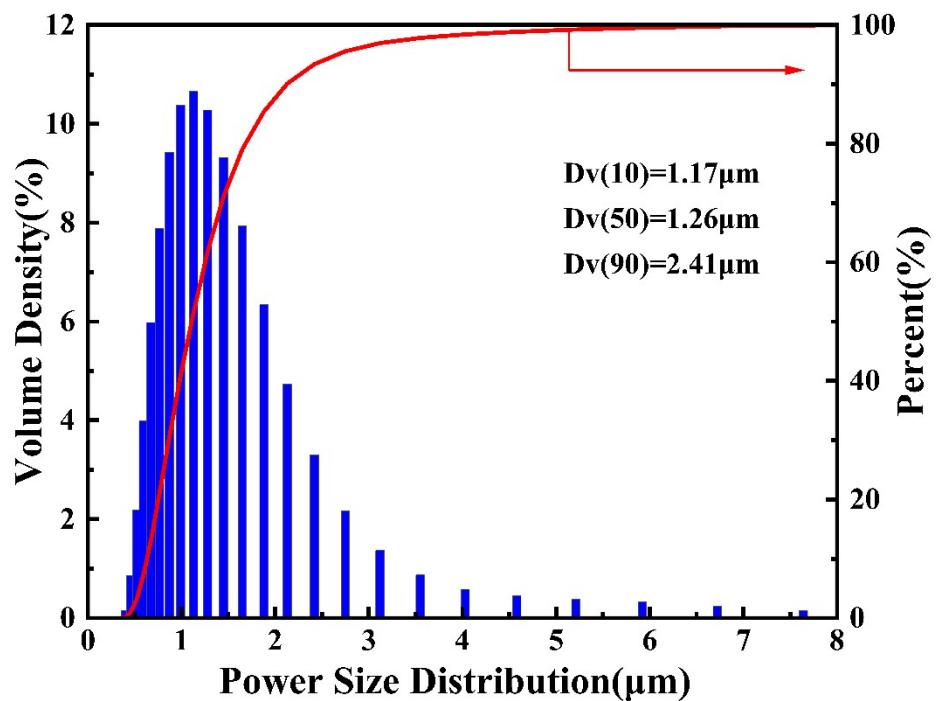
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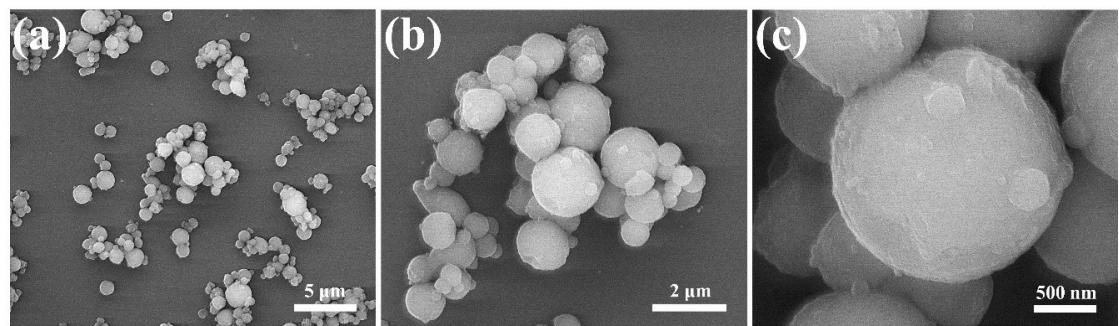
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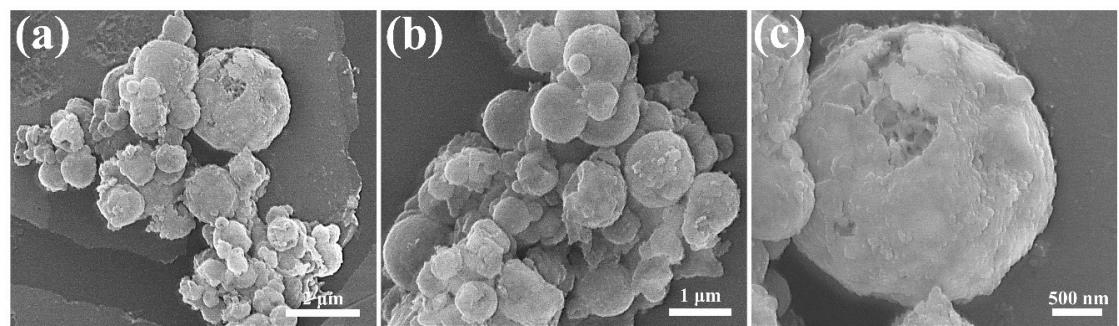
**Figure S1.** SEM and TEM images of the Al-Si powders.



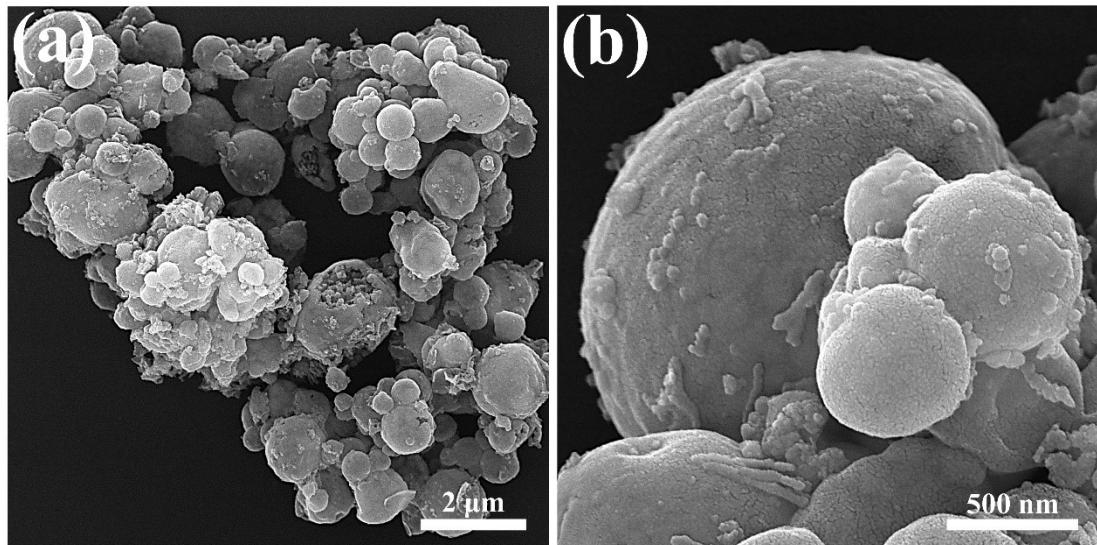
**Figure S2.** Particle size distribution of the Al-Si powders.



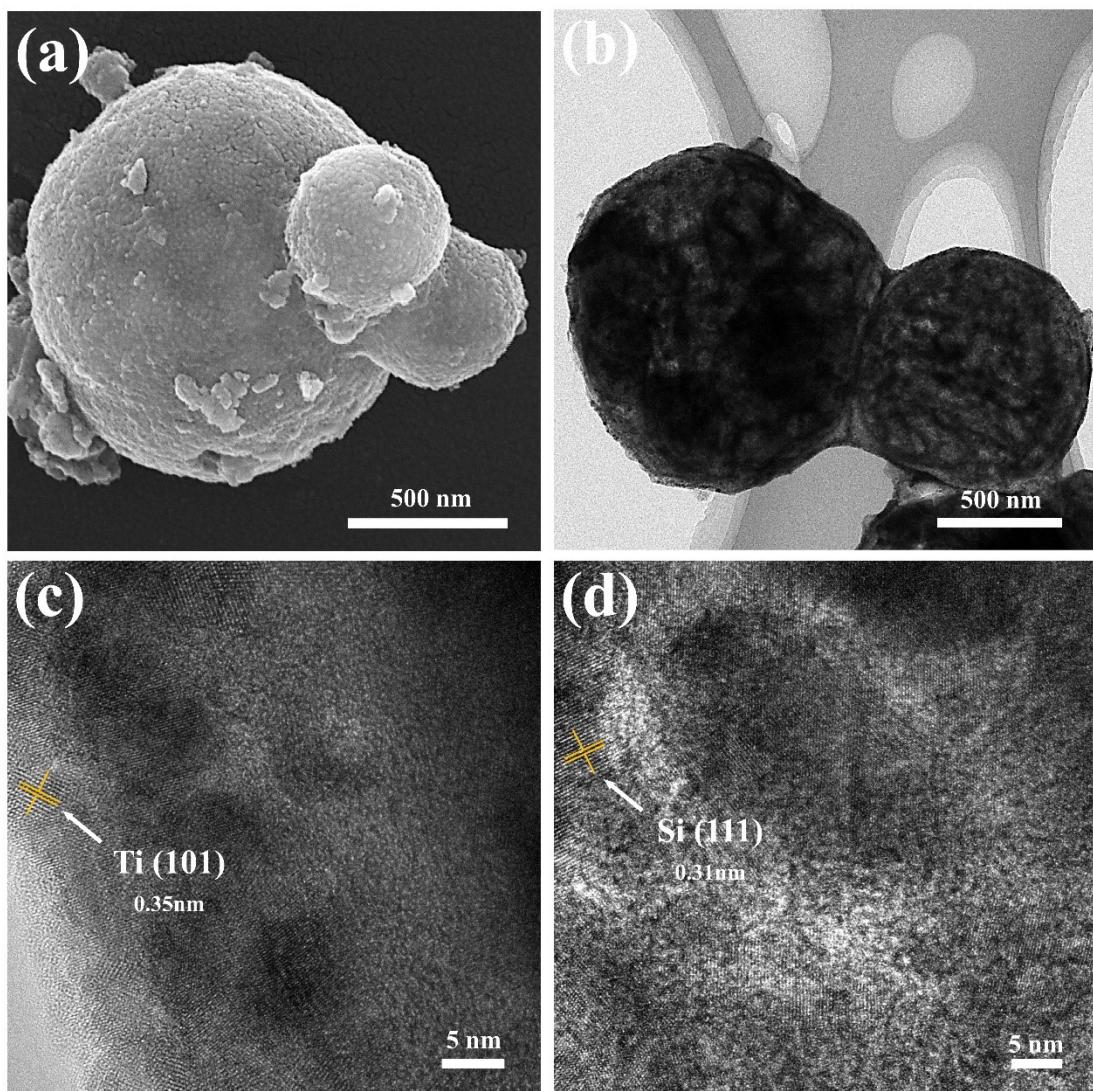
**Figure S3.** SEM images of the Al-Si@RF microspheres.



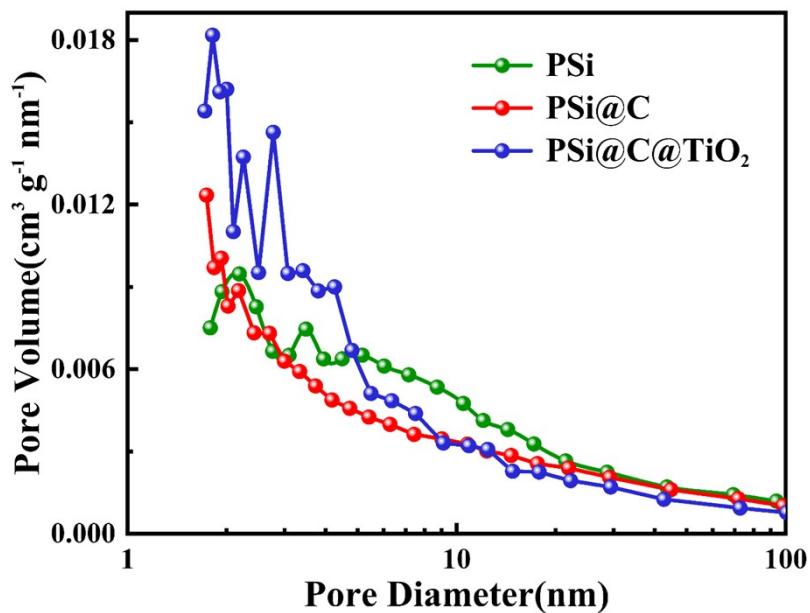
**Figure S4.** SEM images of the PSi@RF microspheres.



**Figure S5.** SEM images of the PSi@C microspheres.



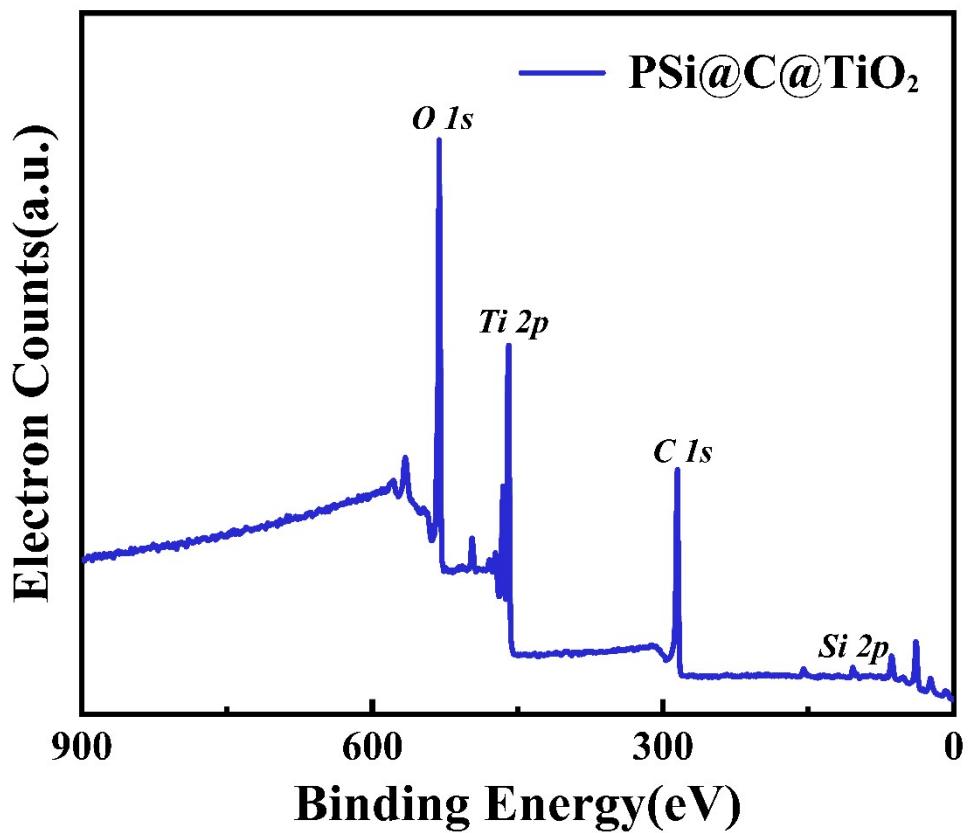
**Figure S6.** SEM and TEM images of the PSi@C@TiO<sub>2</sub> microspheres.



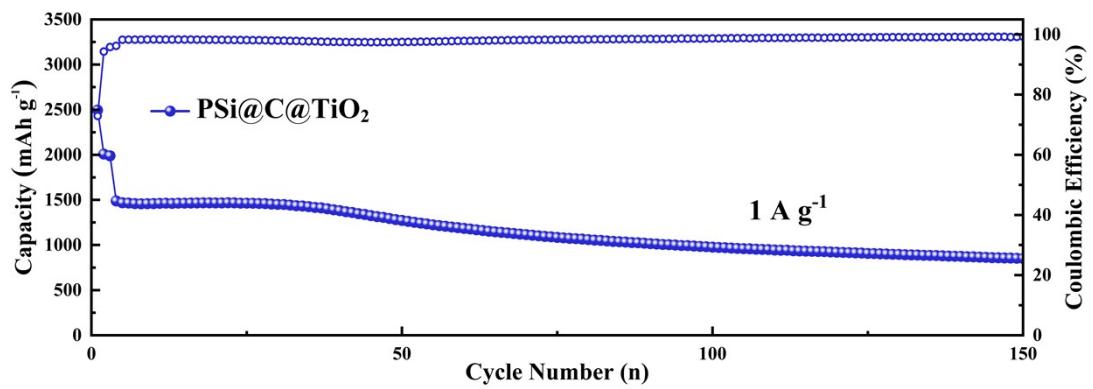
**Figure S7.** The pore size distribution diagrams of the PSi, PSi@C and PSi@C@TiO<sub>2</sub> microspheres.

**Table S1.** Geometric parameters of sample. (Total surface:  $S_{\text{BET}}$ ; Volume of pores in the range of 1.7–300 nm in diameter:  $V_{1.7-300 \text{ nm}}$ ; Average pore size:  $P_{\text{BJH}}$ ).

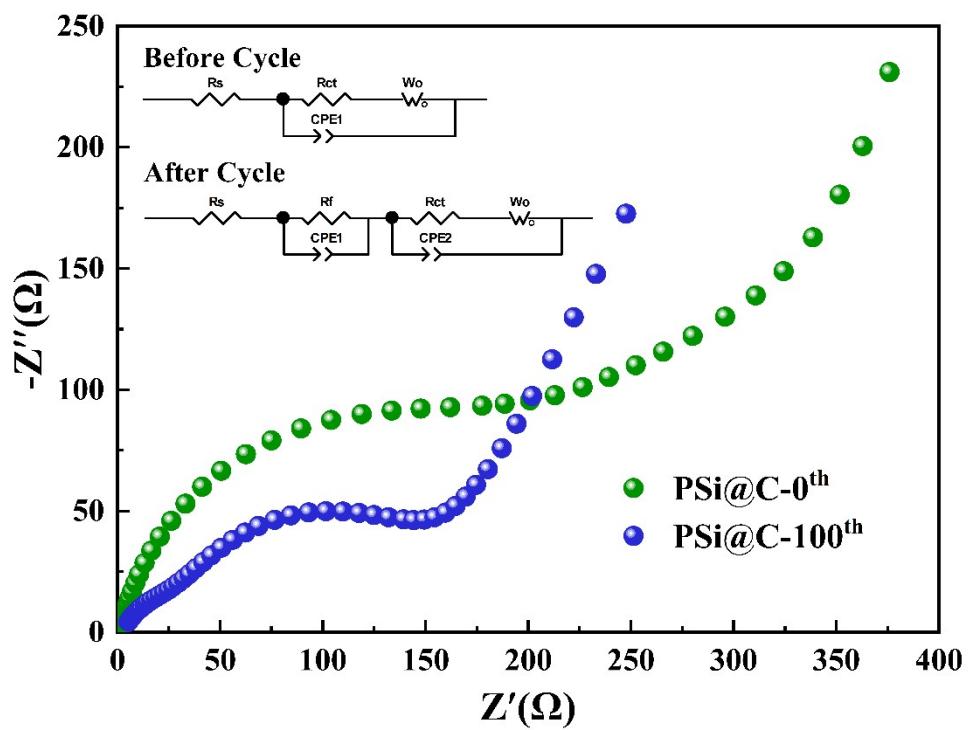
Samples	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_{1.7-300 \text{ nm}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$P_{\text{BJH}}$ (nm)
PSi	68.7	0.293	10.7
PSi@C	143.2	0.268	16.8
PSi@C@TiO <sub>2</sub>	125.3	0.255	12.5



**Figure S8.** XPS survey of the PSi@C@TiO<sub>2</sub> microspheres.



**Figure S9.** The cycling performance of the  $\text{PSi}@\text{C}@\text{TiO}_2$  electrode at  $0.1 \text{ A g}^{-1}$  for the first three cycles and  $1 \text{ A g}^{-1}$  for the subsequent cycles.



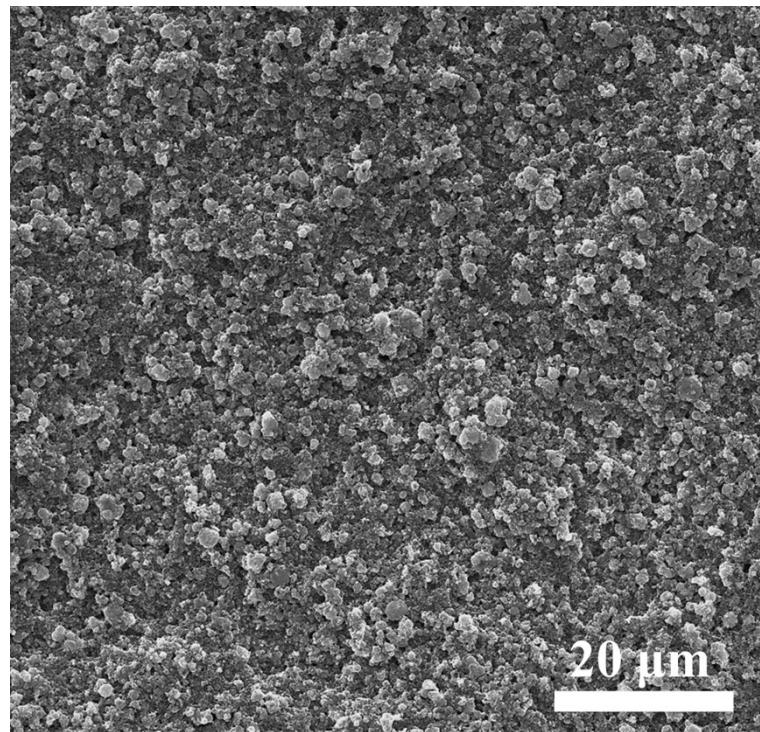
**Figure S10.** Nyquist plots and equivalent circuits of the  $PSi@C$  electrode at different cyclic states.

**Table S2.** Electrode kinetic parameters calculated by fitting the EIS curves in Fig. 5f and Fig. S10.

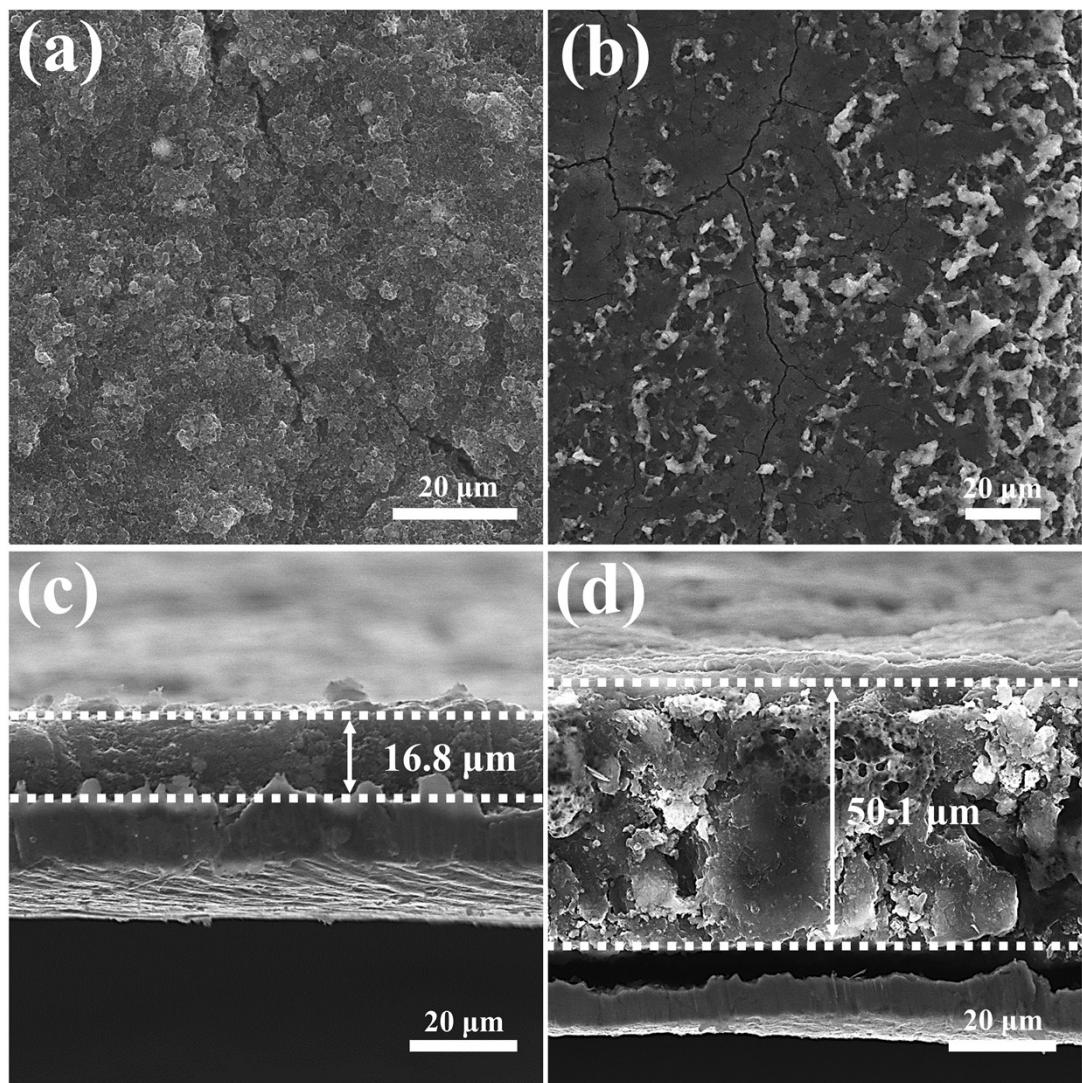
Cycle number	Resistance	PSi	PSi@C	PSi@C@TiO <sub>2</sub>
<b>Before cycle</b>	$R_s(\Omega)$	1.245	1.328	1.093
	$R_{ct}(\Omega)$	141.5	177	92.08
<b>After 100 cycles</b>	$R_s(\Omega)$	5.284	2.615	2.175
	$R_f(\Omega)$	35.38	26.19	7.909
	$R_{ct}(\Omega)$	159.9	124.4	26.05

**Table S3.** The electrochemical performance of the PSi@C@TiO<sub>2</sub> microspheres and other reported Si-based materials as anodes for LIBs.

Materials	Content of Si (%)	Cycling performance (mAh g <sup>-1</sup> )	Rate capacity (mAh g <sup>-1</sup> )	ICE (%)	Electrode thickness swelling	Refs.
Porous Si sponge	40	570 after 1000 cycles at 1 A g <sup>-1</sup>	410 at 4.2 A g <sup>-1</sup>	56	30%	<sup>1</sup>
TC-SiO	-	674.5 after 100 cycles at 0.14 A g <sup>-1</sup>	~800 at 1.4 A g <sup>-1</sup>	71.9	-	<sup>2</sup>
SiO <sub>x</sub> -TiO <sub>2</sub> @C	70.6 (SiO <sub>x</sub> )	910 after 200 cycles at 0.1 A g <sup>-1</sup>	542 at 3.2 A g <sup>-1</sup>	62.5	-	<sup>3</sup>
Hollow Si@TiO <sub>2</sub> @C	67.2	1270 after 250 cycles at 1 A g <sup>-1</sup>	730 at 8 A g <sup>-1</sup>	86.0 6	45.6%	<sup>4</sup>
Compacted SiO <sub>x</sub> /G/C granules	31	487 after 500 cycles at 0.3 A g <sup>-1</sup>	610 at 3 A g <sup>-1</sup>	84.3	13.7%	<sup>5</sup>
Si@TiO <sub>2</sub>	~95	1580 after 50 cycles at 0.42A g <sup>-1</sup>	-	80.8	-	<sup>6</sup>
Si@TiO <sub>2</sub> /NC	-	1070 after 100 cycles at 0.2 A g <sup>-1</sup>	627 at 3 A g <sup>-1</sup>	75.9	-	<sup>7</sup>
p-SiO <sub>x</sub> @TiO <sub>2</sub> @C	~44	801 after 100 cycles at 0.28 A g <sup>-1</sup>	414 at 7 A g <sup>-1</sup>	67	20%	<sup>8</sup>
Si/C@TiO <sub>2</sub>	53	1077 after 100 cycles at 0.2 A g <sup>-1</sup>	749.4 at 5 A g <sup>-1</sup>	75	-	<sup>9</sup>
PSi@C@ TiO <sub>2</sub>	65.2	1041 after 250 cycles at 0.5 A g <sup>-1</sup>	745 at 5 A g <sup>-1</sup>	73	35.3%	In this work



**Figure S11.** SEM images of the pristine PSi@C@TiO<sub>2</sub> electrode.



**Figure S12.** SEM images of the PSi@C electrode after 100 cycles (a-b). Cross-sectional SEM image of the PSi@C electrode: before cycling (c) and after 100 cycles (d) at  $0.5 \text{ A g}^{-1}$ .

## **References:**

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