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## A nanofibrous polypyrrole/silicon composite derived from cellulose substance as anode material for lithium-ion batteries†

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**A bio-inspired nanofibrous polypyrrole/silicon composite derived from natural cellulose substance was synthesized. Due to its unique porous network structure and PPy coating on the silicon fibres, it showed improved reversible capacity, cyclability and rate capability upon long-term charge/discharge cycling when employed as an anode material for lithium-ion batteries.**

Rechargeable lithium-ion battery (LIB) is considered to be one of the most promising energy storage devices because of its wide range applications in electric vehicles and portable electronic devices in the recent decades.<sup>1–3</sup> The electrochemical and structural properties of the electrode materials hold influential roles in the battery performances. Various anode materials other than the graphite-based carbonaceous matters have been attempted to meet the increasing demands of LIBs with higher energy capacity and longer cycle life.<sup>4–7</sup> Among the possible candidates, silicon based materials have drawn considerable attention due to the theoretical capacity as high as 4200 mAh g<sup>-1</sup> corresponding to the formation of Li<sub>4.4</sub>Si phase.<sup>8</sup> However, the serious volume change (*ca.* 400%) occurred during the battery charge/discharge cycling process (*i.e.*, the insertion and extraction reactions of lithium ions) leads to cracking and eventual pulverization of the anode, and consequent rapid capacity fade. To address such issue, one approach is the fabrication of silicon based matters with various nanoscale structures, aiming at releasing the strain force generated from the volume changes during the electrochemical reactions. For instance, silicon nanowires,<sup>9–11</sup> nanotubes<sup>12,13</sup> and three-dimensional porous particles<sup>14,15</sup> were fabricated by specific methods, showing improved cycling performances. In particular, the porous structure provides a superior configuration for accommodating the volume change and facilitates the electron and ion transfer. Another strategy is to synthesize silicon based hybrids that composited with less active or inactive phases such as carbon<sup>16–20</sup> or conductive

polymers.<sup>21–30</sup> It provides a solution to accommodate the severe volume change and increase the electrical conductivity of the composites. As demonstrated by the application of the composite composed of silicon nanoparticles and polypyrrole (PPy)<sup>23</sup> as well as that of silicon nanowires and poly(3,4-ethylenedioxythiophene) (PEDOT)<sup>24</sup> as anode materials, which achieved improved cycling stability and relatively higher discharge capacity compared with bare silicon counterparts. However, there still remains a challenge for the facile and cost effective fabrication of nanostructured composites of silicon and conductive polymers with good electrochemical performance as anode materials for LIBs.

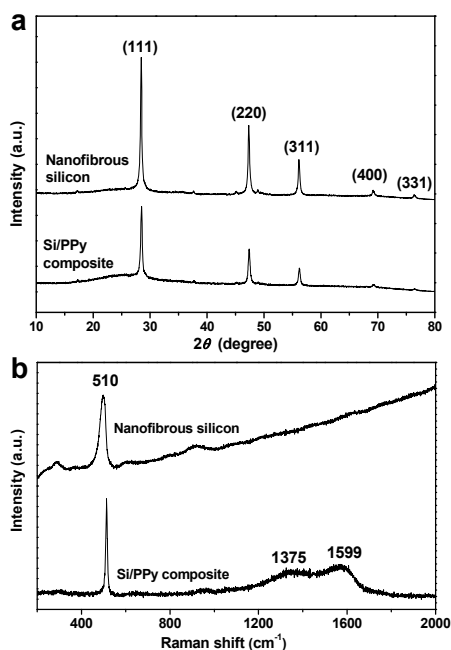
Herein, we report the fabrication of a new bio-inspired nanofibrous polypyrrole/silicon (PPy/Si) composite composed of PPy coated silicon nanowires that derived from natural cellulose substance (*i.e.*, commercial laboratory ashless filter paper). It was employed as an anode material for LIBs, which showed improved capacity retention and rate stability due to the unique three-dimensionally porous network structure of it inherited from the cellulose substance. This structure provides essential space to accommodate the serious volume change of the material during the electrochemical processes. Moreover, the PPy coating offers significant structural stability of the silicon species, the pristine silicon crystalline phase was partially maintained after extensive charge/discharge cycling.

Biomimetic synthetic approaches provide ideal pathways to the fabrication of functional materials,<sup>31–33</sup> where the self-assembly technique has been widely adopted for this purpose.<sup>34–37</sup> We pioneered the nanometer precise replication of natural cellulose substance with metal oxides to give nanostructured materials with both the unique hierarchical structural features of the template substrate and the chemical functionalities of the metal oxides.<sup>38–40</sup> In the present work, the synthesis of the nanofibrous PPy/Si composite (Scheme S1, ESI†) was achieved by an *in-situ* polymerization process to deposit PPy coatings on the silicon nanofibres that resulted from magnesiothermic reduction of the silica replica of the cellulose substance (laboratory filter paper). The silica replica was obtained by a sol-gel nanocoating technique, which allows coating of the template substance without disruption of its initial structures.<sup>41</sup>

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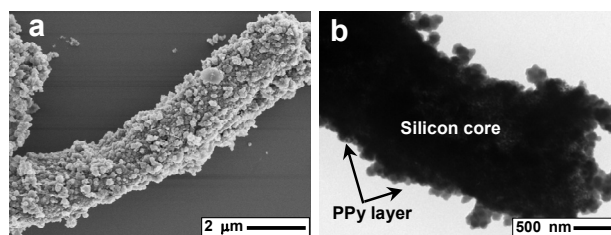
† Electronic Supplementary Information (ESI) available: Experimental details, structural and electrochemical characterizations of the related materials. See DOI: 10.1039/b000000x



**Fig. 1** X-ray diffraction patterns (a) and Raman spectra (b) of the nanofibrous silicon matter derived from natural cellulose substance and the corresponding PPy/Si composite (33.8 wt.% of silicon).

The nanofibrous silicon matter derived from the initial cellulose filter paper existed as hierarchical fibres as replication of the original cellulose fibres. The silicon fibres were surface smooth composed of fine silicon nanocrystallites with sizes about 5 nm, as revealed by the electron microscopes (Fig. S1, ESI<sup>†</sup>). Fig. 1a shows the powder X-ray diffraction (XRD) patterns of the nanofibrous silicon matter and the corresponding nanofibrous PPy/silicon composite with 66.2 wt.% of PPy (*i.e.*, 33.8 wt.% of silicon), as determined by the thermogravimetric and energy dispersive X-ray analyses (Figs. S2 and S3, ESI<sup>†</sup>). Both spectra show the diffraction peaks at 28.4°, 47.4°, 56.2°, 69.2° and 76.5°, which are ascribed to the (111), (220), (311), (400) and (331) planes of crystalline silicon phase, respectively.<sup>18,42</sup> For the PPy/silicon composite, the broad and weak diffraction peak between 20.0° and 25.0° indicates the existing of amorphous PPy therein. The presence of the Raman scattering bands at 510 cm<sup>-1</sup> for both the nanofibrous silicon matter and the PPy/silicon composite is ascribed to the Si–Si stretching mode of crystalline silicon (Fig. 1b).<sup>13</sup> And the bands at 1375 and 1599 cm<sup>-1</sup> in the spectrum of the PPy/silicon composite are attributed to the ring stretching and the backbone stretching of C=C bonds of PPy, respectively.<sup>23,43</sup> These results confirm the formation of the PPy/silicon composite, and the deposition of PPy on the nanofibrous silicon matter does not alter the crystalline nature of the silicon component.

Fig. 2 shows the field-emission scanning electron microscopic (FE-SEM) and the transmission electron microscopic (TEM) images of the resultant nanofibrous PPy/silicon composite (66.2 wt.% of PPy) derived from natural cellulose substance. By comparison to the morphology of the pristine nanofibrous silicon matter (Fig. S1, ESI<sup>†</sup>), the surfaces of the PPy-coated silicon fibres become much rougher



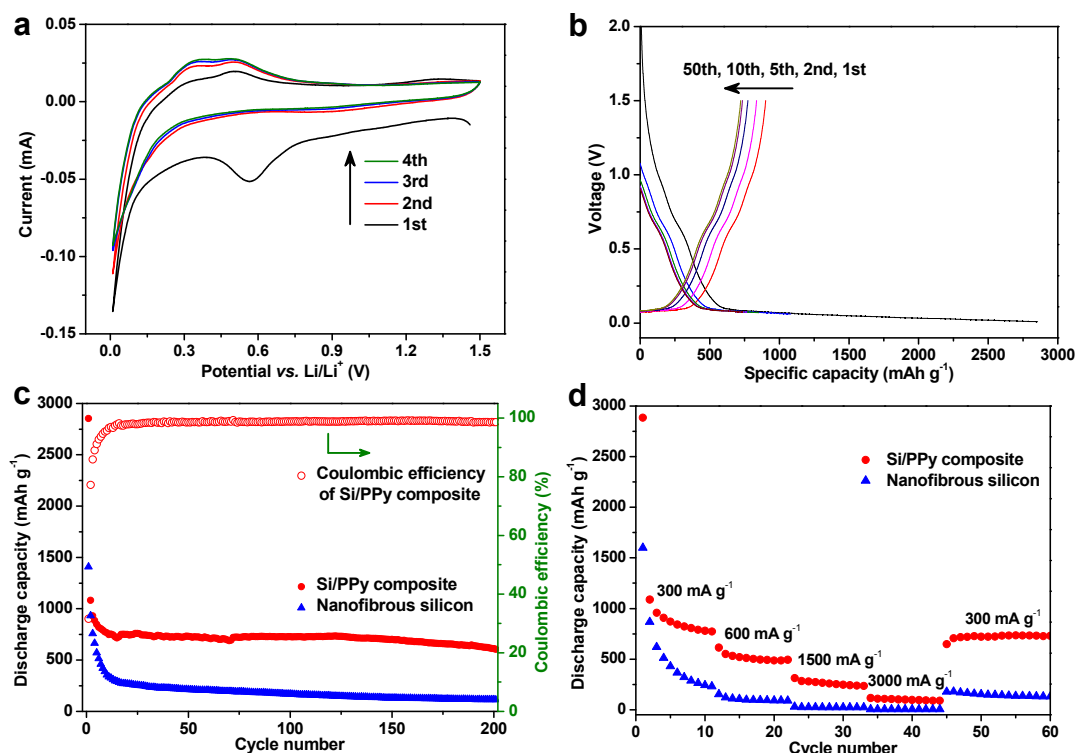
**Fig. 2** Electron micrographs of the nanofibrous PPy/Si composite derived from natural cellulose substance (33.8 wt.% of silicon). (a) FE-SEM and (b) TEM images of the sample, showing the surface of the silicon fibre is coated with PPy layer.

due to the complete coating of PPy particles (with sizes of 50–100 nm) on the surface. While for a PPy/silicon composite with a lower content of PPy (50.1 wt.%), the surfaces of the silicon fibres are just partially coated with the PPy layer. X-ray photoelectron spectroscopy (XPS) of the nanofibrous PPy/silicon composite (66.2 wt.% of PPy) confirm the existing of the metallic silicon and PPy component in the hybrid (Fig. S4, ESI<sup>†</sup>). The Si(2p) peak observed at 99.5 eV indicates the presence of metallic silicon, while the peak at 103.5 eV is indicative of the formation of SiO<sub>x</sub> ( $x < 2$ ) due to the oxidation of the silicon nanocrystals in air.<sup>6,44</sup> In the C(1s) region, the three peaks at 284.5, 285.2 and 286.2 eV are assigned to  $\beta$  and  $\alpha$  carbon types and C=N in PPy;<sup>45</sup> and in the N(1s) region, the doublet peaks at 397.6 and 399.4 eV are ascribed to =N– and –NH– of PPy, respectively.<sup>46</sup>

As a comparison material for the electrochemical study, pure PPy powder was synthesized by the *in-situ* chemical polymerization process. The electron micrographs of it revealed that it was composed of irregular aggregates of PPy particles with sizes of ca. 50 nm (Fig. S5, ESI<sup>†</sup>).

The bio-inspired porous structure of the nanofibrous PPy/silicon composite as well as the PPy coating on the silicon fibres would be beneficial to relieve the severe volume change of the silicon species and hence for the maintenance of the integrity of which when employed as an anode material for LIBs. The nanofibrous PPy/silicon composite with varied PPy contents, the nanofibrous silicon matter, and the PPy powders were used to assemble coin-type half batteries for the study on the corresponding electrochemical performances (see ESI<sup>†</sup> for experimental details).

Fig. 3a shows the cyclic voltammetry (CV) curves of the nanofibrous PPy/Si composite (66.2 wt.% of PPy and 33.8 wt.% of silicon) for the first four cycles in a voltage range between 0.01–1.5 V vs. Li/Li<sup>+</sup> at a scan rate of 0.1 mV s<sup>-1</sup>, which are similar as those of the nanofibrous silicon matter (Fig. S6a, ESI<sup>†</sup>). The CV scan of the pure PPy powder was performed for comparison (Fig. S6b, ESI<sup>†</sup>), the current density is one order of magnitude smaller than that of the PPy/Si composite, which means that the contribution from PPy to the capacity of the whole electrode is negligible. In the first cycle cathodic branch of the PPy/Si composite, the increase of the current between 0.01 and 0.3 V corresponds to the conversion of silicon to the Li<sub>x</sub>Si phase; and the peak at about 0.6 V is attributed to the formation of the solid electrolyte interface (SEI) film. In the anodic process, the two peaks at 0.41 and 0.53 V are due to the



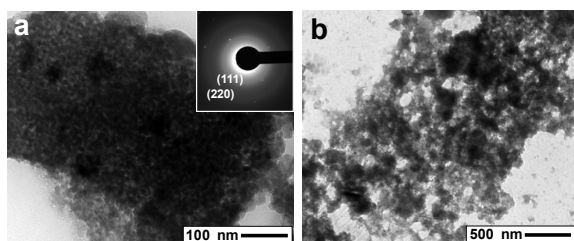
**Fig. 3** Electrochemical performance of the nanofibrous PPy/Si composite (33.8 wt.% of silicon) as employed as an anode material for lithium-ion battery. (a) Cyclic voltammograms at a scan rate of  $0.1 \text{ mV s}^{-1}$  over the potential window of 0.01–1.50 V vs.  $\text{Li/Li}^+$ . (b) The galvanostatic charge–discharge profiles at the 1<sup>st</sup>, 2<sup>nd</sup>, 5<sup>th</sup>, 10<sup>th</sup> and 50<sup>th</sup> cycle under a constant current density of  $300 \text{ mA g}^{-1}$  between 0.01 and 1.50 V. (c) The discharge cycling performance and Coulombic efficiency of the PPy/Si composite at a current density of  $300 \text{ mA g}^{-1}$  with the nanofibrous silicon matter as comparison. (d) The rate capabilities of the PPy/Si composite and the nanofibrous silicon matter at various current densities.

delithiation of  $\text{Li}_x\text{Si}$  to amorphous phase silicon.<sup>24</sup> The CV curve profiles are similar after the second cycle, which indicates the good structural stability and cyclability of the electrode during the following lithium insertion/extraction processes.

Fig. 3b displays the galvanostatic charge/discharge voltage profiles of the nanofibrous PPy/Si anode at a constant current density of  $300 \text{ mA g}^{-1}$  in the voltage range of 0.01–1.50 V. In the first cycle, the potential plateaus at *ca.* 0.1 and 0.7 V are due to the Li–Si alloy and the SEI film formation, respectively; which is in good agreement with the CV results. The first cycle discharge capacity was  $2854 \text{ mAh g}^{-1}$  with a Coulombic efficiency of 31.6%, this low value was caused by the formation of the SEI layer as well as the reduction of the  $\text{SiO}_x$  formed on the surface of the silicon species. The profiles were similar from the second cycle, demonstrating the good cycling stability of the electrode; and the discharge capacity decreased to be  $732 \text{ mAh g}^{-1}$  at the 50<sup>th</sup> cycle, and the Coulombic efficiency increased to be 98.6%. Fig. 3c represents the galvanostatic cycling performance and Coulombic efficiency of the PPy/Si composite at a current density of  $300 \text{ mA g}^{-1}$  (red curves). It was found that the PPy component did not contribute to the capacity (Fig. S7, green curve, ESI<sup>†</sup>). The discharge capacity of the PPy/Si composite decreased within the first 15 cycles, and thereafter reached a relatively stable value with Coulombic efficiency of generally *ca.* 98%. After 200 charge/discharge processes, the discharge capacity was  $611 \text{ mAh g}^{-1}$ . This value was

much higher than that of the nanofibrous silicon matter ( $114 \text{ mAh g}^{-1}$ ; Fig. 3c, blue curve), and that of a PPy/Si composite with lower PPy content (50.1 wt.% of PPy,  $360 \text{ mAh g}^{-1}$ ; Fig. S7, black curve, ESI<sup>†</sup>). These results demonstrate that improved electrochemical performances are offered by the ample coating of PPy on the bio-inspired silicon fibres. And it is needed to be noted that, as compared with the pure silicon nanoparticles<sup>18</sup> and the silicon nanowires synthesized by the vapour–liquid–solid (VLS) method,<sup>7</sup> the current nanofibrous silicon derived from natural cellulose substance possesses higher reversible capacities upon the charge/discharge cycling. This is due to its unique porous network structures that inherited from the initial cellulose substance, which effectively accommodate the volume change. Fig. 3d shows the rate performance of the nanofibrous PPy/Si composite anode at current densities varied from 300 to  $3,000 \text{ mA g}^{-1}$  (red curve), it is seen that the capacity gradually decreased along with the increase of the current density, and almost recovered to the initial value once the current rate went back to  $300 \text{ mA g}^{-1}$ , indicating improved cyclic performances at high current densities as compared with the nanofibrous silicon matter (Fig. 3d, blue curve).

The structural integrity of the nanofibrous PPy/Si composite after extensive charge/discharge cycling processes was confirmed by TEM measurement. In Fig. 4a, the micrograph of the composite (66.2 wt.% of PPy) after 200 cycles is displayed, where the fibrous structure and silicon nanoparticles therein were still clearly to



**Fig. 4** TEM micrographs of the (a) nanofibrous PPy/Si composite (33.8 wt.% of silicon) and (b) the nanofibrous silicon matter employed as anode materials for lithium-ion batteries after 200 cycles of charge/discharge processes. The inset in (a) shows the corresponding selected-area electron diffraction (SAED) pattern of the specimen.

observed. The crystalline nature of the silicon species was partially remained, that is, the PPy coating and the porous material structure relieved the serious volume changes of the silicon particles upon cycling, resulting in significant structural stability of the composite. While for the nanofibrous silicon matter, in sharp contrast, the silicon fibres were completely pulverized and collapsed into amorphous phase after the same number of charge/discharge cycles (Fig. 4b). Moreover, for a nanofibrous PPy/Si composite with lower PPy content (50.1 wt.% of PPy), although the fibrous structure was maintained after 200 cycling, little crystalline silicon particle was observed.

In conclusion, we have fabricated a new bio-inspired nanofibrous polypyrrole/silicon composite that derived from natural cellulose substance. It shows improved electrochemical performances in terms of reversible capacity, cyclability and rate capability as employed as an anode material for lithium-ion batteries. The unique porous network structures as well as the PPy coating in the composite are beneficial to the maintenance of the structural integrity and the crystalline phase of silicon upon long-term charge/discharge cycling. It could demonstrate that bio-inspired chemical synthesis would hold considerable potentials for the design and development of energy-related materials especially for new electrode materials for high-performance lithium-ion batteries aiming at future applications.

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