Supplementary Materials for

Intrinsic Surface-Redox Sodium-Ion Storage Mechanism of Anatase Titanium Oxide toward High-Rate Capability

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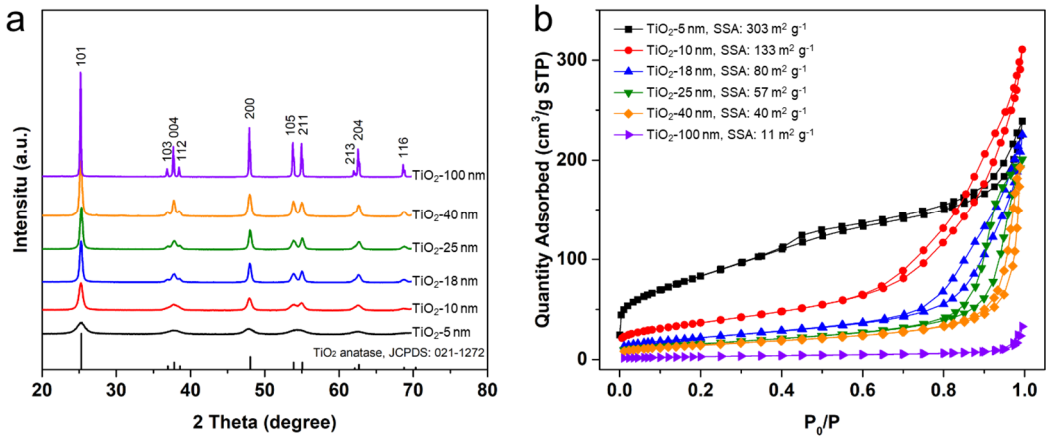
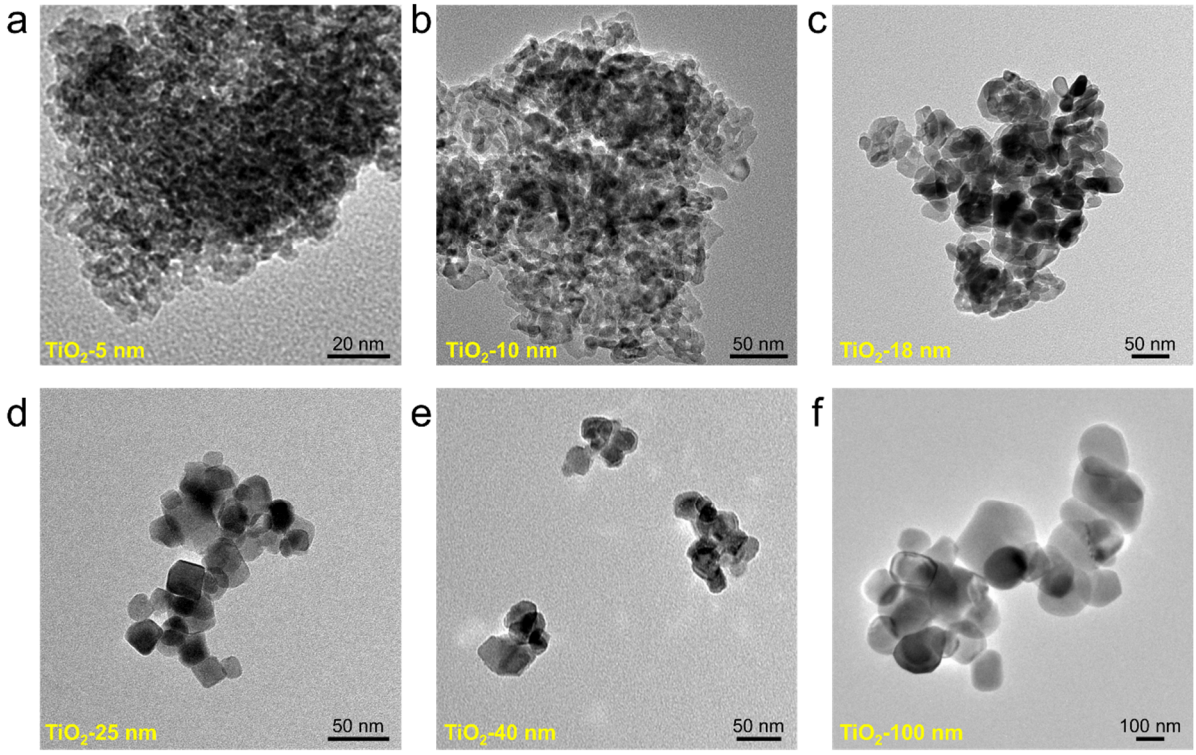
Supplementary Section 1. Materials Characterizations



Supplementary Figure 1. (a) XRD patterns of TiO_2 nanoparticles (NPs) and (b) the N_2 adsorption-desorption isotherms of TiO_2 NPs. The average crystallite sizes of the TiO_2 NPs were calculated according to the Scherrer formula $d = 0.9\lambda_{Cu}/\omega$, where d is the crystallite size, λ_{Cu} = 1.5406 Å is the X-ray wavelength, and ω is full width at half-maximum of the diffraction peak. The calculated results of TiO_2 NPs are ~5, 10, 18, 25, 40 and 100 nm, respectively.



Supplementary Figure 2. TEM images of TiO_2 NPs. (a) TiO_2-5 nm, (b) TiO_2-10 nm, (c) TiO_2-18 nm, (d) TiO_2-25 nm, (e) TiO_2-40 nm, and (f) TiO_2-100 nm.

Supplementary Table 1. Morphology of different TiO_2 NPs.

Sample	NP's size calculated based on Scherrer formula	BET specific surface area (SSA)	NP's size calculated based on SSA
TiO_2-5 nm	4.96 nm	303 m^2 g^{-1}	5.18 nm
TiO_2-10 nm	9.86 nm	133 m^2 g^{-1}	11.81 nm
TiO_2-18 nm	17.93 nm	80 m^2 g^{-1}	19.63 nm
TiO_2-25 nm	24.68 nm	57 m^2 g^{-1}	27.55 nm
TiO_2-40 nm	39.82 nm	40 m^2 g^{-1}	39.27 nm
TiO_2-100 nm	98.23 nm	11 m^2 g^{-1}	142.79 nm

Supplementary Section 2. Specific capacity calculations of TiO_2 NPs.

In this work, composite electrodes consist of the active material (TiO_2), conductive carbon additive (Ketjen black), and binder (carboxyl methyl cellulose [CMC] and styrene butadiene rubber [SBR]). As a rigorous approach to isolate the capacity from the TiO_2 alone, additional sodiation capacity from the conductive carbon additive is measured for removal. The total capacity of electrode (Q_{total}) is measured by an electrochemical workstation, and can be divided into Q_{TiO_2} and Q_{carbon}.

$$Q_{total} = Q_{TiO_2} + Q_{carbon}$$

$$Q_{total} = Q_{S,TiO_2} \times m_{TiO_2} + Q_{S,carbon} \times m_{carbon}$$

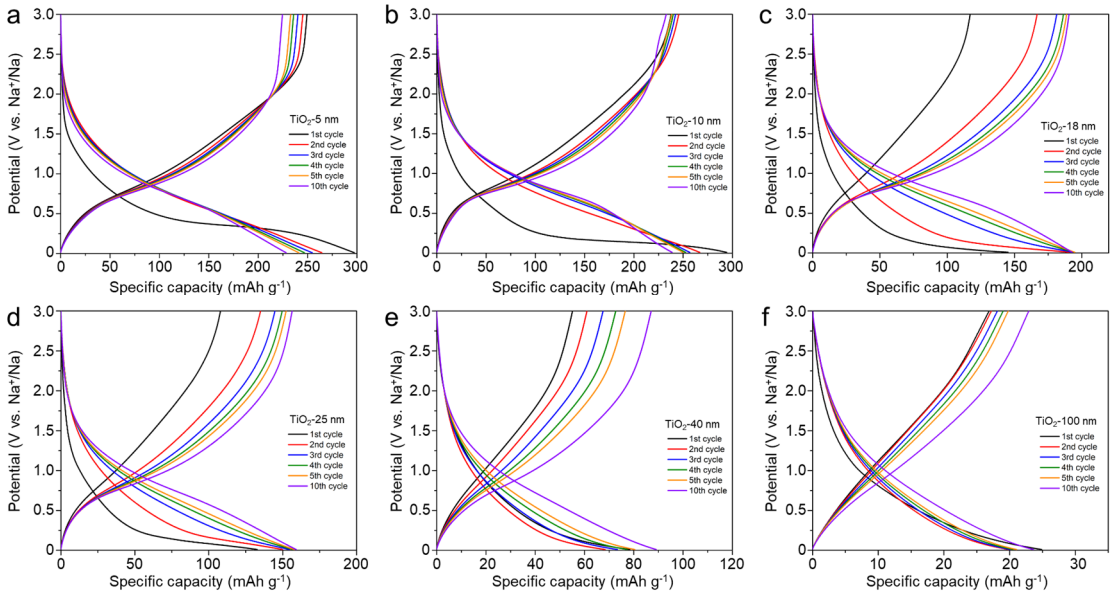
The specific capacity of carbon additive ($Q_{S,carbon}$) was measured through making an electrode consisting of 90 wt.% carbon additive, and 5 wt.% CMC + 5 wt.% SBR. The measured $Q_{S,carbon}$ is 124 mAh g^{-1} at a specific current of 0.05 A g^{-1} in the potential range of 0.01-3 V *vs.* Na^+/Na.

Here, the TiO_2 electrode consists of 85 wt.% TiO_2 NPs, 7 wt.% Ketjen black, and 4 wt.% CMC + 4 wt.% SBR. The weight of an electrode (m_{total}) is measured with an electronic balance. By removing the contribution from the carbon additives, the specific capacity of TiO_2 (Q_{S,TiO_2}) is calculated according to the following equation.

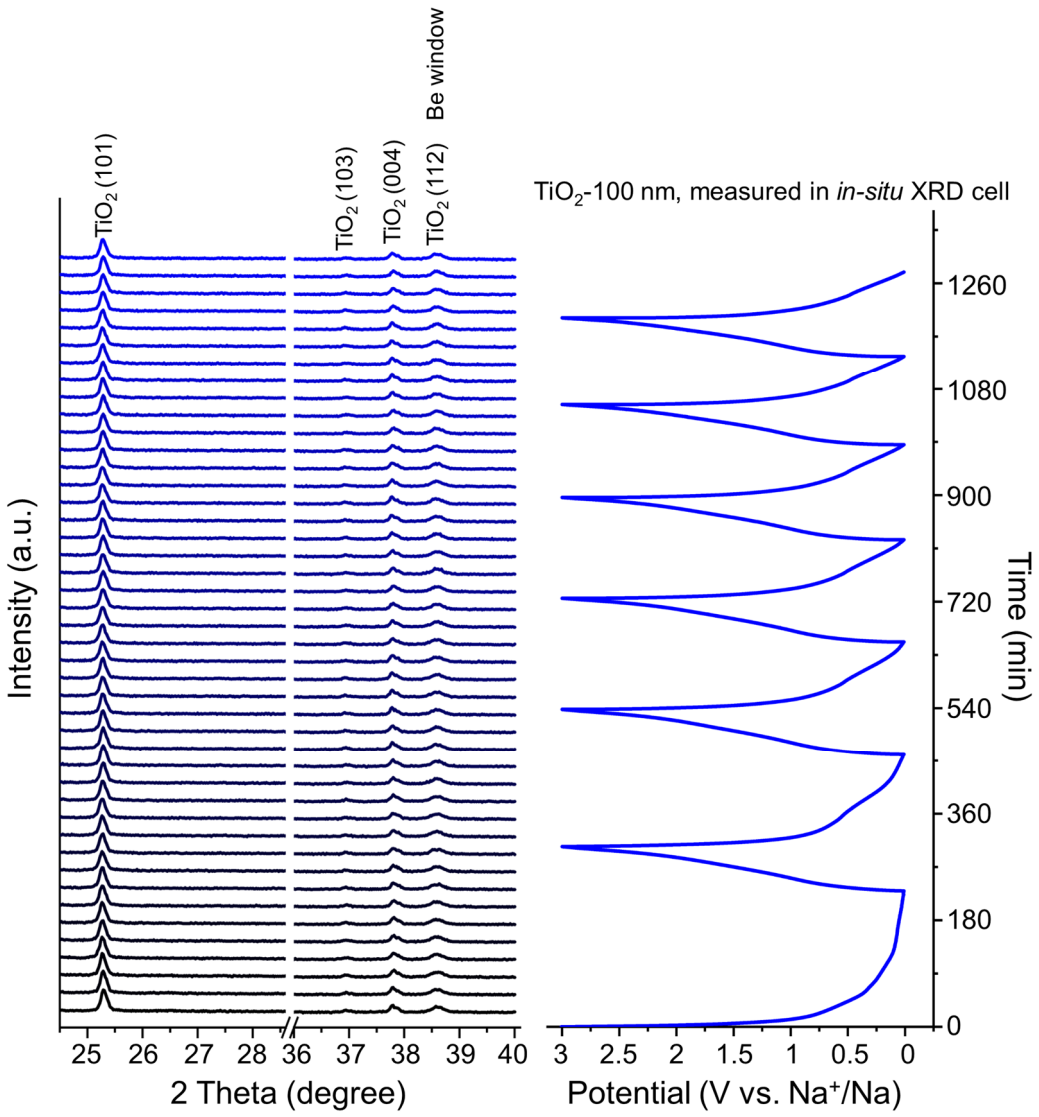
$$Q_{S,TiO_2} = (Q_{total} - 124\ mAh\ g^{-1} \times m_{carbon})/m_{TiO_2}$$

$$Q_{S,TiO_2} = (Q_{total} - 124\ mAh\ g^{-1} \times 0.07 m_{total})/0.85 m_{total}$$

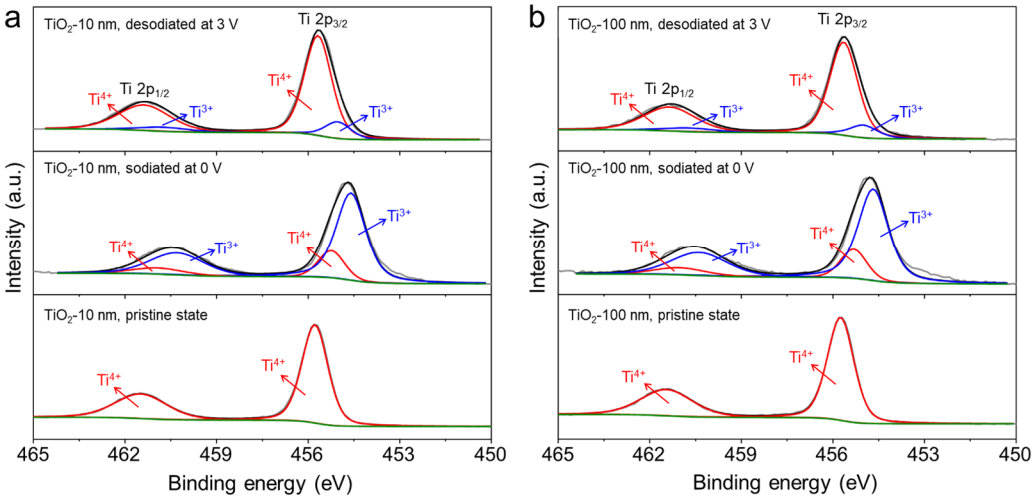
Supplementary Section 3. Electrochemical sodium-ion storage of TiO_2 NPs.



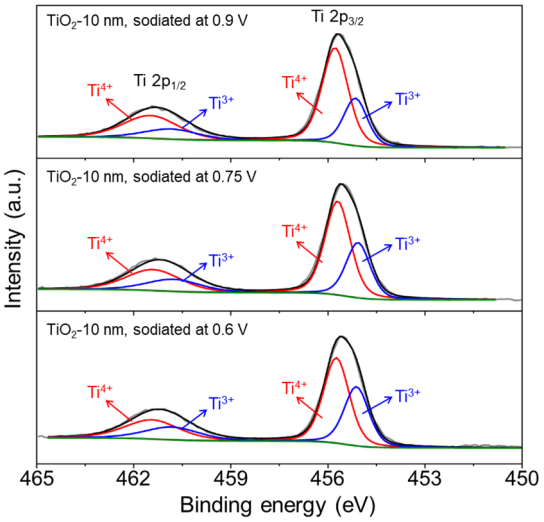
Supplementary Figure 3. The charge and discharge curves of the TiO_2 NPs at 0.1 A g^{-1}. (a) TiO_2-5 nm, (b) TiO_2-10 nm, (c) TiO_2-18 nm, (d) TiO_2-25 nm, (e) TiO_2-40 nm, and (f) TiO_2-100 nm.



Supplementary Figure 4. *In-situ* XRD patterns of TiO_2-100 nm. The electrochemical performance was measured using an in-situ XRD cell using Be foil as both the X-ray transparent window and current collector. As a result of this cell design, side reactions and electrolyte decomposition were more pronounced, leading to the longer initial sodiation curve when compared to the electrochemical performance measured in coin cell (Supplementary Figure 3f).



Supplementary Figure 5. Ex-situ XPS spectra analysis. (a) Ti 2p spectra of the TiO_2-10 nm electrode at different states. (b) Ti 2p spectra of the TiO_2-100 nm electrode at different states. Based on the fitting results (Supplementary Table 2), it is found that both materials exhibit the presence of the same amorphous surface composition (Na_xTiO_2 with $x = 0.8$).



Supplementary Figure 6. Ti 2p spectra of the TiO_2-10 nm electrode at potentials of 0.9 V, 0.75 V and 0.6 V *vs.* Na^+/Na, after 3 cycles. According to Supplementary Table 2, it is found that the sodiation peak at ~0.75 V is mainly based on the redox of Ti^{4+}/Ti^{3+}.

Supplementary Table 2. Analysis of *ex-situ* XPS peaks for the TiO_2-10 nm and TiO_2-100 nm. The peak separation between Ti $2p_{3/2}$ and Ti $2p_{1/2}$ is 5.7 eV and the areas of the peaks are in the ratio of 2:1.

Sample	Position (eV)	Ti $2p_{3/2}$ (4+) 455.8 ± 0.2		Ti $2p_{1/2}$ (4+) 461.5 ± 0.2		Ti $2p_{3/2}$ (3+) 455.1 ± 0.2		Ti $2p_{1/2}$ (3+) 460.8± 0.2	
TiO_2 10 nm, pristine state	area	96818		48409		--		--	
	percentage		100%				--		
TiO_2 10 nm, sodiated at 0.01 V	area	5466		2733		22904		11452	
	percentage		19.3%				80.7%		
TiO_2-10 nm, desodiated at 3 V	area	53980		26990		8590		4295	
	percentage		86.3%				13.7%		
TiO_2-100 nm, pristine state	area	55720		27860		--		--	
	percentage		100%				--		
TiO_2-100 nm, sodiated at 0.01 V	area	1996		998		8114		4057	
	percentage		19.7%				80.3%		
TiO_2-100 nm, desodiated at 3 V	area	17670		8835		2650		1325	
	percentage		87.0%				13.0%		
TiO_2-10 nm, sodiated at 0.9 V	area	22256		11128		9835		4917.5	
	percentage		69.4%				30.6%		
TiO_2-10 nm, sodiated at 0.75 V	area	20796		10398		11444		5722	
	percentage		64.5%				35.5%		
TiO_2-10 nm, sodiated at 0.6 V	area	19322		9661		12940		6470	
	percentage		59.9%				40.1%		

Supplementary Table 3. The specific capacity of the TiO_2 NPs (this work) and previously reported TiO_2 with different particle sizes.

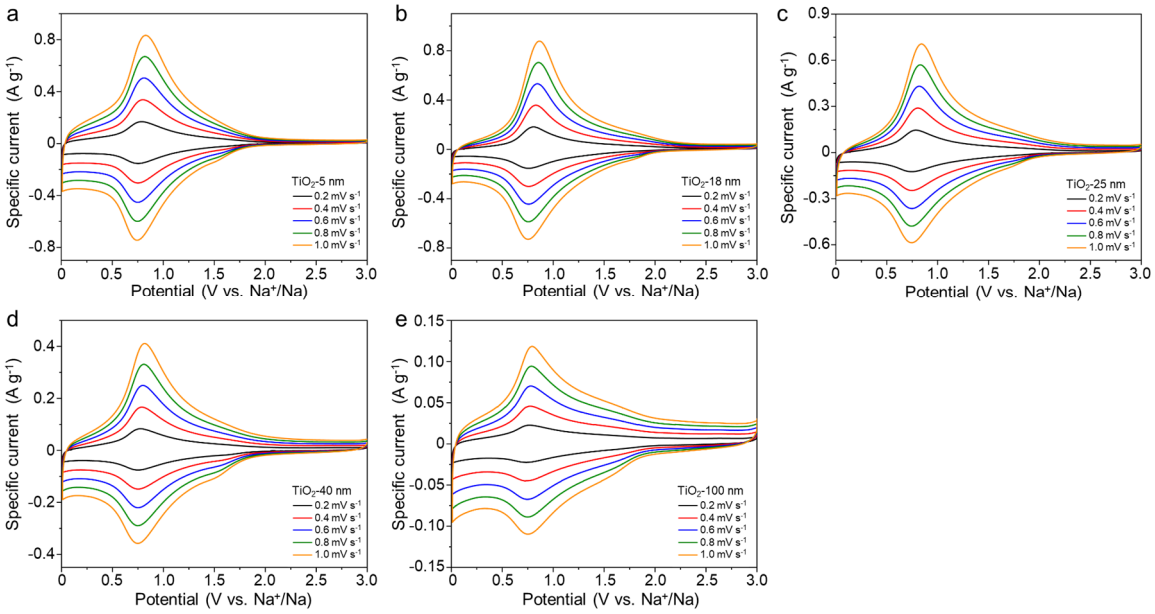
Sample	Particle size (nm)	Specific surface area ($m^2 g^{-1}$)	Specific capacity ($mAh g^{-1}$)	Testing conductions	Electrode composite
TiO_2-5 nm [this work]	4.96*	303	265	at 100 mA g^{-1} in 0.01-3 V	TiO_2:KJB:CMC:SBR =85:7:4:4
TiO_2-10 nm [this work]	10.21*	133	264		
TiO_2-18 nm [this work]	17.93*	80	195		
TiO_2-25 nm [this work]	24.68*	57	161		
TiO_2-40 nm [this work]	39.82*	40	102		
TiO_2-100 nm [this work]	98.23*	11	40		
TiO_2(A) NPs (30 nm) [1]	30	--	150	at 33.5 mA g^{-1} in 0.1-2 V	TiO_2:Super C65:CMC =70:20:10
TiO_2(A)@C NPs (~11 nm) [2]	11	119.8	227	at 33.5 mA g^{-1} in 0.05-2 V	TiO_2:Super C65:PVdF =65:25:10
TiO_2(A) NPs (<25 nm) [3]	<25	--	192	at 0.1 A g^{-1} in 0.01-3 V	TiO_2:CB:PVdF =70:20:10
TiO_2(A) NPs (22.5 nm) [4]	22.5*	80.72	188	at 33.6 mA g^{-1} in 0.01-3 V	TiO_2:SP:CMC =70:15:15
TOC-80 [5]	15*	124	243	at 84 mA g^{-1} in 0.01-2.5 V	TiO_2:SP:CMC =70:15:15
TOC-150 [5]	19*	76	223		
TOC-300 [5]	22*	61	187		

* calculated based on Scherrer formula; CB: carbon black

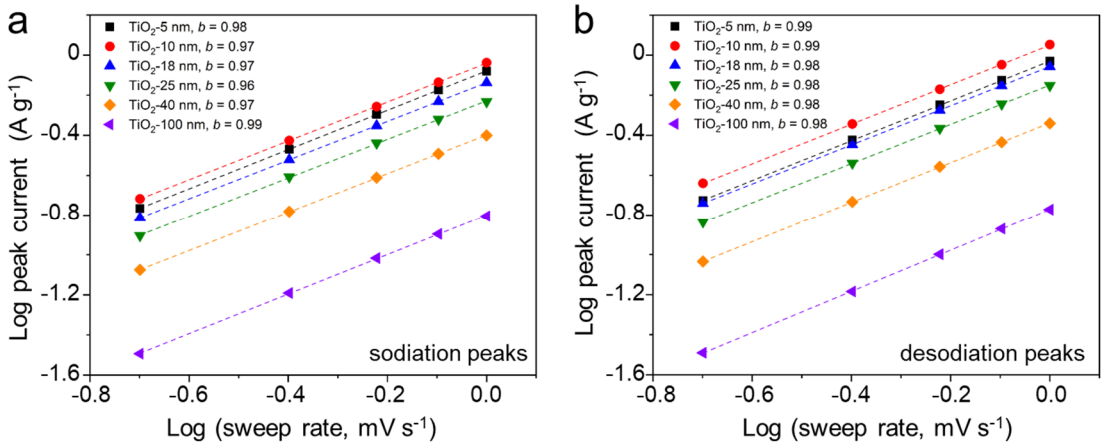
References

1. L. Wu *et al.*, Unfolding the mechanism of sodium insertion in anatase TiO_2 nanoparticles. *Adv. Energy Mater.* **5**, 1401142 (2015).
2. M. N. Tahir *et al.*, Extraordinary performance of carbon-coated anatase TiO_2 as sodium-ion anode. *Adv. Energy Mater.* **6**, 1501489 (2016).
3. Z.-L. Xu *et al.*, Engineering solid electrolyte interphase for pseudocapacitive anatase TiO_2 anodes in sodium-ion batteries. *Adv. Funct. Mater.* **28**, 1802099 (2018).
4. J. Chen *et al.*, Black anatase titania with ultrafast sodium-storage performances stimulated by oxygen vacancies. *ACS Appl. Mater. Interfaces* **8**, 9142-9151 (2016).
5. J. Chen *et al.*, Size-tunable olive-like anatase TiO_2 coated with carbon as superior anode for sodium-ion batteries. *Small* **12**, 5554-5563 (2016).

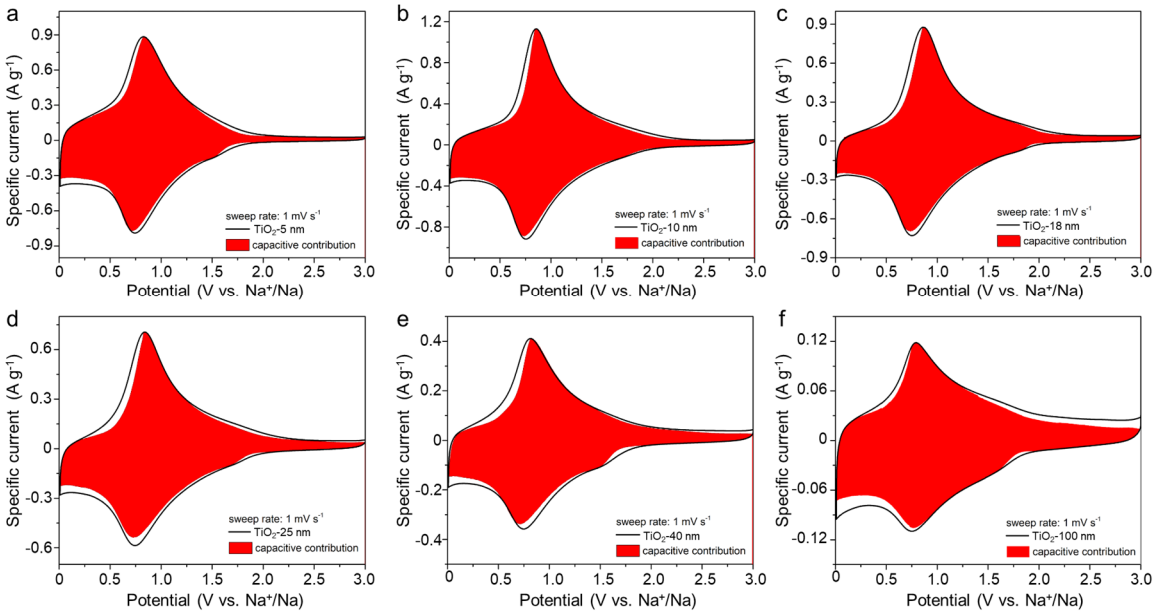
Supplementary Section 4. Kinetics analysis for the sodium-ion storage of TiO_2 NPs.



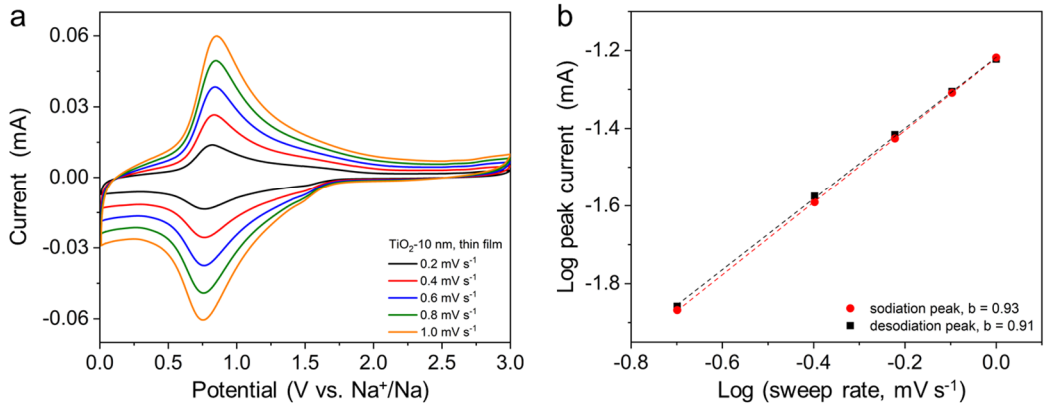
Supplementary Figure 7. CV curves for the sodium-ion storage of TiO_2-NPs at sweep rates from 0.2 to 1 mV s^{-1}: (a) TiO_2-5 nm, (b) TiO_2-18 nm, (c) TiO_2-25 nm, (d) TiO_2-40 nm, and (e) TiO_2-100 nm.



Supplementary Figure 8. *b*-value fitting of the sodiation peaks (a) and desodiation peaks (b) of the TiO_2 NPs, respectively.

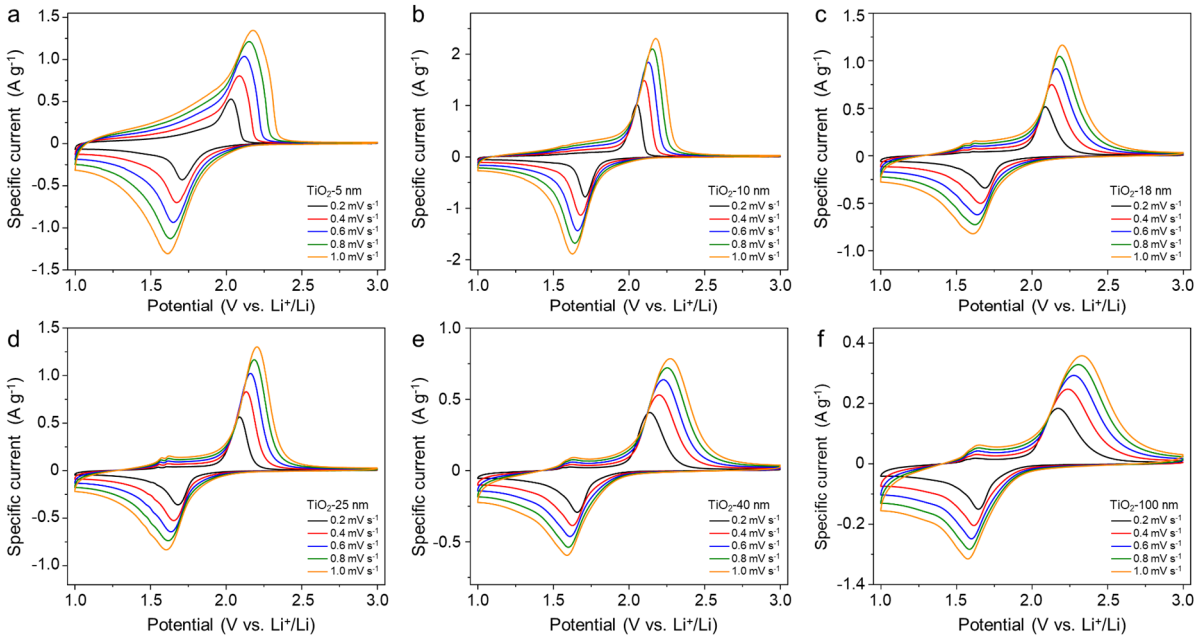


Supplementary Figure 9. Capacitive contributions to sodium-ion storage for TiO_2 NPs at 1.0 mV s^{-1}, (a) TiO_2-5 nm, (b) TiO_2-10 nm, (c) TiO_2-18 nm, (d) TiO_2-25 nm, (e) TiO_2-40 nm, and (f) TiO_2-100 nm.

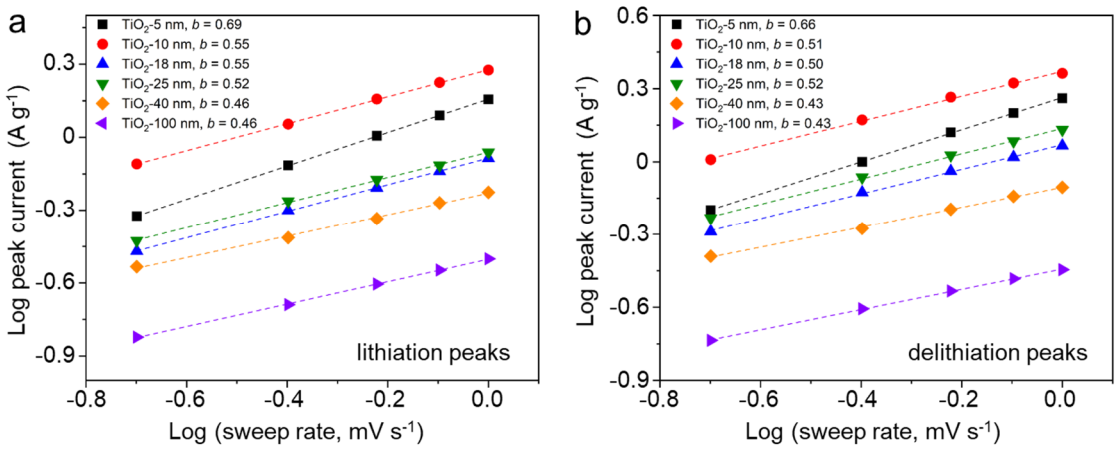


Supplementary Figure 10. (a) CV curves for the thin-film electrode of TiO_2-10 nm (100 μg cm^{-2}, without any binder or carbon additives), at sweep rates from 0.2 to 1 mV s^{-1}. (b) The corresponding *b*-value fitting of the sodiation and desodiation peaks for the thin-film electrode.

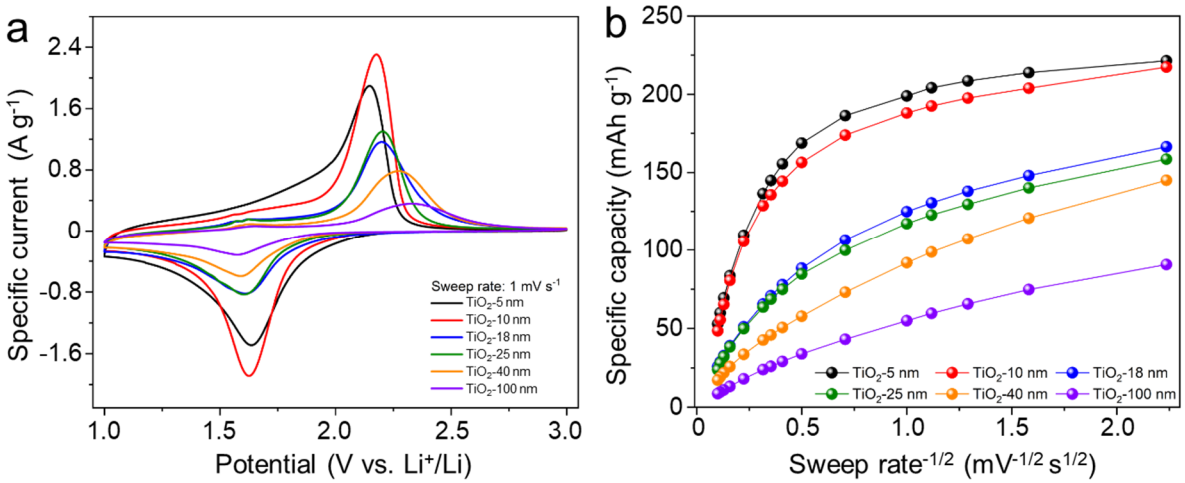
Supplementary Section 5. Kinetics analysis for the lithium-ion storage of TiO_2 NPs.



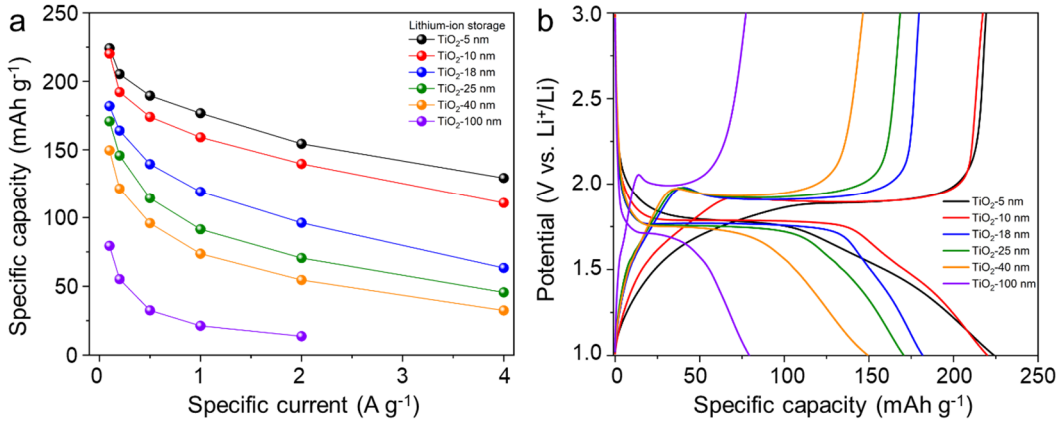
Supplementary Figure 11. The CV curves for the lithium-ion storage of TiO_2 NPs at sweep rates from 0.2 to 1 mV s^{-1}: (a) TiO_2-5 nm, (b) TiO_2-10 nm, (c) TiO_2-18 nm, (d) TiO_2-25 nm, (e) TiO_2-40 nm, and (f) TiO_2-100 nm.



Supplementary Figure 12. *b*-value fitting of the lithiation peaks (a) and delithiation peaks (b) of the TiO_2 NPs, respectively.



Supplementary Figure 13. (a) The CV curves of the different TiO_2 NPs for lithium-ion storage at a sweep rate of 1 mV s^{-1}. (b) Specific capacity *vs.* sweep rate$^{-1/2}$ curves of the TiO_2 NPs.



Supplementary Figure 14. (a) The rate capability of the different TiO_2 NPs for lithium-ion storage. (b) The corresponding charge and discharge curves of the TiO_2 NPs at a specific current of 0.1 A g^{-1}.