## **Supporting information**

# Highly Electrically Conductive Layered Carbon Derived from Polydopamine and Its Functions in SnO<sub>2</sub>-based Lithium Ion Battery Anodes

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### 1. Experimental details

#### Materials

Dopamine chloride (DOPA), tris-(hydroxymethyl) aminomethan (Tris), fluorine-doped tin oxide (FTO)-coated glass slide, anhydrous N-methyl-2-pyrrolidone, polyvinylidene fluoride were purchased from Sigma Chemistry (USA). Silicon wafer was provided by Dreiheit Technologies Pte Ltd (Singapore). Carbon black was purchased from Alfa Aesar. Lithium foil and LiPF<sub>6</sub> solution (1M in a mixture of ethylene carbonate and dimethyl carbonate with 1/1 in v/v) were purchased from Charslton Technologies Pte Ltd (Singapore). All chemicals are used as received.

#### **Sample Preparation**

*Preparation of PDA and C-PDA coatings.* To measure the in-plane and through-plane electrical properties of the C-PDA coating, PDA was deposited on an oxidized silicon wafer and a FTO-coated glass, respectively. To obtain a silicon oxide layer of 500 nm in thickness on a p-

type (100) silicon wafer, a wet oxidization process was carried out in oxygen at 1100 °C for 37 min using a Tystar three-zone atmosphere-pressure tube furnace. DOPA was then polymerized on the surface of the wafer. In a typical experiment, the wafer  $(1 \times 3 \text{ cm}^2)$  was vertically dipped into 80 mL 1.21 mg/mL Tris buffer aqueous solution, and 24 mg DOPA (0.3 mg/mL) was then added into the solution. The polymerization was conducted at room temperature for 2 hrs under continuous magnetic stirring. Upon the immersion of the wafer into the solution, DOPA prefers to self-polymerize on the surface of the wafer owing to the strong affinity of the catechol groups to silicon oxide. The deposited wafer was rinsed with deionized (DI) water for 3 times. A multiple deposition process was used to ensure sufficient coating thickness, which could be well controlled by the number of depositions, for structural characterization. Therefore following the same procedure, the deposition was carried out for another 11 times using newly prepared solution with the same composition to increase the thickness of the coating. The PDA coating on the SiO<sub>2</sub>/Si substrate was then dried in vacuum at 60 °C for 24 hrs. The PDA coating was carbonized in a Carbolite tube furnace with a temperature controller (Type 201) by heating from room temperature to 700 °C at a heating rate of 5 °C/min in Ar environment with an Ar flow rate of 100 sccm, and then annealed at 700 °C for 3 hrs. PDA was deposited on a FTO-coated glass slide (1 x 3  $\text{cm}^2$ ), and carbonized following the same procedure as described above. SnO<sub>2</sub> nanoparticles (NPs) prepared via hydrothermal route<sup>[1]</sup> were dispersed in Tris buffer solution via vigorous ultrasonication. DOPA was added into the above suspension at the concentration of 0.3 mg/mL. The polymerization was conducted at room temperature for 2 hrs under continuous magnetic stirring. In order to achieve a thickness of a few nanometers to facilitate highresolution TEM (HRTEM) examination and achieve excellent electrochemical properties, only one deposition of 2 hrs was carried out. The washing, drying and carbonization were carried out under the same conditions as described above. The obtained C-PDA coated NPs were further oxidized in air environment at 250 °C for 3 hrs and the product is denoted as C-PDA/SnO<sub>2</sub>. The further oxidation was conducted because upon the conversion from PDA to C-PDA at 700 °C in Ar, SnO<sub>2</sub> was reduced to metallic Sn by the C-PDA coating formed. A further annealing in air was therefore necessary to re-oxidize Sn back to SnO<sub>2</sub>.

*Preparation of PDA and C-PDA particles.* To characterize chemical structures of PDA and C-PDA, PDA and C-PDA particles were also prepared. DOPA was added into the Tri buffer solution directly under magnetic stirring at room temperature without the presence of substrate. The concentration of DOPA was 2 mg/mL and the polymerization time was 24 hrs. The product was washed and dried under the same conditions as described above, and the sample is denoted as PDA powder. The PDA powder was carbonized under the same condition as that for PDA coating, and the carbonized sample is denoted as C-PDA powder.

#### Characterization

The morphologies and surface features of the PDA and C-PDA coatings were examined using field-emission scanning electron microscope (FESEM, JEOL 7600F), HRTEM (JEOL 2100) and atomic force microscope (AFM, Weeco DI Dimension 3000). The chemical composition and structure of the PDA and C-PDA were characterized using X-ray photoelectron spectroscopy (XPS, Theta-probe, Thermo Scientific), X-ray diffraction (XRD, Bruker D8 Discover GADDS X-ray diffractometer), confocal Raman microscope (Witec), Fourier transform infrared spectroscope (FTIR, Perkin-Elmer 2000 spectrometer) and thermogravimetric analysis (TGA, Q500). For the elemental composition calculations from XPS, as oxygen (O) could be detected from both the PDA coating and the oxidized silicon wafer, the compositions of PDA and C-PDA were calculated after subtracting the O in SiO<sub>2</sub>. The in-plane and through-plane electrical conductivities of the C-PDA coatings were measured using a Hewlett Packard 4140B pA Meter/DC Voltage source. The I-V characteristic of the C-PDA coating in the basal planes was measured with the oxidized silicon wafer as the substrate. That through the basal plane was carried out on the C-PDA coating deposited on a conductive substrate, FTO-coated glass slide. Gold contacting points was deposited onto the C-PDA coating using patterned masks for the measurement of the in-plane electrical conductivity.

#### **Electrochemical measurements**

The electrochemical properties of C-PDA/SnO<sub>2</sub> NPs were studied as an active anode material in LIBs and compared with that of pristine SnO<sub>2</sub> NPs. Homogeneous slurry of the active materials, polyvinylidene fluoride (binder) and carbon black (conducting agent) in composition of 80, 10 and 10 wt%, respectively, in N-methyl-2-pyrrolidone were prepared via vigorous magnetic stirring and pasted onto copper foil. The paste was then dried and compressed. Lithium foil with 0.4 mm in thickness and 14 mm in diameter, and 1M LiPF<sub>6</sub> in a mixture of ethylene carbonate and dimethyl carbonate (1/1 in v/v) were used as counter electrode and electrolyte, respectively. All the components were assembled into 2032 button coins in argon filled glove box with moisture and oxygen levels of less than 1 ppm. The electrodes were isolated by a separator (Celgard 2325, USA). The electrochemical properties were studied using a battery tester (4200, MACCOR) under the voltage window of 3.0-0.005 V and the current density of 50 followed by 100 mA g<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) study was conducted using an electrochemical workstation (PGSTAT302, Autolab) in a frequency range of  $10^5$  to  $10^{-2}$  Hz and at the a.c. amplitude of 5 mV.

## 2. Figures



**Fig. S1** FESEM images of (a) the PDA and (b) C-PDA coating on SiO<sub>2</sub>/Si substrates, showing the surface morphology. The wafer is completely covered by the PDA and even after the carbonization, the C-PDA coating is still well adhered to the substrate, showing no cracks or peeling. The surface of the C-PDA coating is smoother than that of the PDA coating, which is probably due to the fusion and reactions occurred during the carbonization.



Fig. S2 TEM image of pristine SnO<sub>2</sub> NPs, showing the severe aggregation.



**Fig. S3** TEM of C-PDA coated  $SnO_2$  NPs by 2 times deposition. The thickness of the C-PDA layer is increased to about 10 nm, without the obvious change of the  $SnO_2$  aggregation.



**Fig. S4** Discharge/charge profiles of pristine  $\text{SnO}_2$  NPs at 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> and 10<sup>th</sup> cycle. The voltage window was 3.0-0.005 V, and the current density was 50 mA g<sup>-1</sup> and then raised to 100 mA g<sup>-1</sup>.



Fig. S5 The TGA curve of the C-PDA coated  $SnO_2$  NPs (D-SnO<sub>2</sub>). The TGA was conducted under the following condition: ramped from room temperature to 550 °C at a heating rate of 10 °C/min in air environment. It is indicated that the SnO<sub>2</sub> content in D-SnO<sub>2</sub> is 81.5 wt%.



Fig. S6 TEM images of (a) pristine  $SnO_2$  NPs, (b) C-PDA/SnO<sub>2</sub> NPs after 114 charging cycles at the current rate of 100 mA g<sup>-1</sup>. It is shown that the pristine  $SnO_2$  NPs expand and aggregate after cycling test, forming particles with larger size, while C-PDA/SnO<sub>2</sub> NPs maintain the form of bridged small clusters, which is ensured by the C-PDA coating.

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Fig. S7 Nyquist plots obtained from the impedance spectroscopy of pristine  $SnO_2$  NPs and C-PDA/SnO<sub>2</sub> NPs. The interfacial resistance and charge transfer resistance of C-PDA/SnO<sub>2</sub> NPs is much lower than those of pristine  $SnO_2$  NPs, indicating higher charge conduction of C-PDA/SnO<sub>2</sub> NPs.

<sup>1</sup> Z. Miao, Y. Wu, X. Zhang, Z. Liu, B. Han, K. Ding and G. An, J. Mater. Chem., 2007, 17. 1791.