

# Hydrothermal carbon spheres containing silicon nanoparticles: synthesis and lithium storage performance†

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**Spherically shaped carbon/silicon nanocomposites have been obtained in a one-step procedure using hydrothermal carbonization of glucose in the presence of commercially available silicon nanoparticles and have been tested electrochemically as an anode material for lithium-ion batteries.**

A variety of advanced techniques demand rechargeable lithium-ion batteries exhibiting high energy and high power density. Commercial lithium ion batteries often employ graphitic carbon anodes which provide a theoretical capacity of 372 mA h g<sup>-1</sup>.<sup>1,2</sup> However, new compact and modern portable electronic devices as well as hybrid electric vehicles require higher energy density power sources with improved cyclability and rate capability. In comparison with graphitic carbon, silicon exhibits a theoretical capacity of 4200 mA h g<sup>-1</sup>.<sup>3</sup> However, it is also well known that upon repeated alloying–dealloying processes of Li with silicon, silicon particles show severe volumetric changes which leads to the crumbling of active materials and conduction network breakage, resulting in poor cyclability.<sup>4,5</sup> In order to improve the electrochemical properties of silicon, various composite materials containing well dispersed silicon particles in host matrices have been investigated.<sup>6–10</sup> For instance, Liu and co-workers recently reported amorphous carbon coated Si nanocomposites prepared by a low-temperature spray pyrolysis technique show high capacities and high coulombic efficiencies.<sup>7c,d</sup> In these cases, carbon-based materials have shown advantages as a host matrix. During Li insertion and extraction, carbon materials can buffer the volume changes of silicon particles and guarantee good electrical contact.

Hydrothermal carbonization of carbohydrates represents a cheap, easy and green substitute for the production of carbon spheres.<sup>11,12</sup> These carbon spheres consist of a carbonized hydrophobic core but still contain in the outer shell a high number of functional groups remaining from the carbohy-

drate.<sup>13,14</sup> If the hydrothermal carbonization is performed in the presence of previously synthesized nanoparticles or water-soluble metal salts carbon nanocomposites are easily formed in a one-step reaction.<sup>15</sup>

Here we employ this route to enable a one-step “green” alternative to produce carbon/silicon nanocomposites using hydrothermal carbonization of glucose in the presence of pre-formed silicon nanoparticles with particle size of 20–50 nm. In order to improve the stability and electrical conductivity of the nanocomposite, after hydrothermal carbonization the particles were further carbonized at 900 °C for 2 h in an N<sub>2</sub> oven. The lithium storage performance of the C/Si nanocomposite has been investigated. Contrary to our previously published results<sup>15c</sup> here a higher ratio of carbon source (glucose) was used so that a composite material composed mainly of carbon and a low amount of silicon could be obtained.

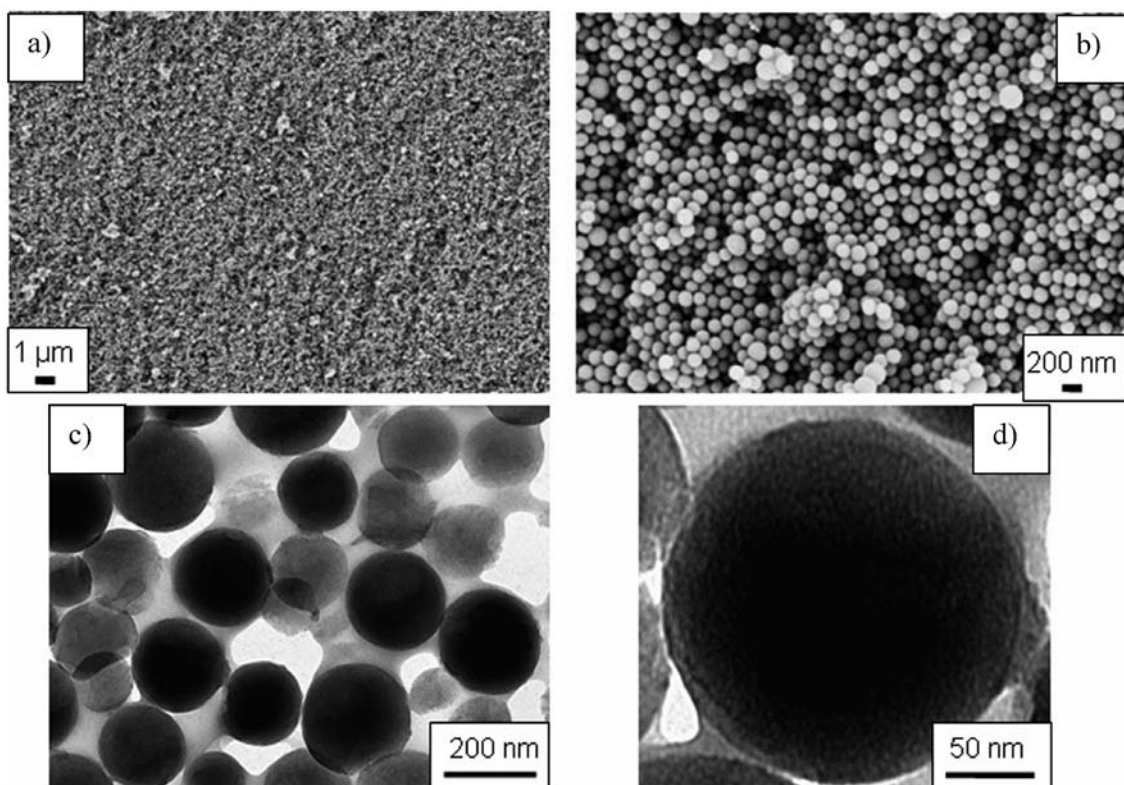
Fig. 1(a) and (b) shows scanning electron microscope (SEM) images of the C/Si spherical nanocomposites. The SEM micrographs show spherical and monodisperse particles of around 200 nm in size. The presence of the silicon nanoparticles inside the carbon spheres can be observed from the microtomed transmission electron microscope (TEM) images (Fig. 1(c) and (d)). These are distributed inside the core of the carbon spheres. According to TGA and elemental analysis (Fig. S1, ESI†) the amount of silicon nanoparticles dispersed inside the carbon matrix is ~15%.

From the X-ray diffraction (XRD) patterns, it can be observed that upon hydrothermal carbonization no SiO<sub>x</sub> crystalline phase was formed whereas a thin layer of amorphous SiO<sub>x</sub> may form on the surface of silicon nanoparticles under such hydrothermal condition as reported elsewhere.<sup>15c</sup> Furthermore, no diffraction peaks corresponding to graphitic carbon were detected in the XRD pattern. However some very weak peaks at *d* = 3.41 and 2.02 Å were observed meaning that our carbon matrix is amorphous (Fig. 2).<sup>11</sup> This was further confirmed by Raman spectroscopy. The characteristic wide D and G bands around 1360 and 1590 cm<sup>-1</sup>, typical for amorphous carbons or disordered graphite are present in the Raman spectrum of the nanocomposite material. The large value of I<sub>D</sub>/I<sub>G</sub> indicated the low graphitic degree in the resulting hydrothermal carbon material (Fig. S2, ESI†). Using the Scherrer equation, the crystallite dimension of silicon nanoparticles along [111] was about 18 nm before, and 19 nm after incorporating into carbon (Fig. 2), indicating that the hydrothermal carbonisation and high temperature

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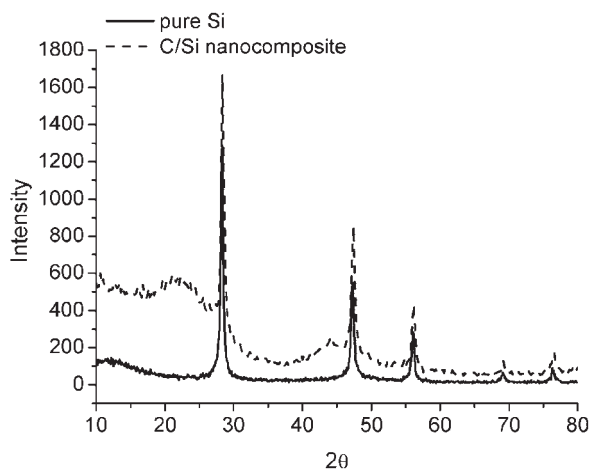
† Electronic supplementary information (ESI) available: Experimental details, thermal (TG) and structural (Raman and BET) characterizations of C/Si nanocomposites as well as electrochemical behaviour of a commercial Si electrode. See DOI: 10.1039/b805671b



**Fig. 1** (a), (b) Scanning electron micrographs of the Si/C nanocomposites at two different magnifications; (c), (d) transmission electron micrographs at two different magnifications.

treatment do not change the crystallite size of the sample as the carbon shell prevents the aggregation and growth of silicon nanoparticles.

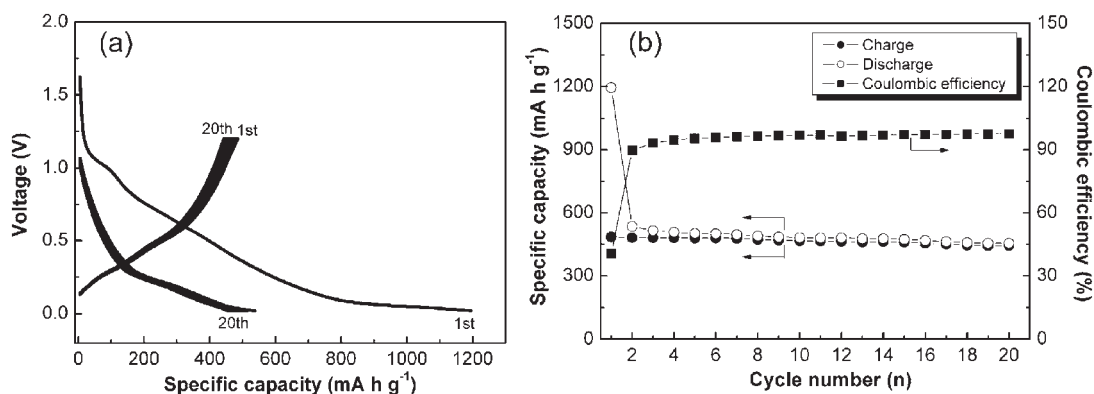
Nitrogen adsorption experiments showed that the obtained C/Si nanocomposite has a surface area of  $260 \text{ m}^2 \text{ g}^{-1}$  and is microporous (Fig. S3, ESI†). This is due to the further carbonization under  $\text{N}_2$  at  $900 \text{ }^\circ\text{C}$  after the hydrothermal carbonization, where further condensation of the carbonaceous material results in functionality loss and development of micropores. The surface area and the adsorption–desorption



**Fig. 2** XRD pattern of the pure Si nanoparticles and the Si/C nanocomposite.

isotherms are similar to those obtained for a pure carbon sample treated under similar conditions.

In order to test the potential applicability in lithium-ion batteries, we investigated the electrochemical properties with respect to Li storage. Galvanostatic discharge–charge experiments were carried out to evaluate the electrochemical performance of the C/Si nanocomposite. For comparison, commercially available nanometer-sized Si was also tested. The discharge (Li insertion)/charge (Li extraction) curves (Fig. 3(a)) of the C/Si nanocomposite electrode were obtained in 1 M  $\text{LiPF}_6$  EC–DMC electrolyte solution containing 2 wt% VC at a current density of  $300 \text{ mA g}^{-1}$ . The C/Si nanocomposite shows highly stable reversible capacity ( $\sim 460 \text{ mA h g}^{-1}$ ) at a high current rate of  $300 \text{ mA g}^{-1}$  in the voltage range of 0.05 to 1.2 V, which is remarkably higher than that of pure hydrothermal carbon under the same electrochemical conditions (*ca.*  $160 \text{ mA h g}^{-1}$ , see Fig. S4, ESI†<sup>16</sup>). In contrast, in the case of pure nanometer-sized Si, although it shows very high charge capacity (*ca.*  $1670 \text{ mA h g}^{-1}$ ) in the first cycle, the capacity decays rapidly in the following cycles (see Fig. S4, ESI†). The significant improvement of the lithium storage properties is attributed to the unique structure of the C/Si nanocomposite with a variety of favorable properties. The carbon shell with high electronic conductivity ensures good electrical contact among particles during Li insertion and extraction processes. The carbon shell also buffers well against the local volume change during the Li–Si alloying–dealloying reactions, thus retaining the structural stability and leading to a good cycling performance. The carbon itself is electroactive for Li storage and



**Fig. 3** The lithium storage performance of the C/Si nanocomposite. (a) Galvanostatic discharge–charge curves at a current density of 300 mA g<sup>-1</sup> in the voltage range of 0.05 and 1.2 V. (b) Variation in discharge–charge capacity and coulombic efficiency vs. cycle number for the C/Si nanocomposite electrode cycled at a current density of 300 mA g<sup>-1</sup>.

contributes to the overall capacity. The present results clearly show the advantage of combining carbon and Si as an anode material in lithium-ion batteries. According to our previous experiments the specific reversible capacity can be improved by using a lower amount of carbon and a higher amount of silicon.<sup>15c</sup> However, since the carbon is formed by hydrothermal carbonization from water-soluble carbohydrates, and the silicon nanoparticles are the highly priced component, these types of composites with a low content of silicon can be cheap and interesting materials to be used as electrodes in lithium ion batteries.

In conclusion a Si-nanoparticles-in carbon material have been synthesized by a cheap, simple and green approach using hydrothermal carbonization of glucose in the presence of Si nanoparticles. The resulting C/Si nanocomposites show an improved lithium storage performance compared with the pure carbon material and Si nanoparticles.

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