

## Supplementary material

### **3.3 nm-sized TiO<sub>2</sub>/carbon hybrid spheres endowed with pseudocapacitance-dominated superhigh-rate Li-ion and Na-ion storages**

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## Supporting Notes

**1. Calculation of electrical conductivity:** 10 measurements of the electrical resistivity  $\rho$  ( $\Omega$  cm) of 3.3-TO/C have been conducted, and the values are depicted in the following table. The electrical conductivity  $\sigma$  ( $S$  cm<sup>-1</sup>) is calculated based on the following equation,

$$\sigma = 1/\rho.$$

The reported  $\sigma$  is an average of 8 values except the largest and the lowest ones. The standard division is given.

1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>	6 <sup>th</sup>	7 <sup>th</sup>	8 <sup>th</sup>	9 <sup>th</sup>	10 <sup>th</sup>
72.01	85.98	75.05	79.26	69.25	78.22	71.67	73.51	70.06	78.52

## 2. Determination of intersection potential of the domain I and the domain II:

The mathematically smoothed  $C_d$  data in a potential range of 0.01 to 0.12 V (vs Li/Li<sup>+</sup>) have been linearly fitted as fitting line 1 (Figure a in the following image), *i.e.*,

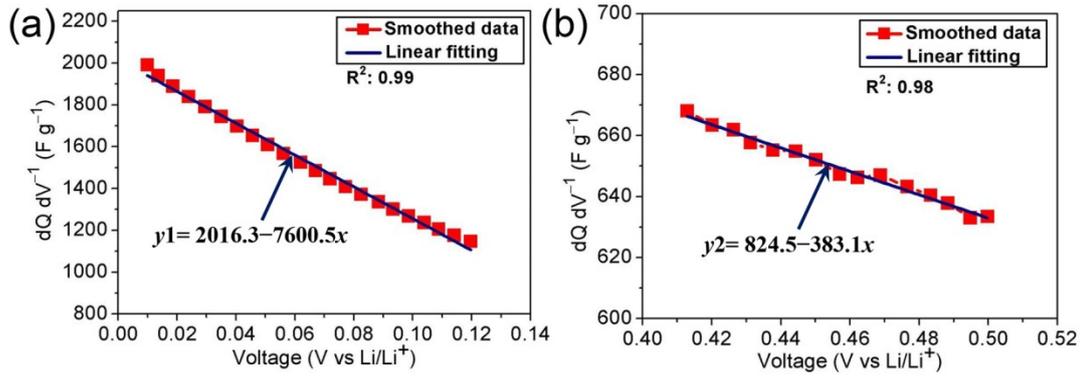
$$y1 = 2016.3 - 7600.5x. \quad (1)$$

The coefficient of determination  $R^2$  is 0.99. Fitting line 2 is derived from the smoothed  $C_d$  data in a potential range of 0.41 to 0.50 V (Figure b), *i.e.*,

$$y2 = 824.5 - 383.1x. \quad (2)$$

The coefficient of determination  $R^2$  is 0.98. The intersection potential thus can be determined by the solution of Equations (1) and (2), *i.e.*,

$$x = 0.17 \text{ V.}$$



**3. Calculation of average voltage  $V_a$ :** The calculation is based on the voltage profiles of 3.3-TO/C at 2 C (Figure 4e). The energy  $E$  is a product of electric charge  $Q$  and voltage  $V$ , *i.e.*,

$$E = QV. \quad (3)$$

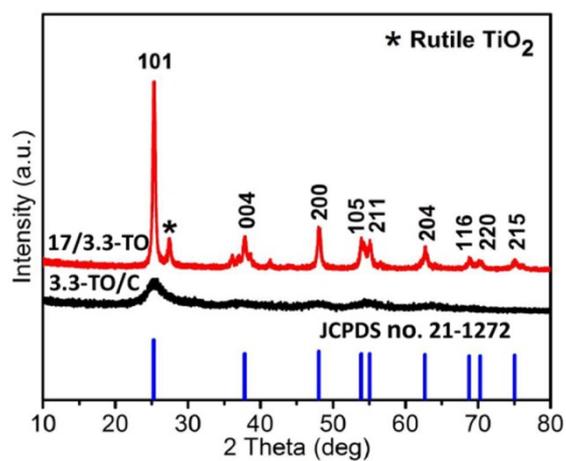
Thus for a given voltage profile,  $E$  is an integration of  $V$  in a full scale of  $Q$ , *i.e.*,

$$E = \int_0^Q V dQ = \int_0^C 3.6V dC. \quad (4)$$

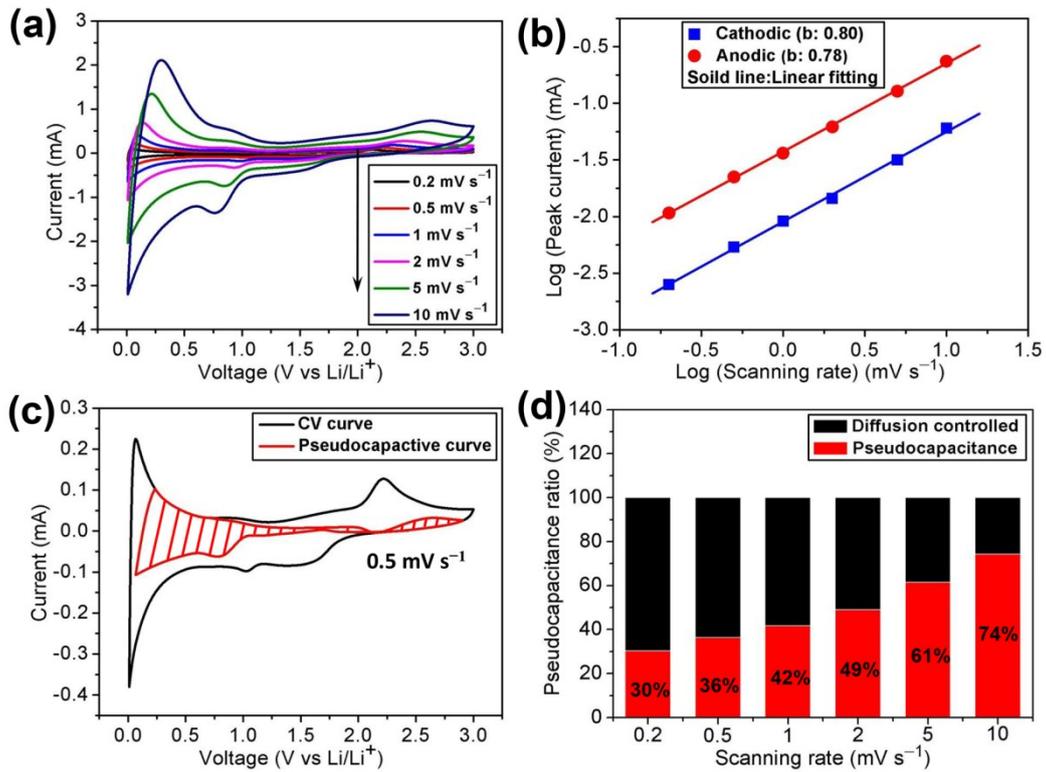
The average voltage  $V_a$  is defined as

$$V_a = \frac{E}{Q} = \frac{\int_0^C 3.6V dC}{3.6C} = \frac{\int_0^C V dC}{C}. \quad (5)$$

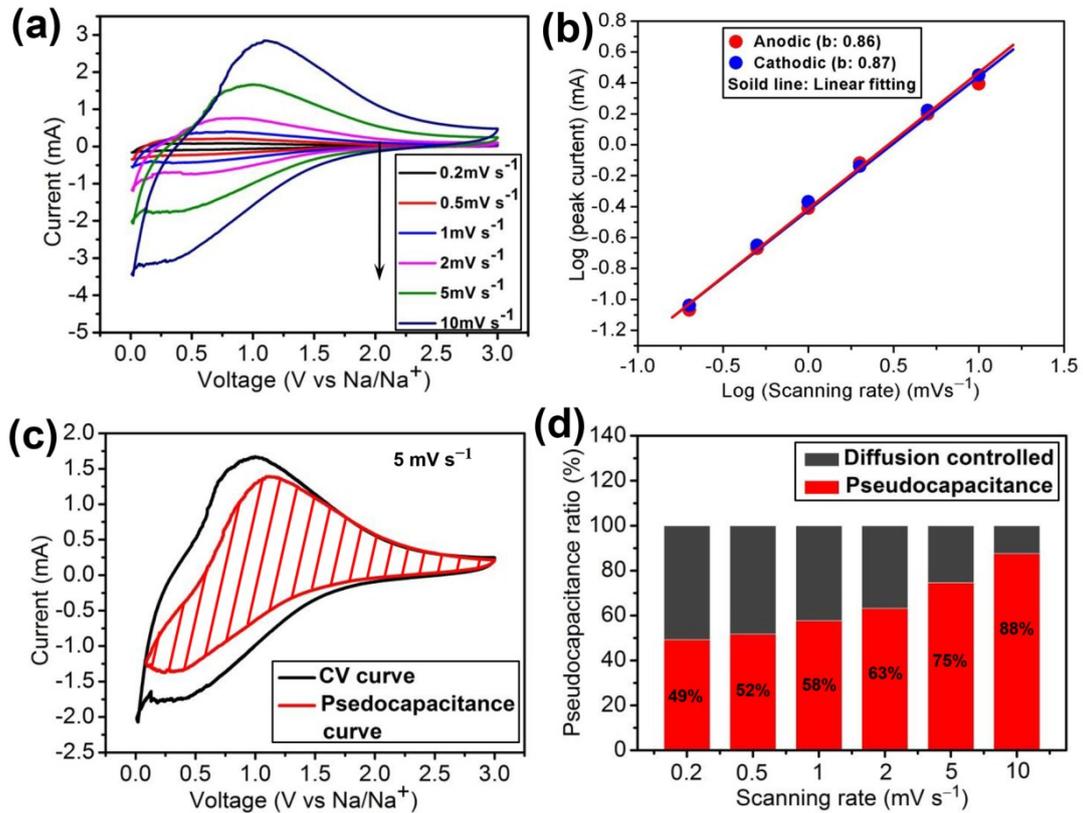
## Supporting Figures



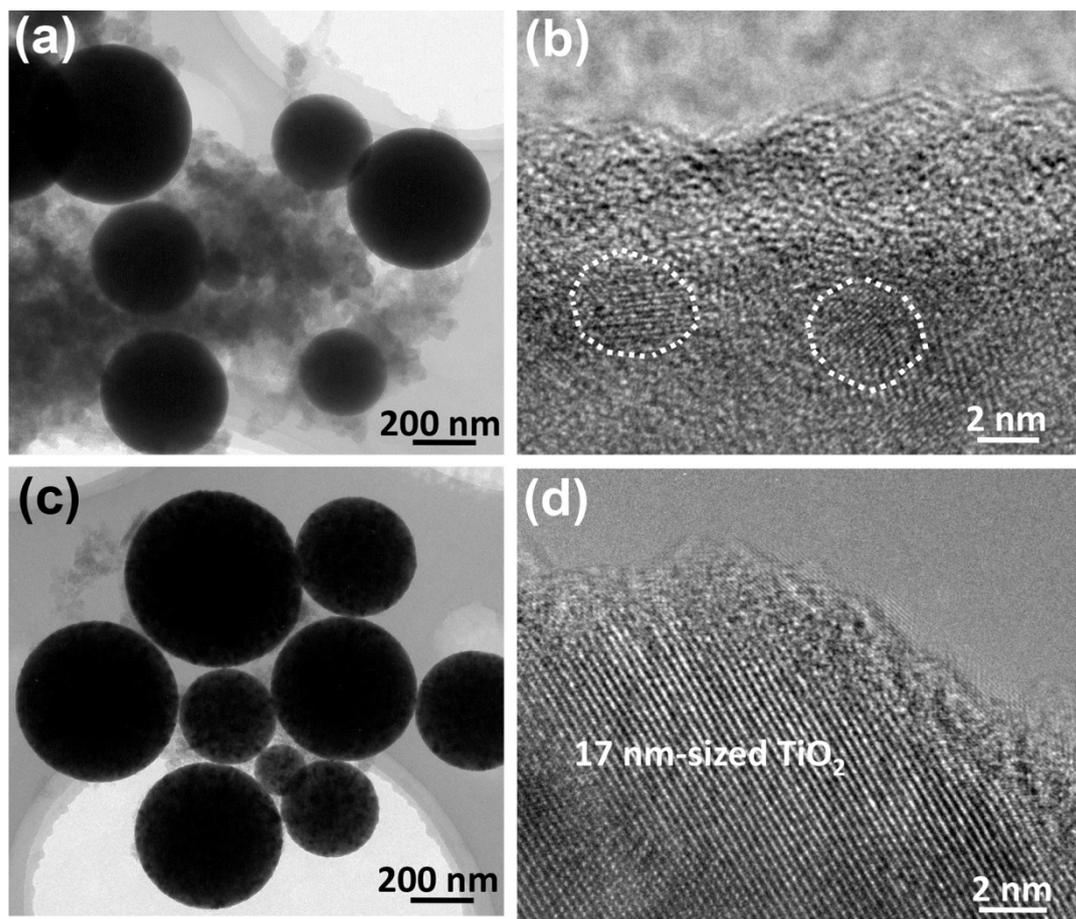
**Fig. S1.** XRD patterns of 3.3-TO/C and 17/5.3-TO.



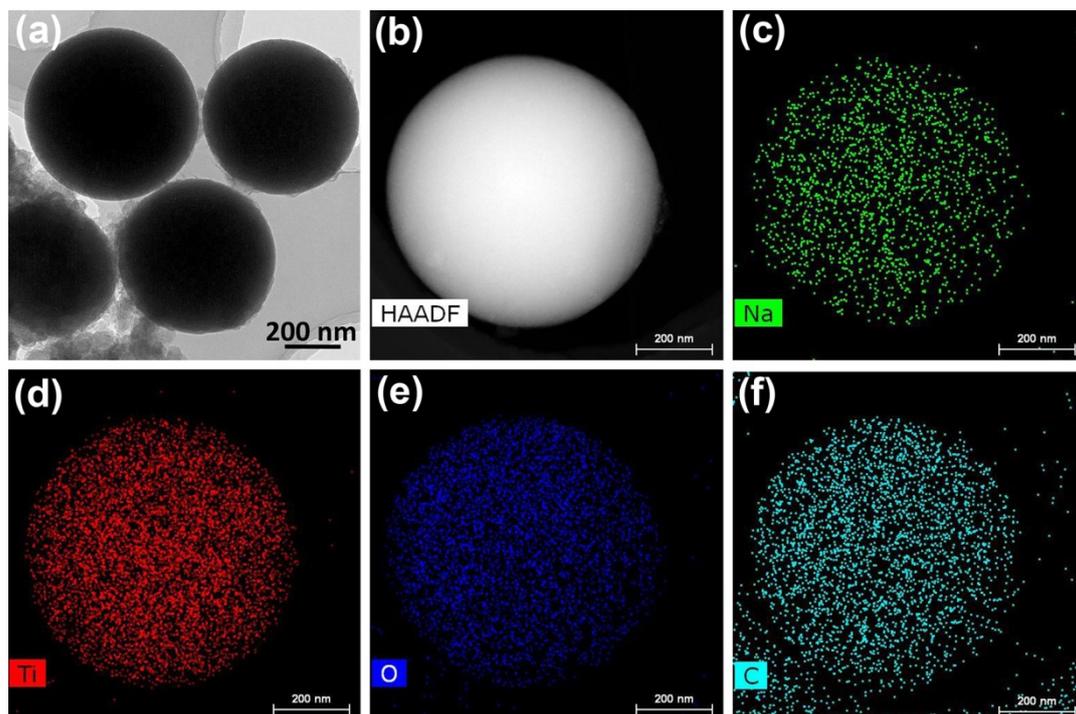
**Fig. S2.** Pseudocapacitive performance of 17/5.3-TO for Li-ion storage. (a) CV curves at various scanning rates. (b) Plots and linear fittings of logarithmic peak current as a function of logarithmic scanning rate of the anodic and the cathodic CV peaks. (c) CV profile and pseudocapacitance contribution represented by the red slashed area at 0.5 mV s<sup>-1</sup>. (d) Variation of the pseudocapacitance contribution with an increase of the CV scanning rate.



**Fig. S3.** Pseudocapacitive performance of 3.3-TO/C for Na-ion storage. (a) CV curves at various scanning rates. (b) Plots and linear fittings of logarithmic peak current as a function of logarithmic scanning rate of the anodic and the cathodic CV peaks. (c) CV profile and pseudocapacitance contribution represented by the red slashed area at 5 mV s<sup>-1</sup>. (d) Variation of the pseudocapacitance contribution with an increase of the CV scanning rate.



**Fig. S4.** Microstructures of 3.3-TO/C and 17/5.3-TO after 600 discharge/charge cycles of Li-ion storage. (a) TEM and (b) HREM of 3.3-TO/C. (c) TEM and (d) HREM images of 17/5.3-TO.



**Fig. S5.** Microstructure and element distributions of 3.3-TO/C after 500 discharge/charge cycles for Na-ion storage. (a) TEM and (b) HAADF image of 3.3-TO/C. Element mappings of (c) sodium, (d) titanium, (e) oxygen and (f) carbon.