



# Tailored synthesis of monodispersed nano/submicron porous silicon oxycarbide (SiOC) spheres with improved Li-storage performance as an anode material for Li-ion batteries



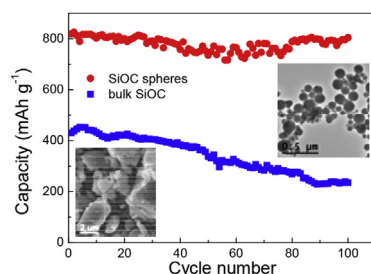
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## HIGHLIGHTS

- Spherical SiOC material was synthesized via a special-tailored synthetic strategy.
- The hollow SiO<sub>2</sub> nanobelts can prevent the pre-ceramic spheres from sintering.
- The material is composed of monodisperse nano/submicron porous SiOC spheres.
- The material exhibits high capacity and good cyclability as a Li-storage anode.
- The material exhibits much superior Li-storage performance over the pristine SiOC.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A spherical silicon oxycarbide (SiOC) material (monodispersed nano/submicron porous SiOC spheres) is successfully synthesized via a specially designed synthetic strategy involving pyrolysis of phenyltriethoxysilane derived pre-ceramic polymer spheres at 900 °C. In order to prevent sintering of the pre-ceramic polymer spheres upon heating, a given amount of hollow porous SiO<sub>2</sub> nanobelts which are separately prepared from tetraethyl orthosilicate with CuO nanobelts as templates are introduced into the pre-ceramic polymer spheres before pyrolysis. This material is investigated as an anode for lithium-ion batteries in comparison with the large-size bulk SiOC material synthesized under the similar conditions but without hollow SiO<sub>2</sub> nanobelts. The maximum reversible specific capacity of ca. 900 mAh g<sup>-1</sup> is delivered at the current density of 100 mA g<sup>-1</sup> and ca. 98% of the initial capacity is remained after 100 cycles at 100 mA g<sup>-1</sup> for the SiOC spheres material, which are much superior to the bulk SiOC material. The improved lithium storage performance in terms of specific capacity and cyclability is attributed to its particular morphology of monodisperse nano/submicron porous spheres as well as its modified composition and microstructure. This SiOC material has higher Li-storage activity and better stability against volume expansion during repeated lithiation and delithiation cycling.

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## 1. Introduction

Searching for green and sustainable electrical energy storage

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technologies such as better batteries to meet the increasing demand of our modern lifestyles is an arduous mission for scientific researchers [1]. Batteries towards applications in some fields, for example, the applications in electric vehicles and green grids, is a great challenge [1,2]. It requires high performances, such as high energy/power density, long service life and good safety. As is well known, rechargeable lithium ion batteries (LIBs) have been widely used as electrochemical energy storage devices in our daily lives because of their high energy density, long cycle life and environmental benignity. However, the theoretical capacity of commercial graphite anode is of only  $372 \text{ mAh g}^{-1}$  that cannot meet the continuously increasing demands of our modern society. Hence, considerable efforts have been put into alternative anode materials with higher specific capacities.

As one category of high-capacity anode materials, silicon-based anode materials such as simple substance silicon, silicon alloys and silicon oxides have gained considerable attentions owing to their high specific capacities and good safety [3–5]. Among these materials, the simple substance silicon possesses a very high theoretical capacity of  $4200 \text{ mAh g}^{-1}$ . However, the major drawback of Si is the excessive volume expansion ( $>300\%$ ) during the lithium-storage alloying reaction, leading to poor cycling performance. Besides, the electrical conductance of amorphous Si is poor. Hence, a great deal of attempts have been devoted to development of various Si/carbon composite materials such as nano-Si/graphene materials [6,7]. These composite materials commonly have reversible capacities of *ca.*  $1500 \text{ mAh g}^{-1}$  or lower because of containing a certain amount of carbon as a conductive additive and in many cases a volume buffer. Nevertheless, fast capacity fading still remains the greatest challenge because of the severe volume expansion and pulverization and therefore the mechanical structure collapse of the active materials upon cycling.

Polymer-derived ceramics (PDCs) represented by silicon oxycarbide (SiOC) are well known as a new type of structural ceramic materials with good high-temperature thermal stability as well as good chemical and mechanical properties [8]. Amorphous SiOC material is commonly obtained by high-temperature pyrolysis of a pre-ceramic polymer precursor derived from siloxane(s). It is composed of Si–O–C glass phase and free carbon ( $C_{\text{free}}$ ) phase with a homogeneous structure at the molecular level (generally expressed as  $\text{SiO}_{2(1-x)}\text{C}_x + yC_{\text{free}}$ , where,  $0 < x < 1$ ), possessing an open structure of nanodomain molecular network with micropores, which can form a path of least resistance for ion diffusion and electron conduction due to the available free carbon. The Si–O–C network is built of Si-centered tetrahedrally coordinated  $\text{SiO}_{4-x}\text{C}_x$  ( $x = 1-4$ ) constitutional units originated from randomly distributed Si–O and Si–C bonds [8–11].

Amorphous SiOC was firstly demonstrated to be capable of electrochemical lithium-storage as a novel anode material in 1994 by Dahn group [12]. Since then, a number of investigations on SiOC-based anode materials have been carried out [13–15]. In recent years, SiOC has attracted increasing attentions as a high-capacity anode for LIBs owing to its high practicable specific capacity ( $500-900 \text{ mAh g}^{-1}$  in general), relatively better cycling stability and potentially low cost [16–29]. Although the Li-storage mechanism of SiOC is not very clear up to now, the Li-storage performance of SiOC-based materials was found to be related to some factors, such as the chemical composition and microstructure including free carbon content (depending on the raw material of siloxane used, the composition and structure characteristics of pre-ceramic polymer precursor including carbon source substance introduced, and the pyrolysis temperature and atmosphere), electrical conductivity, particle size, morphology and micropore structure, etc.

A pyrolysis-derived SiOC material is commonly large-size bulk SiOC duo to the severe sintering of pre-ceramic polymer precursor during heating, and hence its electrochemical performance is not very good under certain conditions. In order to improve the Li-storage performance of SiOC, some research efforts have been devoted to preparing SiOC/carbon composite materials such as SiOC/graphene composite materials, which possess higher electrical conductivity and can accommodate the volume expansion during lithium storage [14,22], or to preparing SiOC materials with special morphologies such as nanofibers [19] and submicron spheres (with smaller sizes and higher specific surface areas) [23]. As Li et al. reported [19], one-dimensional SiOC/C composite nanofibers were prepared by electrospinning followed by pyrolysis of the mixture precursors of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane and polyacrylonitrile. This material can exhibit an initial reversible capacity of  $839 \text{ mAh g}^{-1}$  at  $50 \text{ mA g}^{-1}$ . After 80 cycles, a reversible capacity of  $669 \text{ mAh g}^{-1}$  is remained. Weinberger and coworkers prepared submicron SiOC spheres (average diameter of *ca.*  $200-300 \text{ nm}$ ) through pyrolysis of the pre-ceramic (organosilica spheres derived from sol–gel process of triethoxyphenylsilane) at  $1000 \text{ }^\circ\text{C}$  under argon atmosphere [23]. To prevent the organosilica spheres from sintering during heating, a small amount of tetraethoxysilane was cocondensed with the siloxane before pyrolysis. This SiOC material exhibited reversible capacities of *ca.*  $800-850$ ,  $750$ ,  $400$  and  $250 \text{ mAh g}^{-1}$  at  $50$ ,  $100$ ,  $1000$  and  $3000 \text{ mA g}^{-1}$ , respectively, which are much superior to the bulk SiOC material (pristine SiOC without addition of tetraethoxysilane in the preparation process).

In the present work, we demonstrate a special-tailored synthetic strategy to prepare monodisperse nano/submicron porous SiOC spheres material starting from raw materials of phenyltriethoxysilane (PhTES) and tetraethyl orthosilicate (TEOS). The prepared material has the features of small size and open micropores structure, and therefore an improved electrochemical performance as an anode material for LIBs would be expected. Indeed, as expected, the SiOC spheres material can exhibit much superior lithium-storage performance to the pristine bulk SiOC material prepared under the similar conditions. The unique mechanism for successful formation of the monodisperse SiOC spheres and the reasons accounting for the improved lithium-storage performance are revealed and discussed in this work.

## 2. Experimental

### 2.1. Synthesis of materials

Synthesis of bulk SiOC. All the chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd (China). The bulk SiOC material was prepared according to the literature [23], but with a minor modification (*i.e.*, less amount of ammonia water was used in the polycondensation step in order to obtain smaller pre-ceramic polymer spheres precursor). Briefly,  $0.8 \text{ mL}$  of phenyltriethoxysilane (PhTES) was added into a mixed solution containing  $0.5 \text{ mL}$  of aqueous HCl solution ( $0.01 \text{ M}$ ),  $1.1 \text{ mL}$  of distilled water and  $4 \text{ mL}$  of ethanol under magnetic stirring, and the mixture was further stirred for  $7 \text{ h}$  at room temperature. Thereafter, the resulting hydrolytic product (sol) was quickly added into a solution containing  $0.5 \text{ mL}$  of ammonia water ( $28 \text{ wt}\%$ ) and  $14 \text{ mL}$  of distilled water under stirring, and then a milky suspension (polycondensation product) was rapidly formed. The milky suspension was further stirred for  $48 \text{ h}$  before centrifugation and washing with distilled water and ethanol. Subsequently, the centrifuged product

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