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## Micron-sized $\text{SiO}_x$ /N-doped carbon composite spheres fabricated with biomass chitosan for high-performance lithium-ion battery anodes†

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To achieve superior lithium storage performance,  $\text{SiO}_x$  is usually designed into nanostructured  $\text{SiO}_x/\text{C}$  composites by complex or expensive methods. Here, micron-sized interconnected  $\text{SiO}_x/\text{N}$ -doped carbon (NC) microspheres composed of evenly dispersed  $\text{SiO}_x$  nano-domains and NC have been fabricated by a scalable microemulsion method and following pyrolysis, using vinyltriethoxysilane and chitosan as precursors. The unique structure of the micron-sized  $\text{SiO}_x/\text{NC}$  spheres leads to enhanced structural integrity and enables stable long-term cycling (800 cycles at  $2 \text{ A g}^{-1}$ ). Benefiting from the enhanced electron/ $\text{Li}^+$  diffusion kinetics originated from the unique structure and N-doping,  $\text{SiO}_x/\text{NC}-2$  presents considerable capacitive-controlled Li storage capacity, which leads to outstanding rate capability. Consequently, the assembled  $\text{SiO}_x/\text{NC}-2/\text{LiFePO}_4$  full cell exhibits superior rate capability ( $106 \text{ mA h g}^{-1}$  at  $4\text{C}$ ) and stable long-term cycling at  $2\text{C}$  ( $102 \text{ mA h g}^{-1}$  after 350 cycles). This work opens a new door for the application of chitosan in building micron-sized high-performance  $\text{SiO}_x/\text{C}$  anode materials, and to some extent facilitates the recycling of waste seafood shells.

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### Introduction

With high energy density and long cycle life, rechargeable Li-ion batteries (LIBs) have been widely used as a power source for smartphones and electronic vehicles (EVs), and greatly fueled their development in the past two decades.<sup>1–5</sup> However, traditional LIBs with graphite as anodes cannot satisfy the rapidly growing need for high energy density. Aiming at improving the energy and power density of LIBs, a series of high-capacity new anode materials have been explored. Among them, Si-based materials are considered as the most promising ones for industrial application, because of their super-high theoretical capacity, appropriate working voltage and natural abundance.<sup>6–8</sup> Unfortunately, the Si anode suffers from huge volume change during cycling and poor conductivity, both of which lead to poor cycling stability.<sup>9,10</sup> Benefiting from the reduced volume variation during cycling and the buffering effect of *in situ* generated lithium silicates and  $\text{Li}_2\text{O}$ ,<sup>11,12</sup>  $\text{SiO}_x$  anodes generally maintain better cycling stability than the Si anodes.<sup>12–14</sup> However,  $\text{SiO}_x$  also needs to be combined with other conductive

buffer materials at the nano-scale because of its poor electron/ $\text{Li}^+$  conductivity and non-negligible volume change during charge/discharge processes.

It has been reported that carbon can effectively improve the conductivity and structural integrity of  $\text{SiO}_x$ .<sup>15–17</sup> In order to enhance cycling stability, coulombic efficiency, and rate capability,  $\text{SiO}_x$  is usually designed as nanostructured  $\text{SiO}_x/\text{C}$  composites.<sup>15–32</sup> Stöber method is one of the most commonly used methods for constructing  $\text{SiO}_x/\text{C}$  nanocomposites. But the extensive requirement of solvents lowers its availability. Moreover, to substantially enhance conductivity and mechanical property, graphene (oxides) and carbon nanotubes are massively used in some  $\text{SiO}_x/\text{C}$  composite materials, which inevitably increases the cost of the prepared  $\text{SiO}_x/\text{C}$  composites and hinders their mass production.<sup>20,31,33,34</sup> Thus it is desirable to prepare  $\text{SiO}_x/\text{C}$  anode materials by using more available methods, low-cost and renewable carbon precursors, and achieve superior lithium storage performance.

Chitosan (CS), extracted from waste crab and shrimp shells, is one of the most abundant and least expensive natural polymers on earth.<sup>35,36</sup> Every year, 6–8 million tons of such waste shells are generated from the seafood industry globally, and many of them are directly dumped in landfills or the sea.<sup>37</sup> The industrial application of chitin and CS can not only realize the recycling of waste, but also ease the pressure on the environment.<sup>38,39</sup> Recently, CS has been used to develop CS-based binders and gel polymer electrolytes for LIBs and Li-ion capacitors (LICs).<sup>40–45</sup> Because of its high nitrogen content, CS is also a favored precursor for electrode materials such as N-

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doped activated carbon or nano-composites composed of metal oxides and N-doped carbon (NC).<sup>46–48</sup> N-doping can effectively enhance electronic conductivity and contributes extra pseudocapacitive capacity, thus improving electrochemical performance.<sup>49</sup> Although CS is favored in constructing metal oxides/NC composites, so far, the preparation of  $\text{SiO}_x/\text{NC}$  composite anode materials by CS has not been reported.

In this work, for the first time, chitosan was used as a carbon precursor to fabricate micron-sized spherical  $\text{SiO}_x/\text{NC}$  composites. The strong hydrogen bonding effect between chitosan molecules and the hydrolyzed organosilica nanoparticles facilitates the uniform dispersion of the organosilica nanoparticles, consuming much less solvents than traditional Stöber method and finally ensuring the homogeneous distribution of  $\text{SiO}_x$  and NC.  $\text{SiO}_x/\text{NC}$  microspheres with average diameters less than 3  $\mu\text{m}$  and controllable carbon content were synthesized with a scalable microemulsion method followed by carbonization. The uniform distribution of  $\text{SiO}_x$  nano-domains in NC can effectively enhance the structural integrity of  $\text{SiO}_x$ , leading to excellent long-term cycling performance. Due to the unique structural features and N-doping, the  $\text{SiO}_x/\text{NC}$  composite exhibited considerable capacitive-controlled Li storage capacity, which contributes to superior rate capability. Such electrochemical performances enabled stable full-cell operations when coupled with  $\text{LiFePO}_4$ . Consequently, after 350 cycles at 2C, the assembled  $\text{SiO}_x/\text{NC-2}/\text{LiFePO}_4$  full cell maintains a capacity retention of 89%.

## Experimental section

### Sample preparation

To prepare the  $\text{SiO}_x/\text{NC}$  microspheres, 1 g of chitosan (CS, 200–400 mPa s, deacetylation degree  $\geq 80\%$ , Aladdin Chemistry Co.) and certain amounts of vinyltriethoxysilane (VTES, Aladdin Chemistry Co.) were used as the precursors of NC and  $\text{SiO}_x$ , respectively. The organosilica/chitosan (organosilica/CS) composites synthesized by adding 2, 2.5 and 3 g of VTES were designated as organosilica/CS-1, organosilica/CS-2, and organosilica/CS-3, respectively, and the corresponding carbonization products were labelled as  $\text{SiO}_x/\text{NC-1}$ ,  $\text{SiO}_x/\text{NC-2}$ , and  $\text{SiO}_x/\text{NC-3}$ , respectively.

To synthesize  $\text{SiO}_x/\text{NC-2}$ , 1 g of chitosan was dispersed in 25 ml 1.5% acetic solution to form a transparent solution. After slowly adding 2.5 g of VTES, the solution was continuously stirred overnight at room temperature to obtain viscous organosilica/CS-2 solution. A well-mixed suspension containing 120 ml of liquid paraffin and 5.5 g of sorbitan trioleate (Span 85) was dispersed in a reactor and stirred at 1000 rpm for 0.5 h. Then the organosilica/CS-2 solution was added into the reactor and stirred at 1400 rpm for 1 h. Then, 3 g polyoxyethylene sorbitan trioleate (Tween 85) was added into the suspension and kept stirring at 1400 rpm for another 1 h. Subsequently, a solution containing 3 ml ammonia (28%) in 10 ml isopropanol was added dropwise into the vessel and stirred at 1400 rpm for 1 h to coagulate the organosilica/CS droplets. After vacuum filtration and washing with petroleum ether, ethanol, and deionized water (DW), the sample was dried in a freeze-

dryer at  $-60\text{ }^\circ\text{C}$  for 24 h. To obtain the black  $\text{SiO}_x/\text{NC-2}$  powder, the freeze-dried white organosilica/CS-2 powders were carbonized at  $1000\text{ }^\circ\text{C}$  in a tube furnace for 3 h, in  $\text{Ar}/\text{H}_2$  (95/5) atmosphere.

The synthesis of  $\text{SiO}_x/\text{NC-1}$  and  $\text{SiO}_x/\text{NC-3}$  were similar to that of  $\text{SiO}_x/\text{NC-2}$ , except the weight of VTES was 2 g and 3 g, respectively. Bare NC sample was prepared by etching  $\text{SiO}_x/\text{NC-2}$  microspheres with 10% HF solution for 6 h.

### Materials characterization

The Brunauer–Emmett–Teller (BET) specific surface area measurements of the  $\text{SiO}_x/\text{NC}$  composites were performed on a Micromeritics ASAP 2020 analyzer. To investigate the phase composition of the  $\text{SiO}_x/\text{NC}$  composites, a PANalytical X'Pert X-ray diffractometer was used to measure the X-ray diffraction (XRD) patterns. Thermo gravimetric analysis (TGA) data were collected by a STA-449C thermogravimetric apparatus in air atmosphere. X-ray photoelectron spectrum (XPS) data of the samples were obtained on a VG Multi Lab 2000 apparatus. Transmission-electron-microscopy (TEM) and scanning electron microscopy (SEM) images of the  $\text{SiO}_x/\text{NC}$  samples were taken by using a Tenia G200 FEI STEM/EDS microscope and a Nova NanoSEM 450 scanning electron microscope, respectively.

### Measurements of electrochemical performances

The electrochemical performances of the  $\text{SiO}_x/\text{NC}$  composites and NC were tested by using CR2032 coin cells. The  $\text{SiO}_x/\text{NC}$  composite or bare NC, Super-P, and sodium alginate (75 : 10 : 15, by weight) were mixed in DW to form a slurry. Then the formed slurry was casted to a Cu foil. The mass loading of the active material was controlled at  $0.9\text{--}1.2\text{ mg cm}^{-2}$ . The foil was dried at  $100\text{ }^\circ\text{C}$  in a vacuum oven over night. The electrolyte was 1.3 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in a mixed solution of ethylene carbonate/diethylene carbonate/fluoroethylene carbonate (EC/DEC/FEC, 30 : 60 : 10, by volume). The rate capability and cycling performance of the assembled half and full cells were tested galvanostatically on a Neware battery testing system. Cyclic voltammetry (CV) at various sweep rates was tested by using a Solartron 1470E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) of the  $\text{SiO}_x/\text{NC}$  composites was tested by using a CHI600E electrochemical workstation. The N/P ratio of the  $\text{SiO}_x/\text{NC-2}/\text{LiPFeO}_4$  (LFP) full cells was about 1.2. The weight ratio of LFP : Super-P : PVDF in the cathode was 80 : 10 : 10. The  $\text{SiO}_x/\text{NC-2}$  anodes were pre-lithiated in half cells to contemplate the lithium loss of the initial lithiation process. The galvanostatic charge/discharge test of  $\text{SiO}_x/\text{NC-2}/\text{LFP}$  full cells were performed at 0.2–4C in a voltage range of 2.2–3.8 V. The capacities of the full cells are calculated based on the weight of LFP ( $1\text{C} = 170\text{ mA h g}^{-1}$ ).

## Results and discussion

The micron-sized  $\text{SiO}_x/\text{NC}$  microspheres were fabricated by a simple and scalable microemulsion method followed by high-



temperature carbonization, as illustrated in Fig. 1a. The microemulsion used in this work can be classified as water-in-oil (W/O) system. Before emulsification, VTES was slowly hydrolyzed and condensed in an acetic acid solution of CS to form organosilica nanoparticles. As shown in Fig. S1,† compared with raw CS, the obvious redshift of the vibration peaks of  $-\text{NH}_2$  and  $-\text{OH}$  in organosilica/CS composite demonstrates the strong hydrogen binding effect between CS and the formed organosilica nanoparticles. In addition, with the hydrolysis and condensation of VTES, the CS solution gradually becomes more and more viscous, further confirming the strong hydrogen binding effect. Such strong hydrogen binding effect is beneficial for the uniform dispersion of the organosilica nanoparticles in the water phase. The water phase droplets were coagulated when ammonia was dropped into the emulsion system. After freeze-drying, the white organosilica/CS powder with homogeneous distribution of the organosilica nanoparticles in the CS matrix was obtained. The  $\text{SiO}_x/\text{NC}$  microspheres can be readily fabricated by pyrolysis of the organosilica/CS powder in  $\text{Ar}/\text{H}_2$  atmosphere.

It is noteworthy that most of the  $\text{SiO}_x$  and nano-Si anode materials prepared by Stöber method consume extensive

solvent (Table S1†). Consequently, the reported materials cannot be produced in a large scale. As shown in Table S1,† the solvent consumption in the hydrolysis process in this work is greatly reduced compared with the literature, which enables the large-scale synthesis of the  $\text{SiO}_x/\text{NC}$  composites. It is believed that the organosilica/CS solution can also be applied in the spray-drying method, which will facilitate more efficient preparation of micron-sized  $\text{SiO}_x/\text{NC}$  spheres.

The organosilica/CS samples are interconnected microspheres with smooth surface and compact structure (Fig. 1b, S2a and S3a†). As the organosilica content increases, the average diameter of the microspheres increases. After calcination, the  $\text{SiO}_x/\text{NC}$  samples inherited the smooth spherical morphology and compact structure of the organosilica/CS spheres (Fig. 1b, c, S2b and S3b†). According to the SEM and TEM observation, the average diameter of the  $\text{SiO}_x/\text{NC}$  microspheres also increases slightly with the increase of  $\text{SiO}_x$  content. According to the SEM and TEM (Fig. 1d) observation, the average particle sizes of  $\text{SiO}_x/\text{NC-1}$ ,  $\text{SiO}_x/\text{NC-2}$ , and  $\text{SiO}_x/\text{NC-3}$  are estimated to be  $\sim 0.8$ ,  $1.5$ , and  $2.5$   $\mu\text{m}$ , respectively. Compared with nanomaterials, such micron-sized  $\text{SiO}_x/\text{NC}$  composites possess lower specific surface and higher tap



Fig. 1 (a) Fabrication process of  $\text{SiO}_x/\text{NC}$  microspheres, (b) SEM image of organosilica/CS-2, (c) SEM image of  $\text{SiO}_x/\text{NC-2}$ , (d) TEM and (e) HAADF-STEM images of  $\text{SiO}_x/\text{NC-2}$ , (f-i) EDS elemental mapping images corresponding to (e).



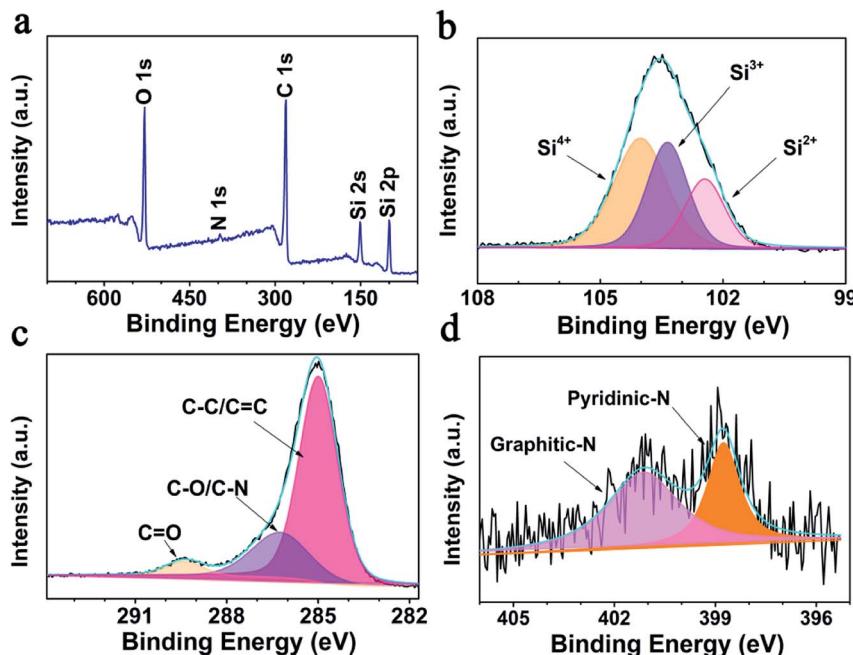


Fig. 2 XPS analysis of  $\text{SiO}_x/\text{NC}-2$  (a) survey spectrum, (b–d) Si 2p, N 1s, and C 1s high-resolution spectra, respectively.

density, which is favorable for less side reaction and higher volumetric capacity.<sup>50</sup> The elemental mapping results (Fig. 1e–i) demonstrate that C, N, O, and Si distribute evenly in micron-sized  $\text{SiO}_x/\text{NC}$  spheres, indicating that the  $\text{SiO}_x$  nano-domains are also uniformly dispersed in NC matrix. The XRD patterns (Fig. S4†) of the  $\text{SiO}_x/\text{NC}$  composites are almost identical. Only some broad diffraction peaks can be identified, indicating that both the  $\text{SiO}_x$  and NC are amorphous. The broad diffraction peaks centered at  $\sim 23^\circ$  and  $\sim 43^\circ$  belong to  $\text{SiO}_x$  and NC, respectively. The Raman spectra of the  $\text{SiO}_x/\text{NC}$  composites are presented in Fig. S5.† The intense peaks located at approximately  $1330$  and  $1600\text{ cm}^{-1}$  are corresponding to the D-band and G-band of NC, respectively. The  $I_D/I_G$  ratio for  $\text{SiO}_x/\text{NC}-1$ ,  $\text{SiO}_x/\text{NC}-2$ , and  $\text{SiO}_x/\text{NC}-3$  are estimated to be  $1.12$ ,  $1.14$ , and  $1.05$ , respectively, suggesting that a large number of defects have been introduced by N-doping. Two bumps of the 2D-band also appear at around  $2650$  and  $2900\text{ cm}^{-1}$ , indicating the existence of graphitized carbon.<sup>32</sup>

The specific surface areas as well as pore size distribution of the  $\text{SiO}_x/\text{NC}$  composites are analyzed *via* nitrogen adsorption method (Fig. S6†). The obtained specific surface areas of the  $\text{SiO}_x/\text{NC}-1$ ,  $\text{SiO}_x/\text{NC}-2$ , and  $\text{SiO}_x/\text{NC}-3$  micron-sized spheres are  $17.4$ ,  $10.5$ , and  $6.0\text{ m}^2\text{ g}^{-1}$ , respectively. The pore volumes of  $\text{SiO}_x/\text{NC}-1$ ,  $\text{SiO}_x/\text{NC}-2$ , and  $\text{SiO}_x/\text{NC}-3$  are  $0.07$ ,  $0.04$ , and  $0.03\text{ cm}^3\text{ g}^{-1}$ , respectively. Such a micron-sized moderate porous spherical structure of  $\text{SiO}_x/\text{NC}$  is very favorable for obtaining high tap density, minimizing side effect as well as achieving high volumetric energy density. Thermogravimetric analysis (TGA) was performed in the air to estimate the  $\text{SiO}_x$  content of the  $\text{SiO}_x/\text{NC}$  composites. Based on the TGA results (Fig. S7†), the  $\text{SiO}_x$  contents of  $\text{SiO}_x/\text{NC}-1$ ,  $\text{SiO}_x/\text{NC}-2$ , and  $\text{SiO}_x/\text{NC}-3$  are calculated to be about  $65\%$ ,  $59\%$ , and  $51\%$ , respectively. The

actual  $\text{SiO}_x$  content of the  $\text{SiO}_x/\text{NC}$  composites should be slightly lower than the calculated results, because  $\text{SiO}_x$  domains are oxidized to  $\text{SiO}_2$  during TGA testing.

Consistent with the EDS results, the XPS survey spectrum (Fig. 2a) reveals that the  $\text{SiO}_x/\text{NC}-2$  sample is composed of Si, O, C, and N. After calcination at  $1000\text{ }^\circ\text{C}$ , the N 1s signal is very weak, and the N content of NC is determined to be  $0.76\text{ wt\%}$  by XPS elemental analysis. As shown in Fig. 2b, the broad high-resolution Si 2p peak are divided into three peaks, corresponding to  $\text{Si}^{2+}$ ,  $\text{Si}^{3+}$ , and  $\text{Si}^{4+}$  respectively. The  $\text{Si}^{2+} : \text{Si}^{3+} : \text{Si}^{4+}$  ratio is calculated to be  $21.36\% : 33.62\% : 45.02\%$ , and an average valence state of  $3.24$  is determined (corresponding to an  $x$  value of  $1.62$ ). The calculated average valence state value is very close to the theoretical one ( $3.0$ ). The C 1s spectrum (Fig. 2c) can be divided into three peaks, locating at  $284.9$ ,  $286.2$ , and  $289.4\text{ eV}$ , corresponding to  $\text{C-C/C=C}$ ,  $\text{C-N/C-O}$ , and  $\text{C=O}$  bonds, respectively.<sup>51,52</sup> Fig. 2d presents the high resolution N 1s spectrum. The peak located at  $401.1\text{ eV}$  is attributed to graphitic-N, and the one centered at  $398.9\text{ eV}$  corresponds to pyridinic-N.<sup>25</sup> It has been reported that N-doping is beneficial to improve the electron/ion conductivity of the carbon matrix.<sup>53</sup>

As shown in Fig. 3a and S8,† the initial CV curves of the  $\text{SiO}_x/\text{NC}$  electrodes scanned at  $0.1\text{ mV s}^{-1}$  are similar in shape. In the first cathodic process, the peak at  $\sim 1.2\text{ V}$  corresponds to the formation of the solid electrolyte interface (SEI) layer.<sup>19</sup> The peak located at  $\sim 0.75\text{ V}$  cannot be observed in the following cycles. This peak relates to the irreversible reaction between Li and  $\text{SiO}_x$ , and the formation of Si,  $\text{Li}_2\text{O}$ , and various lithium silicates.<sup>19</sup> The sharp cathodic peak close to  $0.01\text{ V}$  is ascribed to lithiation of the *in situ* formed Si. The broad anodic peak below  $1.2\text{ V}$  is associated with the delithiation of  $\text{Li}_x\text{Si}$  alloy and the formation of amorphous Si.<sup>19</sup> A reduction peak at  $\sim 0.22\text{ V}$



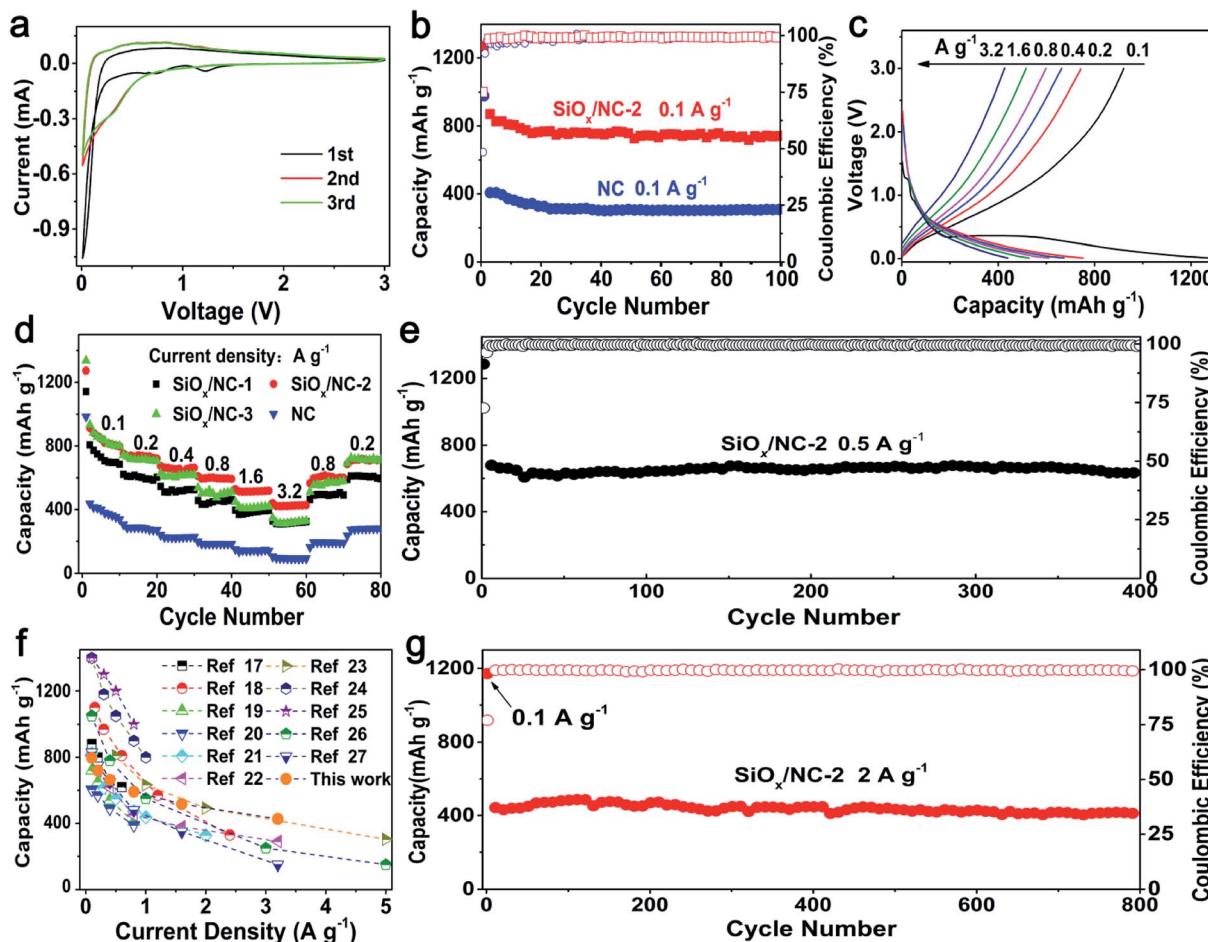


Fig. 3 (a) CV curves of  $\text{SiO}_x/\text{NC-2}$ , (b) cycling performance of  $\text{SiO}_x/\text{NC-2}$  and NC at  $0.1 \text{ A g}^{-1}$ , (c) galvanostatic charge–discharge curves of  $\text{SiO}_x/\text{NC-2}$  and NC at  $0.1\text{--}3.2 \text{ A g}^{-1}$ , (d) rate performance of the NC and  $\text{SiO}_x/\text{NC}$  electrodes, (e) cycling performance of  $\text{SiO}_x/\text{NC-2}$  at  $0.5 \text{ A g}^{-1}$ , (f) comparison of the rate performance of  $\text{SiO}_x/\text{NC-2}$  and literature, (g) long-term cycling performance of  $\text{SiO}_x/\text{NC-2}$  at  $2 \text{ A g}^{-1}$ .

appeared in the subsequent cycles, corresponding to the lithiation of the amorphous Si. The perfect overlap of the second and third curves indicates that the lithiation/delithiation reaction is highly reversible.

The cycling performance of  $\text{SiO}_x/\text{NC-2}$  and bare NC at  $0.1 \text{ A g}^{-1}$  are shown in Fig. 3b.  $\text{SiO}_x/\text{NC-2}$  maintains a discharge capacity of  $742 \text{ mA h g}^{-1}$  after 100 cycles, corresponding to a capacity retention of 81.1% to the 2<sup>nd</sup> capacity. On the contrast, the bare NC electrode only maintains a specific capacity of  $307 \text{ mA h g}^{-1}$ , demonstrating that  $\text{SiO}_x$  contributes most of the capacity of the  $\text{SiO}_x/\text{NC}$  composites. The selected charge–discharge profiles of  $\text{SiO}_x/\text{NC-2}$  at  $0.1 \text{ A g}^{-1}$  are presented in Fig. S10.†  $\text{SiO}_x/\text{NC-2}$  manifests an initial discharge capacity of  $1270 \text{ mA h g}^{-1}$  as well as an initial coulombic efficiency (ICE) of 74.9%. Such ICE is higher than many recently reported  $\text{SiO}_x$  anodes.<sup>17,19,20,22,23,28</sup>

Fig. 3c displays the typical charge–discharge curves of  $\text{SiO}_x/\text{NC-2}$  at  $0.1\text{--}3.2 \text{ A g}^{-1}$  and Fig. 3d reveals the rate capability of bare NC and the  $\text{SiO}_x/\text{NC}$  electrodes. The corresponding discharge specific capacity data are listed in Table S2.† These samples exhibit a stable cycling even at  $3.2 \text{ A g}^{-1}$ . The electrodes can recover nearly 100% of the initial capacities, when the

current density decreases to  $0.2 \text{ A g}^{-1}$ , demonstrating the structural integrity of bare NC and the  $\text{SiO}_x/\text{NC}$  microspheres. The capacity difference between  $\text{SiO}_x/\text{NC-2}$  and  $\text{SiO}_x/\text{NC-3}$  is negligible at  $0.1$  and  $0.2 \text{ A g}^{-1}$ . While at  $0.8, 1.6$ , and  $3.2 \text{ A g}^{-1}$ ,  $\text{SiO}_x/\text{NC-2}$  achieves discharge capacities of  $592, 518$ , and  $427 \text{ mA h g}^{-1}$ , respectively, evidently higher than the corresponding ones of  $\text{SiO}_x/\text{NC-3}$ , although  $\text{SiO}_x/\text{NC-3}$  has a higher content of  $\text{SiO}_x$ . The lower capacities of  $\text{SiO}_x/\text{NC-3}$  at high current densities can be explained by its higher charge-transfer resistance, which can be confirmed by the EIS spectra (Fig. S9†). At  $0.2$  and  $3.2 \text{ A g}^{-1}$ , the bare NC electrode only delivers a capacity of  $271$  and  $92 \text{ mA h g}^{-1}$ , respectively, confirming that  $\text{SiO}_x$  is the primary active material. Fig. 3f compares the rate performance of  $\text{SiO}_x/\text{NC-2}$  and many reported  $\text{SiO}_x/\text{C}$  composites with  $x$  values close to 1.5.<sup>17–27</sup> For some reported  $\text{SiO}_x/\text{C}$  composites, the rate performance are tested at current densities lower than  $2 \text{ A g}^{-1}$ , and their capacities decrease sharply with the increase of current density. Some  $\text{SiO}_x/\text{C}$  composites deliver much higher capacities than  $\text{SiO}_x/\text{NC-2}$  at  $0.1$  and  $0.2 \text{ A g}^{-1}$ , but at about  $3.2 \text{ A g}^{-1}$ , their discharge capacities are lower than that of  $\text{SiO}_x/\text{NC-2}$ . At  $3.2 \text{ A g}^{-1}$ ,  $\text{SiO}_x/\text{NC-2}$  exhibits a discharge capacity of  $427 \text{ mA h g}^{-1}$ , which is quite competitive among the



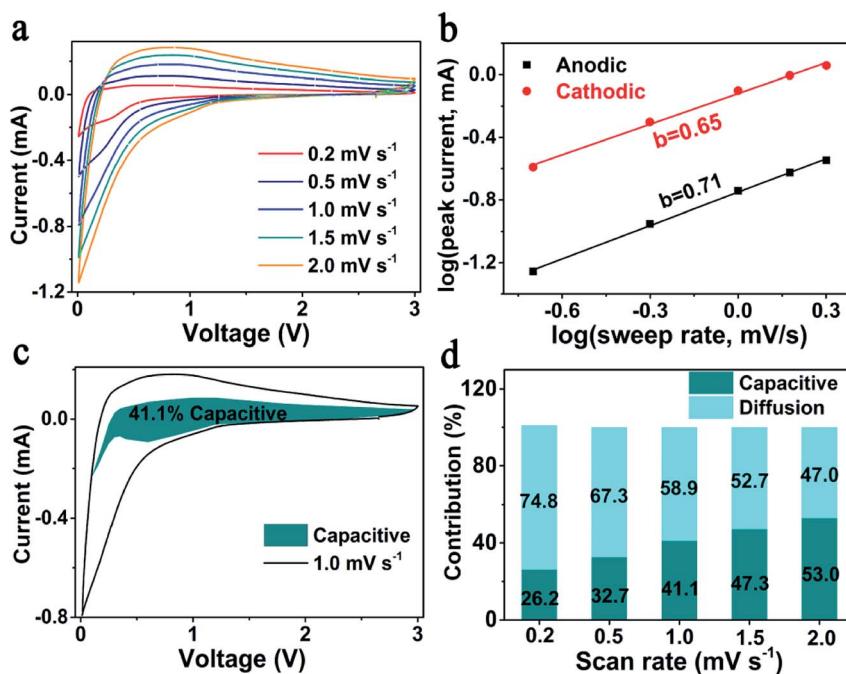


Fig. 4 (a) CV curves of  $\text{SiO}_x/\text{NC-2}$  at  $0.2\text{--}2.0\text{ mV s}^{-1}$ , (b) plots of  $\log(i_p)$  vs.  $\log(v)$ , (c) capacitive-controlled contribution at  $1\text{ mV s}^{-1}$ , (d) capacitive-controlled contribution at  $0.2\text{--}2.0\text{ mV s}^{-1}$ .

recently reported  $\text{SiO}_x$ -based composite electrodes. The superior rate capability of  $\text{SiO}_x/\text{NC-2}$  may be derived from the uniform dispersion of  $\text{SiO}_x$  as well as N-doping.<sup>17,32,46</sup>

As shown in Fig. 3e and g, the  $\text{SiO}_x/\text{NC-2}$  also shows excellent long-term cycling performance at both  $0.5$  and  $2\text{ A g}^{-1}$ . After 400 deep charge-discharge cycling at  $0.5\text{ A g}^{-1}$ ,  $\text{SiO}_x/\text{NC-2}$  maintains a discharge capacity of  $637\text{ mA h g}^{-1}$ , slightly lower than the capacity of the  $\text{SiO}_x/\text{C}$  microspheres prepared with resorcinol/

formaldehyde and VTES by Liu *et al.*<sup>17</sup> However, the  $\text{SiO}_x/\text{NC-2}$  displays outstanding long-term cycling capability at a high current density of  $2\text{ A g}^{-1}$ , and retains a discharge capacity of  $416\text{ mA h g}^{-1}$  after 800 cycles, corresponding to a capacity retention of 81% from the 4<sup>th</sup> cycle. The excellent cycling stability of  $\text{SiO}_x/\text{NC-2}$  benefits from its outstanding structural integrity. As shown in Fig. S11,† after 100 cycles, the  $\text{SiO}_x/\text{NC-2}$  preserves the micron-sized spherical geometry, demonstrating

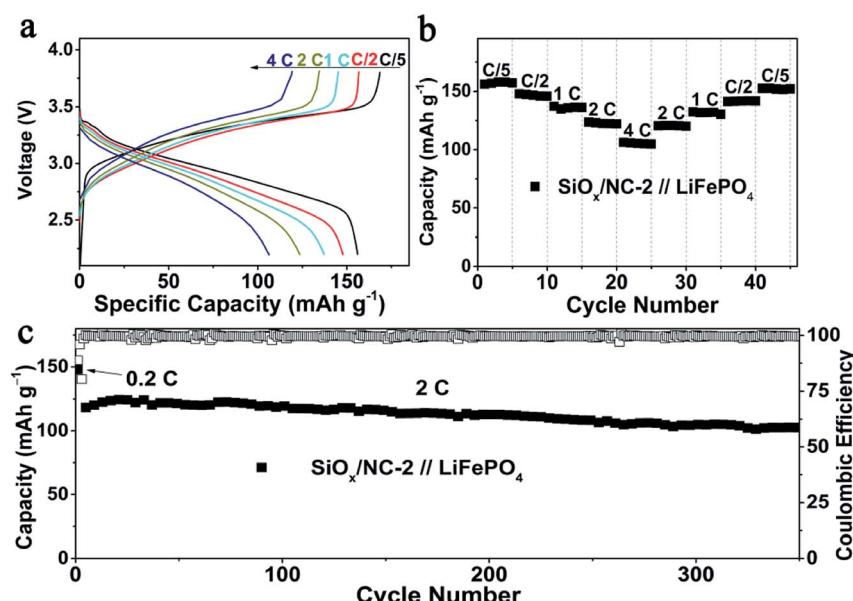


Fig. 5 Electrochemical performance of the  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell, (a) galvanostatic charge/discharge profiles at  $0.2\text{--}4\text{C}$ , (b) rate capability at  $0.2\text{--}4\text{C}$ , (c) galvanostatic long cycling performance at  $2\text{C}$ .

its structural integrity. The structural integrity originates from the unique structural features of  $\text{SiO}_x/\text{NC-2}$ : (a) the  $\text{SiO}_x$  species are divided into ultrafine nano-domains by the 3D NC matrix, thus the pulverization of  $\text{SiO}_x$  can be effectively inhibited. (b) The NC matrix ensures the structural integrity of the micron-sized composite spheres by buffering the volume change of the  $\text{SiO}_x$  nano-domains and preventing their aggregation.

According to previous reports, the outstanding rate performance may be related with the capacitive-controlled Li storage mechanism.<sup>54,55</sup> Here, CV measurements at sweep rates of 0.2–2.0 mV s<sup>-1</sup> were performed, to explore the Li storage mechanism of  $\text{SiO}_x/\text{NC-2}$ . The obtained CV curves showed similar shapes with broad peaks (Fig. 4a). Generally, the capacitive behavior can be judged based on eqn (1).<sup>54</sup>

$$i_p = av^b \quad (1)$$

Here,  $i_p$  and  $v$  correspond to peak current and sweep rate, respectively.  $a$  is a constant, and  $b$  is the slope of the  $\log(v) - \log(i_p)$  plots. It is commonly accepted that a  $b$ -value of 0.5 and 1 indicates a diffusion-controlled and a capacitive-controlled Li storage mechanism, respectively. As displayed in Fig. 4b, the determined  $b$ -value of the anodic peak is 0.71, and the one of the cathodic peak is 0.65. These  $b$ -values suggest that both the capacitive-controlled and diffusion-controlled Li storage mechanisms contribute to the  $\text{SiO}_x/\text{NC-2}$  electrode. At a specific scan rate ( $v$ ) and voltage ( $V$ ), based on the relationship between current ( $i(v)$ ), capacitive-controlled contribution ( $k_1v$ ), and diffusion-controlled contribution ( $k_2v^{1/2}$ ):  $i(V) = k_1v + k_2v^{1/2}$ , the ratio of capacitive-controlled capacity to the total Li storage capacity can be calculated quantitatively.<sup>54,55</sup> Typically, at 1 mV s<sup>-1</sup> (Fig. 4c), capacitive-controlled capacity accounts for about 41.1% of the total Li storage capacity. The ratio of capacitive-controlled capacity to the total capacity increases with the sweep rate (Fig. 4d), demonstrating that the capacitive-controlled mechanism facilitates more efficient  $\text{Li}^+$  insertion/extraction at higher scan rate. As a result, the  $\text{SiO}_x/\text{NC-2}$  electrode exhibits high rate capability and stable cycling at 2 A g<sup>-1</sup>. The pseudocapacitive effect of  $\text{SiO}_x/\text{NC-2}$  can be attributed to three factors: (a) the huge interfaces between  $\text{SiO}_x$  nano-domains and NC matrix provide numerous active sites for Li storage; (b) N doping causes sufficient defects in the carbon matrix, thus enhances electron/ion transfer kinetics; (c) the uniform distribution of  $\text{SiO}_x$  in NC matrix reduces the diffusion distance of electron and  $\text{Li}^+$ , leading to further improved electrochemical kinetics.

To evaluate the validity of the  $\text{SiO}_x/\text{NC-2}$  in LIBs,  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cells were assembled by using commercial LFP and  $\text{SiO}_x/\text{NC-2}$  as a cathode and anode, respectively. The N/P ratio of the full cell is controlled at around 1.2. Before the full cell assembly, the  $\text{SiO}_x/\text{NC-2}$  electrodes were pre-lithiated in a half cell to obtain a stable SEI layer. Base on the weight of LFP, at 0.2, 0.5, 1, 2 and 4C, the  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell manifests specific capacities of 156, 148, 137, 123 and 106 mA h g<sup>-1</sup>, respectively (Fig. 5a). Due to the excellent rate capability of  $\text{SiO}_x/\text{NC-2}$ , the assembled  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell displays stable cycling at 4C (Fig. 5b). A specific capacity of 152 mA h g<sup>-1</sup> is achieved, when

the C-rate gradually decreases to 0.2C, demonstrating superior rate capability. The superior rate capability of the  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell can be attributed to the enhanced structural integrity and the dual-model (battery-capacitive) Li storage mechanism of  $\text{SiO}_x/\text{NC-2}$ . Consequently, the as assembled  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell achieves a stable long-term cycling at a relatively high rate of 2C (Fig. 5c). After 350 cycles, the  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell maintains a specific capacity of 103 mA h g<sup>-1</sup>, retaining 89% of the 3<sup>rd</sup> capacity. The superior rate capability and outstanding cycling stability demonstrate that the  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell can serve as a potential high energy density power source with a certain quick-charge capability.

The superior rate capability and excellent cycling stability of  $\text{SiO}_x/\text{NC-2}$  can be ascribed to the following points: (a) the electron and  $\text{Li}^+$  diffusion kinetics of active  $\text{SiO}_x$  is significantly enhanced by its even distribution in the NC matrix. (b) The NC matrix ensures the structural integrity by alleviating the volume change and preventing the pulverization of  $\text{SiO}_x$ . (c) The capacitive-controlled Li storage mechanism enables the high rate capability.

## Conclusions

In summary, micron-sized  $\text{SiO}_x/\text{NC}$  interconnected microspheres with tunable  $\text{SiO}_x$  content (51–65 wt%) have been produced *via* a scalable microemulsion method with chitosan and VETS as the NC and  $\text{SiO}_x$  precursor, respectively. With the uniform distribution of ultra-small  $\text{SiO}_x$  domains in amorphous NC matrix, the  $\text{SiO}_x/\text{NC-2}$  microspheres exhibit considerable capacitive-controlled Li storage capacity and outstanding structural integrity, which contribute to the superior rate capability and excellent cycling stability. After 350 cycles at 2C, the assembled  $\text{SiO}_x/\text{NC-2} // \text{LFP}$  full cell can maintain a specific capacity of 103 mA h g<sup>-1</sup>. This work provides an effective approach for constructing micron-sized high-performance  $\text{SiO}_x/\text{C}$  anode materials by using chitosan as N-doped carbon precursor, and to some extent facilitates the recycling of waste seafood shells.

## Conflicts of interest

There are no conflicts to declare.

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