



Liquid-phase plasma synthesis of silicon quantum dots embedded in carbon matrix for lithium battery anodes



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ABSTRACT

Silicon quantum dots embedded in carbon matrix (SiQDs/C) nanocomposites were prepared by a novel liquid-phase plasma assisted synthetic process. The SiQDs/C nanocomposites were demonstrated to show high specific capacity, good cycling life and high coulombic efficiency as anode materials for lithium-ion battery.

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1. Introduction

Rechargeable lithium ion batteries are the most useful energy storage devices due to their high energy density and very high efficiency [1,2]. Whereas, the limited specific charge storage capacity of lithium ion batteries lead to their performance still lying behind the demands of higher energy density, higher power density, and longer cycle life for future applications. To overcome these issues, elemental materials which can form alloys with lithium (such as Si [2–4] and Sn [5,6]) and transition metal oxides (such as Fe₃O₄ and TiO₂ [7–9]) have been studied and shown to possess multiple times higher specific capacity than the state of the art graphitic anodes and to be potential as next generation electrodes. Among these functional materials, Si-based anode materials [10–13] have attracted much more attentions because of their abundance in nature, low cost, low discharge potential, and the highest known theoretical charge capacity (4200 mAh g⁻¹). However, the low electrical conductivity and significant volume changes by 400% of Si anodes during electrochemical alloying and de-alloying with lithium can lead to the pulverization of Si and rapid capacity fading [2,6], which restrict the battery performance

of Si-based anode materials. To improve the battery performance, several novel Si-based anode materials have been developed, including the nanosized active materials [2,3], active/inactive composites materials [4], and Si-based carbon composites [10,11]. Particularly, in Si/carbon (Si/C) composites system, carbon acts as a buffering matrix with good mechanical properties to accommodate the mechanical strains experienced by Si, which ensures electrode integrity during battery operating. For Si/C composites, the large sized Si particles can lead to serious pulverization and rapid capacity fading during battery operating [14–19]. Then, reducing the particle size of anode materials has a positive influence on the cycling behaviour because of the reduced mechanical stress during the lithiation process [20–25]. Consequently, to obtain Si/C nanocomposites with much smaller sized Si component as anode materials may be an effective way to improve lithium ion batteries performance [22].

Si quantum dots (SiQDs) with ultra-small size (within 5 nm) and monodispersity are ideal candidates for Si/C nanocomposites as anode materials for lithium ion batteries. However, the fabrication of this kind of SiQDs/C nanocomposites is still a huge challenge for material chemistry due to the small size, high chemical activity, and low density of SiQDs with Si–H terminated surface. In this communication, we report a convenient synthetic method for the preparation of SiQDs/C nanocomposites by a liquid-phase plasma assisted synthetic process. The as-prepared SiQDs/C nanocomposites were demonstrated to show an excellent

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performance as anode materials for lithium ion batteries with contribution of SiQDs for lithiation capacity reached up to about 3140 mAh g⁻¹, good cycling life and high coulombic efficiency.

2. Experimental

2.1. Materials

Si wafer (phosphorus-doped (p-type), 0.002 Ω sensitivity), hydrofluoric acid (HF), hydrogen peroxide, absolute ethanol were purchased from Sigma-Aldrich. All chemicals were used as-received without additional purification.

2.2. Synthetic method of SiQDs/C nanocomposites

In a typical procedure, SiQDs (synthesized by our reported method [26]) were dispersed in a beaker (100 mL) containing 60 mL absolute ethanol solution by ultrasonication for 5 min. Then the beaker containing mixed solution was placed in the chamber of the radio frequency (RF) generator setup [27]. Modulating the RF power and keeping at 300 W, the tungsten electrode tip of the RF microelectronic device will generate spark in chamber. Keeping the sparking for 20 min, the SiQDs/C nanocomposites were prepared.

To remove the SiQDs in the nanocomposites, the SiQDs/C composites (1.0 g) were put into the mixed solution of HF (50 mL, 10%) and H₂O₂ (5 mL, 30%) and stirring for 5 h. Then, the obtained carbon materials were separated by centrifugation, washed with deionized water and absolute ethanol, and then dried in vacuum oven at 60 °C.

In the control experiments, carbon materials were also prepared by liquid-phase plasma synthesis technique. The procedure and reaction conditions are similar to that for preparing the SiQDs/C nanocomposites, and the only difference is that the absolute ethanol solution of SiQDs was replaced by absolute ethanol.

2.3. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a FEI G2 transmission electron microscope. The normal TEM samples were prepared by dropping the solution onto a copper grid with polyvinyl formal support film and dried in air, respectively. Raman spectra were collected on an HR 800 Raman spectroscopy (J Y, France) equipped with a synapse CCD detector. Fourier transform infrared (FTIR) was recorded on a Ventrix (Bruker) spectrophotometer in the wavelength range of 550–3800 nm.

2.4. Electrochemical experiment

The electrodes were prepared by mixing 87 wt.% composite powders as active material, 5 wt.% acetylene black as electronic conductor and 8 wt.% polyvinylidene fluorides (PVDF) dissolved in N-methylpyrrolidinone (NMP) as binder. The as-prepared slurry was coated onto a copper foil followed by drying under vacuum at 120 °C over 12 h. The electrodes were cut into disks (14 mm in diameter). The model cells were assembled in the argon filled glove box using metallic lithium as the counter electrode, 1 M LiPF₆ dissolved in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight ratio) as electrolyte solution. The cells were tested at a different rate of 0.05–5 C with voltage cut off of 1.2/0.01 V versus Li/Li⁺.

3. Results and discussion

Fig. 1(a) shows the setup scheme for the liquid-phase plasma synthetic route. Briefly, the copper and tungsten (with a quartz

shell) electrodes were put into the ethanol solution containing SiQDs (photograph i). After continuous sparking discharge treatment for 20 min, grey SiQDs/C composites (photograph ii) were successfully obtained. Photograph iii shows the spark during the tungsten electrode discharging process. Fig. 1(b) shows the TEM image of the SiQDs used as raw materials, revealing their diameter within 5 nm and the single crystalline nature with (1 1 1) spacing about 0.313 nm of Si crystal. Fig. 1(c) depicts the TEM image of the obtained SiQDs/C nanocomposites, and shows that the SiQDs are embedded in large sized amorphous carbon particles, resulting into the formation of SiQDs/C nanocomposites. The HRTEM image of the obtained SiQDs/C nanocomposites was shown in Fig. 1(d), and the inset image highlights the SiQDs in the nanocomposites maintaining the good crystalline nature with lattice fringe space about 0.313 nm of (1 1 1) plane of Si crystal [26].

In our experiments, Raman spectrum ($\lambda_{\text{ex}} = 633 \text{ nm}$) was recorded to further confirm the structure and composition of the obtained SiQDs/C nanocomposites. As shown in Fig. 2(a), the Raman spectrum shows the presence of D and G bands of C and Si bands at 1340, 1585 and 520 cm⁻¹, respectively. The intensity of D band corresponding to C is stronger than that of G band, indicating the high density of defects and structural disorder in carbon [28]. FTIR spectroscopy provides further support for the strong binding between carbon and SiQDs. As can be seen in Fig. 2(b), the FTIR spectrum gives a broad absorption peak at $\sim 3430 \text{ cm}^{-1}$ corresponding to hydrogen bond O–H stretching vibrations. The absorption bands at 2800–3000 cm⁻¹ are attributed to CH_x, where $x = 1, 2, \text{ and } 3$. The peaks at ~ 1640 and $\sim 1400 \text{ cm}^{-1}$ are related to O–C–O asymmetric and symmetric vibrations, respectively [10a,29]. The peaks at $\sim 1050 \text{ cm}^{-1}$ and $\sim 870 \text{ cm}^{-1}$ are due to the Si–O vibrations [30], and the sharp absorption band at $\sim 750 \text{ cm}^{-1}$ are corresponding to Si–C vibrations. Both Raman and FTIR spectra confirm the formation of SiQDs/C nanocomposites. Furthermore, the energy dispersive X-ray spectroscopy (EDS, supporting information, Fig. S1) shows that this kind of SiQDs/C nanocomposites are composed of Si, O and C with weight ratio of 8.12, 3.85, and 88.03 wt.%, respectively.

The electrochemical performance of SiQDs/C nanocomposites electrodes was systematically investigated. Figs. 3 and 4 summarize the discharge (lithiation) and charge (delithiation) capacity data for SiQDs/C nanocomposites electrodes. The calculated capacities were based on the active material of SiQDs/C nanocomposites in the electrode. In Fig. 4, the plots tagged by (▲) and (▼) show the cycling behaviour of the SiQDs/C nanocomposites electrode at a cycle rate of C/20 ($C = 3579 \text{ mAh g}^{-1}$). As calculated, an initial charge capacity of 635 mA h g⁻¹ and a discharge capacity of 560 mAh g⁻¹ for SiQDs/C nanocomposites were obtained by using a nonrestricted cycling procedure. And the coulombic efficiency is high up to 88.2%, which is due to the role of the coated carbon in diminishing the side reactions with the electrolytes [21]. After 50 cycles, the charge and discharge capacities still keep at 490 and 480 mAh g⁻¹, respectively. The ratio of the irreversible capacity in the SiQDs/C nanocomposites system was only about 23.0%.

We further investigated the cycling stability of SiQDs/C nanocomposites electrode at different C rates. The rate capability testing results are shown in Fig. S2. It delivers discharge capacity over 527 mAh g⁻¹ at current rate of C/20, 485 mAh g⁻¹ at C/10, 415 mAh g⁻¹ at C/5, 304 mAh g⁻¹ at 1 C, 126 mAh g⁻¹ at 2 C, 85 mAh g⁻¹ at 5 C and finally recovered to around 508 mAh g⁻¹ at C/20, respectively.

In further experiments, simple carbon materials were obtained by treating the SiQDs/C nanocomposites by hydrofluoric acid (HF) to remove SiQDs, and their electrochemical performance was also investigated for comparison. As shown in the curves tagged by ◆

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