

Hollow porous silicon nanospheres with 3D SiC@C coating as high-performance anodes

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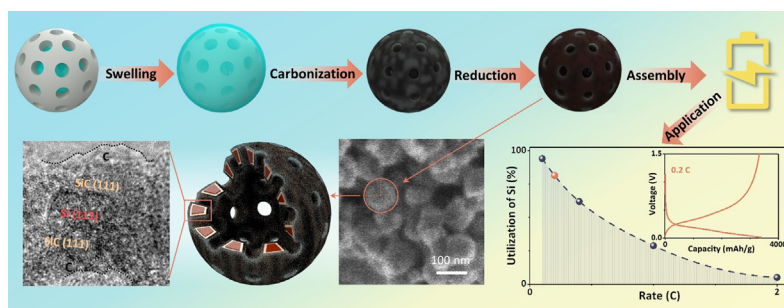
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HIGHLIGHTS

- A facile synthetic route using a polymer template has been developed to prepare hollow porous Si nanospheres with 3D SiC on C coating.
- The polymer template prevents the waste of organic components and the post-introduction of foreign carbon sources during the synthesis of the hollow Si nanospheres.
- High capacity (3200 mAh/g) and exceptional stability upon cycling (decay of 0.7% per cycle) are obtained for the anodes prepared from the hollow Si nanospheres.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon is regarded as one of the most promising anode candidates for next-generation Li-ion batteries because of its high theoretical capacity (4200 mAh g^{-1}). However, the main challenge for the practical application of Si anodes is the huge volume change during (de)alloying with lithium, which leads to the pulverization of the active material and severe loss of electrical contact after cycling. Here, we develop hollow porous silicon nanospheres with three-dimensional carbon coating and SiC transition interlayer (C@SiC@Si@SiC@C) via a simple and straightforward polymer-directed strategy in order to tackle the challenges met with Si anodes. The accordingly synthesized C@SiC@Si@SiC@C anode shows high utilization of the active substance, high measured capacity (3200 mAh g^{-1}) with almost 100% Coulombic efficiency and stable cycling performance (0.7% per cycle decay rate at 0.2C). Such superior performances are related to the uniquely designed structure. Firstly, the 3D carbon coating provides high electronic conductivity, and extremely small size of silicon shortens the diffusion distance for Li ions and electrons. Secondly, the stable cyclability originates from the nanoscale silicon particles reinforced by a SiC transition interlayer which effectively prevents fracture and provides robust outer layers, respectively.

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1. Introduction

Rechargeable Li-ion batteries (LIBs), which feature high energy density and long cycle life, are utilized in a wide range of practical applications, e.g., portable electrical devices, electric vehicles, aerospace industry and so forth [1–3]. While the ever-growing energy requirements of our society are still not satisfied with the energy density of current LIB technologies, electrodes and electrolyte materials with superior performance are highly pursued. In terms of anode materials, compared with graphite ($\sim 372 \text{ mAh g}^{-1}$), silicon presents more than ten times higher theoretical storage capacity ($\sim 4200 \text{ mAh g}^{-1}$ for the $\text{Li}_{22}\text{Si}_5$ alloy), and endows with moderate lithium-uptake electrochemical potential ($\leq 0.4 \text{ V}$ vs Li/Li^+) [4]. Therefore, Si has been regarded as one of the most promising anode candidates for next-generation LIBs [5]. However, the biggest challenge for its practical application is the huge volumetric variation (greater than 300 %) during the lithium insertion and extraction processes [6]. The resulting lithiation-delithiation strains incur the pulverization of active silicon materials as well as the repeated destruction of the solid electrolyte interface (SEI) layer, which, as a consequence, leads to severe loss of active material and electrical contact [7]. Inevitably, the overall capacity degrades along with long-time running.

To date, significant advances have been achieved to solve the above-mentioned problems, which can be generally divided into two categories. The first strategy comprises decreasing the dimension of silicon particles. In this respect, Liu *et al.* reported that the fracture of silicon nanoparticles during lithiation strongly depends on the particle size, with a critical “no-fracture” size of $\sim 150 \text{ nm}$ [8]. Therefore, considerable efforts have been devoted to downsizing Si particles by nano-engineering, e.g. by preparing nanowires [9–13], nanoparticles [14–17], nanodots [5], and hollow structures [18–21]. For instance, hierarchically porous Si nanospheres with a thickness of 75 nm effectively prevent fracture and also accommodate volume expansion, achieving excellent cyclability for hundreds of cycles [18]. The second method is to encapsulate silicon with an outer coating layer (e.g. core-shell [22–25], yolk-shell [26–29], and their derivatives [6,30]) which has been proved as an effective strategy to alleviate the volumetric expansion characteristic not only of silicon-based anode materials but also of other anode materials suffering from the same problem [31,32]. In particular carbon as the outer layer has attracted wide attention, due to its supplement of electrical conductivity for the inner Si material. A successful example is shown in a pomegranate-inspired design of silicon nanoparticles encapsulated by a carbon layer that protects from pulverization, stabilizes the SEI, and ensures good electrical connection between particles, resulting in high capacity and superior cyclability [30]. In those previously reported studies, carbon coating invariably requires post introduction of foreign carbon by e.g. chemical vapor deposition (CVD) [5,20] or post impregnation [21]. However, introduction of extrinsic carbon source requires additional organic precursors and complicated processes which increase the resources and energy consumption. Moreover, a single layer of amorphous carbon is reported to be brittle and to break when exerted to mechanical stress during the expansion of silicon [33]. Therefore, the development of novel nanoscale silicon anodes wrapped by robust and conductive coatings obtained *via* cost-effective and straightforward approaches is of great importance and interest.

Herein, we introduce a novel and innovating strategy to synthesize an original Si anode material characterized with a hollow porous nanostructure, 3D carbon shells and SiC interlayer. Thanks to the spontaneous migration of the polymer segments to the external polarity change of the solvent, the poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate) (PTMPM) polymer template directs the

formation of three-dimensional carbon outer layers. In addition, a hard SiC interlayer is further formed by the reaction between Si and C during the reduction of the SiO_2 precursor. Such a uniquely designed structure of nanoscale silicon core/functional shell effectively inhibits the fracturing of Si particles, enhances their electrical conductivity and shortens the pathway of electrons and Li^+ ions in the active materials, further allowing outstanding LIB performance. The originality of our approach is not only related to the unique nanosized design of the Si-based electroactive nanoparticles as but also on the disclosed fabrication method based on a stimuli-responsive polymer template. The ability of polymer chains to migrate through the nanopores of the precursor SiO_2 shell upon exposure to a specific solvent offers the possibility to wrap the particles by a polymer layer. This unique reorganization process of the polymer template is at the origin of the three-dimensional design of the particles investigated in this study. Furthermore, this fabrication process does not require external sources of carbon precursor.

2. Experimental section

2.1. Materials

2,2,6,6-Tetramethyl-4-piperidyl methacrylate (TMPM, $\text{C}_{13}\text{H}_{23}\text{NO}_2$), and vinylene carbonate (VC) were supplied by TCI. Ethanol (EtOH, 99.97 %), hydrochloric acid (HCl, 37 %), ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$, 32 %), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4 , 95 %) were supplied by VWR. 2,2'-Azobis(2-methylpropionamide) dihydrochloride ($\text{C}_8\text{H}_{18}\text{N}_6\cdot 2\text{HCl}$) was supplied by Acros Organics. CTAB ($\text{C}_{19}\text{H}_{42}\text{BrN}$) was supplied by Carl Roth. TEOS, magnesium (20–230 mesh, 98 %), and lithium hexafluorophosphate (LiPF_6) solution in ethylene carbonate (EC) and diethyl carbonate (DEC) were supplied by Sigma-Aldrich. Lithium metal foils were supplied by Alfa Aesar. *N*-methylpyrrolidone (NMP) was supplied by Fisher. Super P and polyvinylidene difluoride (PVDF) were supplied by XIAMEN TOB. Glass fiber membrane was supplied by Whatman. All chemicals were used as received without any further treatment. Milli-Q water was used.

2.2. Sample synthesis

2.2.1. Synthesis of TMPM-Cl

TMPM (5 g) were dissolved in EtOH (25 mL) at room temperature, and further stirred for 30 min. Then a HCl solution (6.5 mL, 4.1 M) was added into the solution, at a syringe speed of 13 mL h^{-1} , and stirring was continued for 1 h. The dry TMPM-Cl was obtained by removing the solvent with a rotary evaporator followed by drying in a vacuum oven at 40°C overnight.

2.2.2. Synthesis of PTMPM

TMPM-Cl (1 g) was dissolved into a mixture of water (3 mL) and EtOH (3 mL). Then $\text{C}_8\text{H}_{18}\text{N}_6\cdot 2\text{HCl}$ (50 mg) was added into the above solution. After thoroughly degassing with argon, the mixed solution was placed in an oil bath of 70°C for 3 h. Finally, PTMPM was obtained.

2.2.3. Synthesis of C@SiC@Si@SiC@C nanospheres.

(a). Synthesis of PTMPM-silica composite nanospheres.

PTMPM (0.3 mL) and water (9.7 mL) were mixed and stirred for 1 h. Afterwards, a NaOH solution (1 mL, 1.25 M) was dropwise added into the above solution and stirred overnight. The suspension was centrifuged at 5000 rpm for 20 min. The precipitate was collected and washed by water until the pH reached a value of 7–8. The washed sample was

dissolved into EtOH (8 mL), and dropwise added into a CTAB solution (20 mL, 3.75 mg mL⁻¹). Successively, NH₃·H₂O (30 µL) and TEOS (200 µL) were thoroughly mixed into the solution. The mixed solution was heated in an oil bath at 38 °C for 24 h. The P@SiO₂ particles were finally collected by centrifugation at 9000 rpm for 20 min.

- (b). **Swelling of PTMPM and *in-situ* carbonization.** The P@SiO₂ sample was swelled in EtOH for 24 h and freeze-dried, to obtain the swollen sample, denoted as P@SiO₂@P. P@SiO₂@P (0.2 g) was impregnated by a H₂SO₄ aqueous solution (0.6 mL, 10 wt%) for 2 h at room temperature, followed by 12 h at 100 °C, and finally 12 h at 160 °C. The pre-carbonized sample was calcined for 2 h at 900 °C in a tubular furnace under argon atmosphere, with a ramp rate of 2 °C min⁻¹. The carbonized sample was obtained and denoted as C@SiO₂@C.
- (c). **Magnesiothermal reduction reaction.** C@SiO₂@C sample, magnesium powder, and NaCl were thoroughly mixed in an agate mortar, where the molar ratio of SiO₂ (in C@SiO₂@C) and Mg was 1:2.1, and the mass ratio of Mg and NaCl was 1:10. The mixture was then sealed in a boron nitride reactor under argon. In a typical magnesiothermal reduction reaction, the reactor was heated at 650 °C for 2.5 h under argon atmosphere, with a ramp rate of 10 °C min⁻¹ below 400 °C and a ramp rate of 1 °C min⁻¹ from 400 °C to 650 °C. The reduced sample was washed by HCl (1 M) and HF (1 vol%) solutions more than three times, to achieve the C@SiC@Si@SiC@C composite material.

2.3. Material characterization

Transmission electron microscopy (TEM) imaging was performed on a FEI Tecnai G220 system at an acceleration voltage of 120 kV and the layers structure of C@SiC@Si@SiC@C was investigated with a JEOL JEM-2100 (JEOL GmbH, Eching, Germany) at an acceleration voltage of 200 kV. Samples have been prepared by applying a finely grinded powder onto a carbon coated TEM grid (Quantifoil, Germany). Scanning electron microscopy (SEM) images were collected with a JEOL 7600F electron microscope. An ALV/CGS-3 compact goniometer system (ALV GmbH, Germany) was used to measure the average hydrodynamic radius of the samples using dynamic light scattering (DLS). The CONTIN algorithm available in the ALV software was used to analyze DLS data. Nitrogen sorption isotherms were measured with a Micromeritics ASAP 2020 analyzer at 77 K. X-ray diffraction (XRD) patterns were collected on a STOE Stadi P transmission diffractometer system using Cu-Kα ($\lambda = 1.54 \text{ \AA}$) or Mo-Kα ($\lambda = 0.71 \text{ \AA}$) radiation. X-band electron spin resonance (ESR) spectra were acquired on an EMXmicro CW-EPR spectrometer from Bruker, Germany (EMX micro EMM-6/1/9-VT control unit, ER 070 magnet, EMX premium ER04 X-band microwave bridge equipped with EMX standard resonator, EMX080 power unit). The powdery samples were investigated at room temperature and the data handling was done using the Bruker Xenon software package, version 1.1b86. Raman analysis was carried out using a DXR Raman microscope with laser excitation at 532 nm from Thermo Fisher Scientific. FT-IR spectra were recorded with the KBr method on a Nicolet iN10 IR Microscope from Thermo Fisher Scientific. Thermogravimetric analysis (TGA) was conducted in a TGA/SDTA851 instrument from Mettler Toledo under air flow with a heating ramp of 5 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was realized at room temperature by using a SSI X-Probe (SSX 100/206) photoelectron spectrometer from FISONS equipped with a monochromatized microfocus Al-Kα X-ray source.

2.4. Battery fabrication and electrochemical measurements

C@SiC@Si@SiC@C, super P, and PVDF (5 wt% in NMP) were mixed with a mass ratio of 7:2:1 to form a slurry. After casting the slurry onto a copper foil, the electrode was dried in a vacuum oven overnight at 70 °C. A polished lithium metal foil was used as a reference and counter electrode. A glass fiber membrane was used as a separator. The electrolyte consisted of LiPF₆ (1 M) in EC and DEC (1:1 v/v), with VC (1 vol%) as an additive. All coin-cells (2032) were assembled under an argon atmosphere (H₂O and O₂ less than 0.1 ppm) in a MBraun glovebox. The cells were cycled galvanostatically between 0.01 V and 1.5 V vs Li/Li⁺ on a NEWARE system. Galvanostatic intermittent titration technique (GITT) was used after two cycles of activation at 0.02C, wherein the current density of pulse current was 0.02C for 10 min, followed by 1 h as rest time. Electrochemical impedance spectroscopy (EIS) tests were carried out using a Bio-Logic BSC-COM instrument. Charge/discharge rates were calculated based on the theoretical capacity of silicon (C = 4200 mA g⁻¹).

3. Result and discussion

The strategy used in this contribution for the synthesis of low porous C@SiC@Si@SiC@C nanospheres with 3D SiC@C coating is illustrated in Fig. 1A and is directed by the swelling behavior of PTMPM (structural formula in Figure S1) polymer template. This novel and innovating strategy is based on four successive main steps: (i) synthesis of PTMPM-silica composite nanospheres, (ii) swelling of PTMPM, (iii) *in-situ* carbonization, and finally (iv) magnesiothermal reduction.

Firstly, PTMPM-silica composite nanospheres with a porous silica shell have been synthesized, using our previously reported procedure [34]. This approach relies on a mini-emulsion process resulting in monodisperse PTMPM spherical nanoparticles stabilized by cetyltrimethylammonium bromide (CTAB) surfactant molecules which are denoted as P@CTAB. In a further step, both PTMPM and CTAB are used as templating agents. More precisely, the condensation reaction of tetraethoxysilane (TEOS) is realized on the P@CTAB nanoparticles, and core-shell nanoparticles that consist of a PTMPM core and a porous silica shell (denoted as P@SiO₂) are obtained after removal of the excess of TEOS and CTAB. The porosity in the SiO₂ shell originates from the partial removal of CTAB molecules and/or CTAB micelles located at the surface of the PTMPM nanoparticles, which is in agreement with our previous report [35,36]. The transmission electron microscope (TEM) image presented in Fig. 1B shows that the P@SiO₂ composite has a regular spherical shape with a uniform diameter around 100 nm. The magnified insert image in Fig. 1B shows the rough edges of the nanospheres resulting from the porous SiO₂ shells.

Secondly, the P@SiO₂ nanospheres have been brought into contact with ethanol, resulting in the swelling of the PTMPM polymer. The swelling of PTMPM does not result in the breaking of the porous SiO₂ layer but rather in swollen PTMPM polymer chain segments passing through the pores from the inside of P@SiO₂ nanospheres to their outside. This results in a three-dimensional wrapping of PTMPM around the porous SiO₂ shells, and the resulting swollen materials are denoted as P@SiO₂@P. Compared to other reported synthetic methods for Si@C composites (Table S1), the carbon precursor in the P@SiO₂@P sample originates from the PTMPM templating agent rather than from an extrinsic carbon source. Moreover, PTMPM polymer chains direct the formation of the future three-dimensional carbon outer layers obtained after calcination. The spontaneous migration of PTMPM polymer chain segments in response to the external polarity change of the solvent is at the origin of this behavior. This unique re-wrapping process of

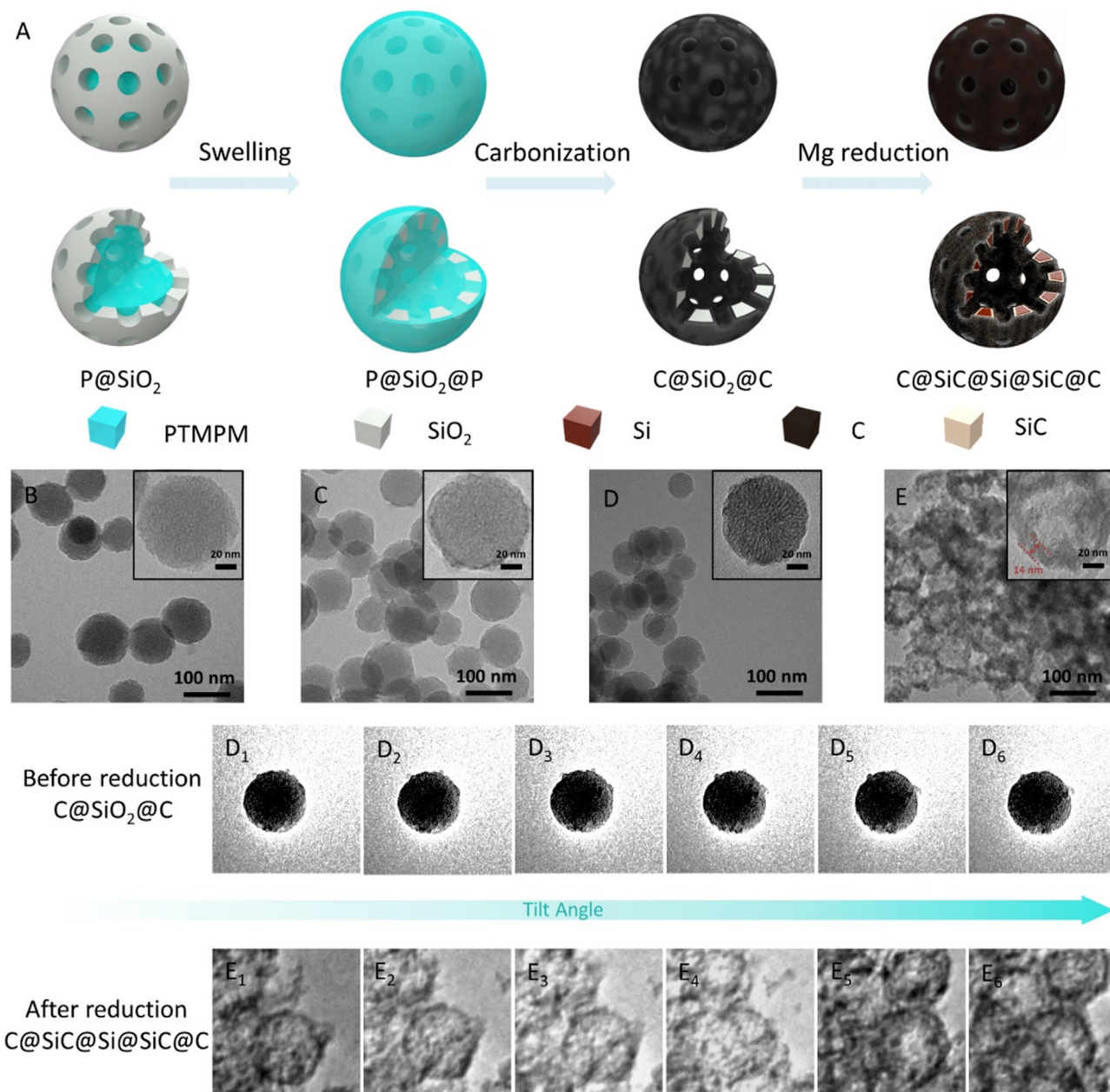


Fig. 1. Synthetic pathway towards $C@SiC@Si@SiC@C$ hollow porous nanospheres (A). TEM images of $P@SiO_2$ (B), $P@SiO_2@P$ (C), $C@SiO_2@C$ (D), and $C@SiC@Si@SiC@C$ (E) with the corresponding high magnification inserts. Projection images of $C@SiO_2@C$ (D₁-D₆, Supplementary Movie 1) and of $C@SiC@Si@SiC@C$ (E₁-E₆, overview in Supplementary Movie 2) with various tomography tilt angles.

the precursor nanoparticles by PTMPM allows to get rid of additional steps in order to generate the targeted 3D structure, further saving additional material and energy costs. Practically, the migration of PTMPM chain segments leads to extra outer margins for the nanoparticles, as shown in Fig. 1C. The swelling behavior of PTMPM in ethanol is further confirmed by dynamic light scattering (DLS). As shown in Fig. 2A, the particle radius of swollen $P@SiO_2@P$ samples is 95.7 nm, which is obviously larger than that of the initial $P@SiO_2$ (78.4 nm). Besides, the polydispersity index (PDI) measured by DLS for $P@SiO_2@P$ (PDI of 0.116) is smaller than that of $P@SiO_2$ (PDI of 0.137), suggesting a more homogeneous size distribution for the nanoparticles after PTMPM swelling. This observation is further confirmed by TEM images before and after swelling. Compared to the rough edges of $P@SiO_2$, $P@SiO_2@P$ nanoparticles display a smooth surface, since the porous SiO_2

nanospheres are wrapped by a conformal and uniform PTMPM coating layer (Fig. 1B and 1C). The change in porosity of the nanoparticles associated with the swelling of PTMPM has been also tracked by N_2 adsorption-desorption isotherms. As shown in Fig. 2B, $P@SiO_2$ and $P@SiO_2@P$ display isotherms of similar tendency, with a gradual increase in adsorption quantity in the relative pressure range of 0–0.3, and another sharp capillary condensation step in the relative pressure range of 0.9–1.0, indicating the co-existence of two types of pores in these two samples. The smaller pores are attributed to the porosity generated in the SiO_2 shell by the arrangement of CTAB molecules, while the larger pores refer to the inside of the nanospheres filled with PTMPM. The pore size distribution curves derived from the adsorption branch based on the Barrett-Joyner-Halanda model show a bimodal porous structure with highly uniform small pores centered

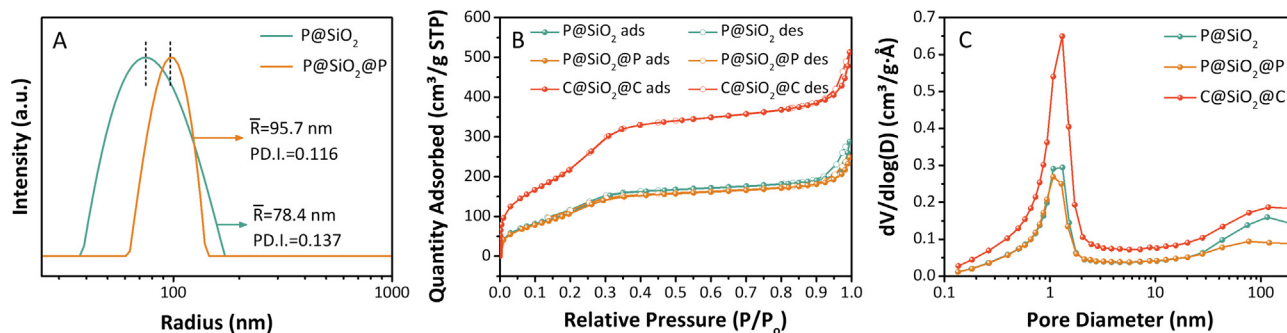


Fig. 2. DLS analysis of P@SiO₂ and P@SiO₂@P (A). N₂ adsorption–desorption isotherms (B), and the corresponding pore size distribution curves (C) of P@SiO₂, P@SiO₂@P, and C@SiO₂@C.

at ~ 1 nm and larger pores with a relatively broad size distribution ranging from 40 nm to 200 nm (Fig. 2C). Textural properties (Table 1) calculated from the N₂ sorption isotherms indicate that, before swelling, P@SiO₂ exhibits a large surface area (424 m²/g) and large pore volume (0.34 cm³ g⁻¹). After swelling, the size of both small and large pores in the P@SiO₂@P sample decreases as well as the surface area (420 m²/g) and the pore volume (0.32 cm³ g⁻¹) since swollen PTMPM occupies more volume and is filling the pores.

^{a)} Surface area calculated from the adsorption branches at 0.02–0.2 on the basis of Brunauer-Emmet-Teller method; ^{b)} Pore diameter calculated by Barrett-Joyner-Halenda method from the adsorption branch of isotherms; ^{c)} Pore volume calculated from the adsorbed amount at p/p_0 of 0.995.

Thirdly, the swollen PTMPM and remaining CTAB molecules have been transformed *in-situ* into carbon material by pretreatment with sulfuric acid followed by high-temperature carbonization. Sulfuric acid, by initiating reactions of dehydration and sulfonation, is well-known to allow the immobilization of carbonaceous substances during calcination [37,38]. After calcination under argon atmosphere, 3D carbon layers are therefore generated *in-situ* on the inner and outer surface of the porous silica shell and replicate the initial templating structure of P@SiO₂@P nanoparticles. Remarkably, the spherical morphology of those carbonized materials (denoted as C@SiO₂@C) is highly preserved after high-temperature calcination, as a proof of the good thermal stability of the obtained composites (Fig. 1D). The preservation of the spherical morphology is further confirmed by continual multi-angle tomographic images (Fig. 1D1–D6), with corresponding video in Supplementary Movie 1. As expected, the carbonization of swollen PTMPM and CTAB molecules to thin carbon layers results in increased pore size, surface area and pore volume for C@SiO₂@C nanoparticles compared to the P@SiO₂@P precursor, confirming the important porosity of the nanoparticles after the carbonization process (Fig. 2B and 2C, and Table 1).

Finally, silica has been reduced to silicon by a magnesiothermic reduction reaction. Meanwhile a silicon carbide interlayer is generated at the contact region between silicon and carbon, assisted by magnesium [39–41]. Thus, the targeted hollow porous silicon nanospheres coated with a 3D SiC@C structure have been obtained

and are denoted as C@SiC@Si@SiC@C (Fig. 1E and S2). Those uniform hollow nanostructures are clearly observed in tomography characterization (Fig. 1E1–E6, with overview in Supplementary Movie 2), and further show a large difference compared to samples before reduction. The shell thickness of the final hollow spheres is ~ 14 nm as measured by TEM (Fig. 1E). Those shells are consisting of a sandwich-like structure, listed from the inside to the outside as C, SiC, Si, SiC, and C, which is further confirmed by high-resolution TEM (Fig. S3A) and justifies the C@SiC@Si@SiC@C acronym. As a consequence, it could be inferred that the actual thickness of the inner silicon layer is less than 14 nm (Fig. S3B). Such an ultrathin silicon layer with SiC@C functional coating is highly sought in the design of silicon-based anode materials, since it could easily accommodate severe volumetric expansion during lithium insertion and display improved electronic conductivity.

The composition of the C@SiC@Si@SiC@C nanospheres has been further analyzed by X-ray diffraction (XRD) as shown in Fig. 3A. As a comparison, the XRD pattern of the C@SiO₂@C precursor displays only one broad peak attributed to amorphous silica. This broad peak disappears after reduction for the C@SiC@Si@SiC@C sample and is replaced by a series of intense peaks located at 28.5°, 47.5°, and 56.3°, corresponding to (111), (220), and (311) of the Fd3m silicon phase (JCPDS 77–2107), respectively. In addition, the peak at 35.3° is indexed to silicon carbide (JCPDS 74–2307). These results confirm the successful conversion of silica to silicon, as well as the consecutive reaction of silicon and carbon to form a small amount of silicon carbide. According to the existing reports and the structural characteristics of C@SiC@Si@SiC@C nanospheres, the silicon carbide formation could be attributed to the close areal contact of reactants between silicon and carbon with the assistance of magnesium [39–41]. The presence of amorphous carbon could not be detected in the XRD pattern, but will be further evidenced below by other experimental techniques.

In order to confirm the presence of carbon layers in the synthesized samples, electron spin resonance (ESR) has been employed to study the electron states of the Si surface with and without the carbon layer (Fig. 3B). Under air atmosphere, strong ESR signals are detected in the C@SiC@Si@SiC@C sample, which originate from unpaired electrons on the Si surface while, without carbon coating, the signals associated to hollow porous pure Si material dramati-

Table 1
Textural properties of P@SiO₂, P@SiO₂@P, and C@SiO₂@C.

Sample	S_{BET} (m ² g ⁻¹) ^{a)}	Pore diameter (nm) ^{b)}		Pore volume (cm ³ g ⁻¹) ^{c)}
		small	large	
P@SiO ₂	424	1.3	114.6	0.34
P@SiO ₂ @P	420	1.1	76.8	0.32
C@SiO ₂ @C	827	1.3	117.3	0.66

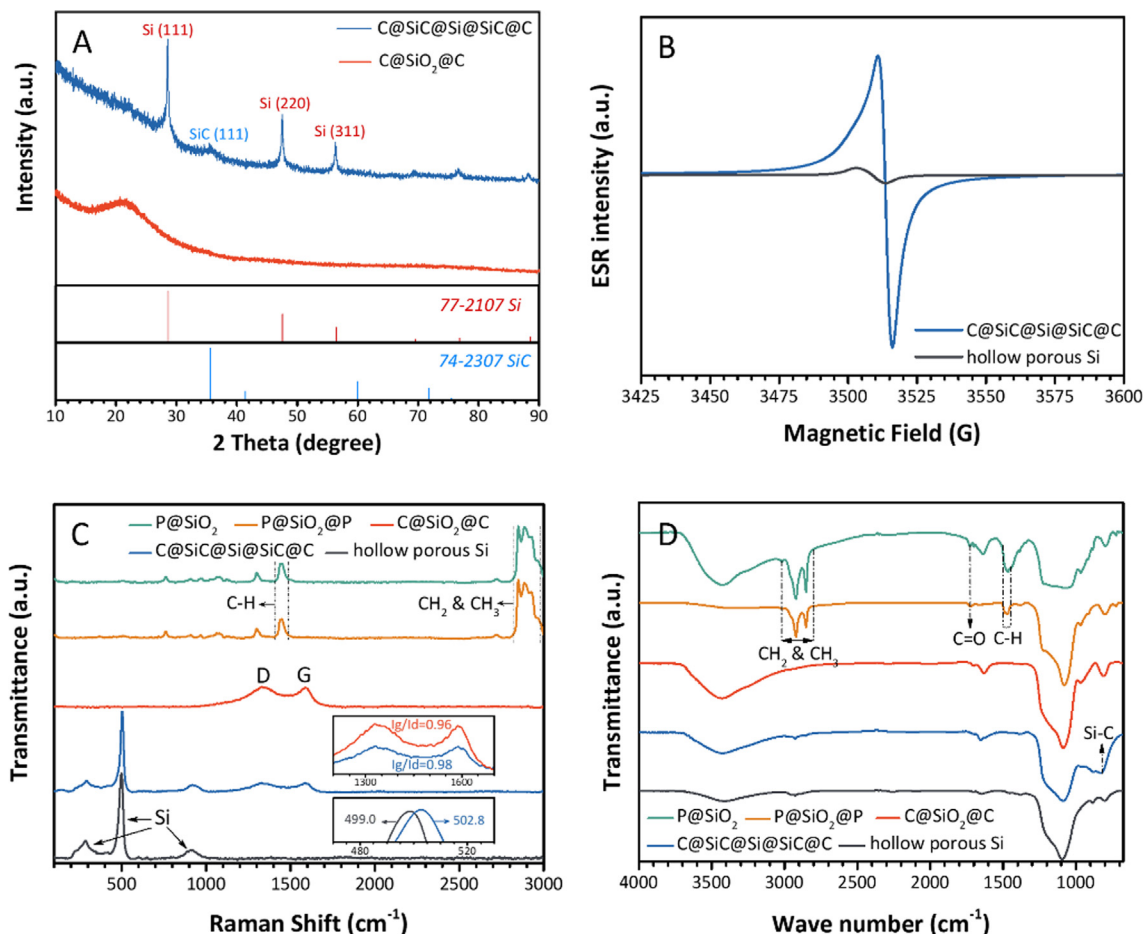


Fig. 3. XRD patterns of C@SiC@Si@SiC@C and C@SiO₂@C samples (A). ESR spectra of C@SiC@Si@SiC@C and Si (B). Raman spectra (C) and FT-IR spectra (D) of P@SiO₂, P@SiO₂@P, C@SiO₂@C, and C@SiC@Si@SiC@C.

cally weaken (the synthetic process towards hollow porous pure Si is detailed in the [Supporting Information](#), SEM image and XRD pattern are presented in [Figure S4](#)), because the unpaired electrons on the Si surface are mostly captured by O₂ when silicon is exposed to air without any coating [24,25]. These results unambiguously demonstrate that the porous Si in the C@SiC@Si@SiC@C sample is protectively encapsulated by outer carbon layers. Raman spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy have then been used to monitor structural and compositional changes among carbonaceous species in the four synthetic stages. In the Raman spectrum before carbonization, the C—H bands from PTMPM and CTAB in P@SiO₂ and P@SiO₂@P are detectable ([Fig. 3C](#)). After carbonization, all C—H bands disappear, while the two strong D band at 1331 cm⁻¹ and G band at 1588 cm⁻¹ are detected due to the formation of sp² carbon, indicating that organic matter has been completely transformed to carbon black during high-temperature calcination. After reduction, the D and G bands are both preserved. Notably, the I_G/I_D ratio increases to 0.98 after reduction compared to 0.96 before reduction, indicating that the graphitization level slightly increases after reduction [42]. Furthermore, a series of characteristic Si bands appears at 292, 503, and 920 cm⁻¹ [43]. Besides, compared to the hollow porous pure silicon, the main Si band of the C@SiC@Si@SiC@C sample exhibits a blue shift from 499.0 cm⁻¹ to 502.8 cm⁻¹. Based on the phonon confinement effect, this blue shift suggests that the size of the composite particles increases due to the presence of the outer coating layers [44]. In the corresponding FT-IR spectra, both P@SiO₂ and P@SiO₂@P show characteristic bands of the CH₂ and CH₃

stretching vibrations at 2800–3000 cm⁻¹, the C=O stretching vibration at 1726 cm⁻¹, and the C—H bending vibration at 1461 cm⁻¹, all ascribed to the presence of PTMPM and CTAB before carbonization ([Fig. 3D](#)) [42]. After carbonization, all above-mentioned organic bands disappear, in agreement with the complete conversion of the organic materials into carbon, echoed by the results of Raman spectra. As expected, after Mg reduction, a single band characteristic of Si-C at 822 cm⁻¹ is detected for the C@SiC@Si@SiC@C sample. As a reference, there is no characteristic carbonaceous band in the hollow porous pure Si material. These additional characterizations are further supporting the successful formation of the C@SiC@Si@SiC@C hollow porous nanostructures.

The composition of the C@SiC@Si@SiC@C hollow porous nanoparticles was quantitatively determined by combining X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) ([Figure S5](#)) [43]. The weight ratio of elemental silicon in the C@SiC@Si@SiC@C sample is determined to be equal to 24 %, with the detailed data shown in the [Supporting Information](#).

The lithiation-delithiation properties of C@SiC@Si@SiC@C hollow porous nanospheres as an anode material have been investigated by galvanostatic charge–discharge measurements within a voltage range of 0.01–1.50 V (vs Li/Li⁺). As shown in [Fig. 4A](#) and [Figure S6](#), the electrode has been activated for the first five cycles at a low current rate of 0.02C and the capacities have been normalized to the total weight of the composite materials. The C@SiC@Si@SiC@C electrode displays high specific discharge capacities up to 2625 mAh g_{total}⁻¹ at the first cycle and tends to maintain stable at 1300 mAh g_{total}⁻¹ from the second cycle. The extremely large capac-

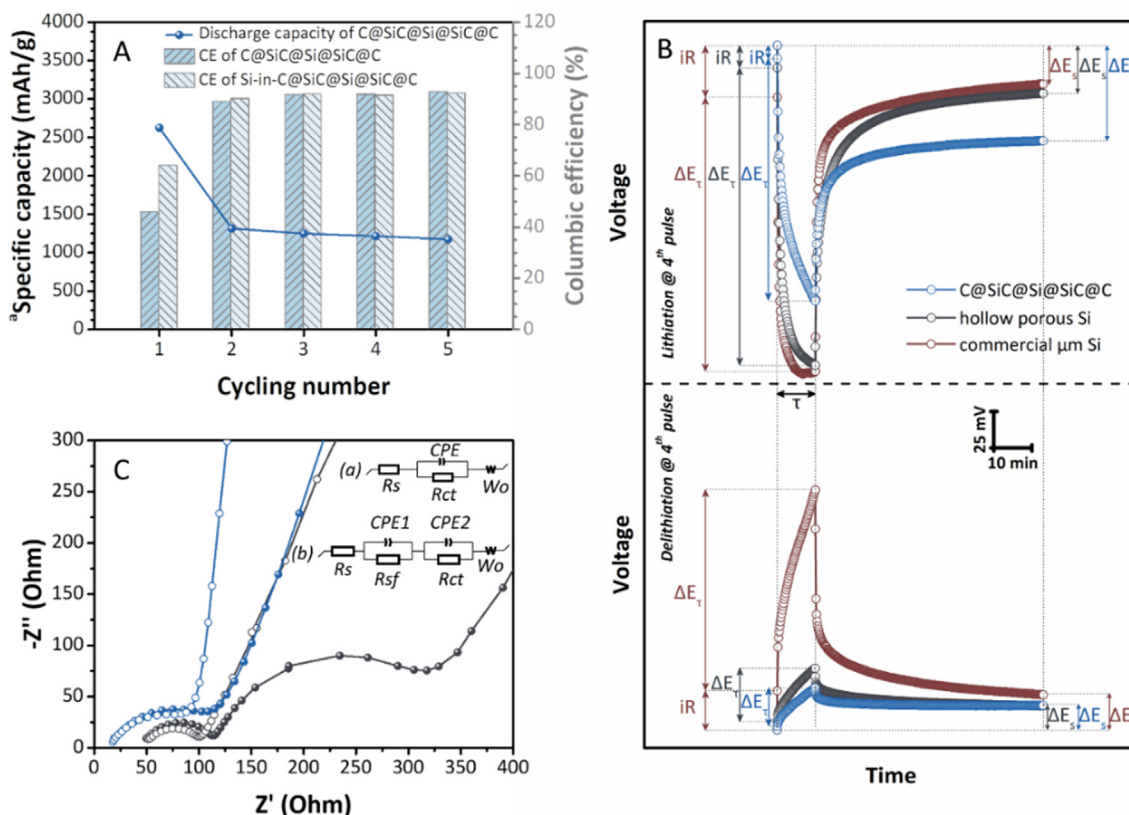


Fig. 4. Cycling performance (A) of C@SiC@Si@SiC@C electrode at a current rate of 0.02C from the 1st to the 5th cycle, with the corresponding CE of Si content in the C@SiC@Si@SiC@C material. Schematic illustration (B) for C@SiC@Si@SiC@C, hollow porous Si, and commercial micron Si at the 4th pulse of lithiation and delithiation during GITT tests. Nyquist plots (C) of C@SiC@Si@SiC@C (in blue) and hollow porous pure Si reference electrode (in black), before cycling (plotted by hollow circles) and at the 4th cycle (plotted by solid spheres). ^aSpecific capacities are based on the total mass of composite materials. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ities are mainly due to the following reasons: i) the hollow porous nanostructure greatly shortens the conduction paths of electrons and Li^+ ions in the active materials, thereby improving the utilization of active materials during the cycling; ii) the additional capacities from composite components under low current density, e.g. Si, C, and SiC [45–47].

To confirm the benefit of hollow porous nanostructures, the Li^+ diffusion coefficients (D_{Li}) of C@SiC@Si@SiC@C, hollow porous Si and commercial μm size Si have been compared by galvanostatic intermittent titration technique (GITT). A typical analysis of one single step is illustrated in Fig. 4B. More details are presented in Figure S7 and Table S2. Derived from GITT data, the average D_{Li} of C@SiC@Si@SiC@C during lithiation or delithiation is slightly larger than that of hollow porous Si and the values measured for both nanoscale samples are obvious higher than for the commercial μm size Si. Compared to the microscale structure, the hollow porous nanostructure obviously possesses the shorter conduction pathways for the diffusion of Li ions, further promoting the utilization of active materials. Moreover, C@SiC@Si@SiC@C provides the smallest overpotential in GITT analysis among the three investigated samples, implying the optimized electrochemical reaction and electrical energy efficiency [29].

In order to further clarify the specific contribution of SiC and C components, C@SiC@C nanospheres with similar hollow porous structures have been synthesized (synthetic process shown in Supplementary Information, SEM image and XRD pattern in Figure S8). At a low current density of 0.02C, the capacity of the C@SiC@C sample even reaches 1478 mA h g^{-1} at the first discharge process with low initial coulombic efficiency (ICE) of 14.9 %, and averages at 215

mA h g^{-1} for the next 4 cycles (Figure S9). However, when the charge/discharge rate increases to 0.1C or higher, the capacity substantially decreases. In short, the capacity of C@SiC@Si@SiC@C includes specific contributions of Si, SiC and C under low current density. When the current density increases at a higher value than 0.1C, the capacity mainly originates from Si and the contribution from SiC@C can be considered negligible (Table S3). The particularly high capacity and low ICE of C@SiC@C in the first cycle indicate the generation of the SEI. Therefore, the SEI formation of Si in the composite electrode (denoted as Si-in-C@SiC@Si@SiC@C) could be estimated by eliminating the capacity contribution of C@SiC@C from that of C@SiC@Si@SiC@C, combined with the proportion of each component in the C@SiC@Si@SiC@C sample. Consequently, ICE of Si-in-C@SiC@Si@SiC@C is calculated to be 64.0 %, which is obviously higher than 45.7 % for the C@SiC@Si@SiC@C sample. Furthermore, the CEs of the C@SiC@Si@SiC@C surpass 90 % from the 2nd cycle indicating that the SEI quickly reaches stabilization. Thus, we can hypothesize that the formation of the SEI on the SiC@C layer eventually prevents excessive SEI formation on the surface of Si and improves the stability of the composite electrode during the cycling.

Furthermore, the formation of the stable SEI in the composite electrode can also be demonstrated by electrochemical impedance spectroscopy (EIS) measurements (Fig. 4C and Table S4), which have been conducted on the C@SiC@Si@SiC@C and hollow porous pure Si samples. Before cycling, the Nyquist plots of the C@SiC@Si@SiC@C and the hollow porous pure Si anodes both exhibit a depressed semicircle in the high-frequency region and a sloped line in the low-frequency regions, equivalent to the circuit models

shown in the insert of Fig. 4C. The surface resistance (R_{sf}) of the high-frequency region is equal to 60.6Ω for the C@SiC@Si@SiC@C electrode, which is similar with the R_{sf} of the hollow porous pure Si anode (the solution resistance has been eliminated, see Table S4). After four cycles, the resistance of C@SiC@Si@SiC@C electrodes is equal to 75.8Ω , which is much smaller than the value measured for the hollow porous pure Si (247.8Ω). Notably, after cycling, only one semicircle is detected in the curve of the C@SiC@Si@SiC@C sample, while two semicircles are observed for the hollow porous pure Si [48]. This suggests that a new interface is formed after cycling for the hollow porous pure Si, while the interface impedance of C@SiC@Si@SiC@C basically remains unchanged in agreement with the formation of a stable SEI on the surface. Besides, at low-frequency region, the steeper inclined line of C@SiC@Si@SiC@C indicates the enhanced Li^+ diffusion compared to hollow porous pure Si materials, which is consistent with GITT results.

After the activation process at 0.02C, the rate capacity performance of the C@SiC@Si@SiC@C electrode has been tested at various current densities from 0.1 to 2 C (Fig. 5A). The composite electrode displays high utilization of Si at different current densities, up to 94.0 % at 0.1 C, 81.4 % at 0.2 C, 61.9 % at 0.4 C, and 28.9 % at 1 C, which represents outstanding rate performances compared to the previously reported samples from literature and described in Table S1. Notably, after running at high current density of 2 C, the capacity recovers to 93.4 % of the initial value at 0.2 C, confirming the high stability of C@SiC@Si@SiC@C anodes. Such property can also be demonstrated by high CEs (close to 100 %). In contrast, although the nanostructures have been mostly maintained for the pure Si electrode before cycling (see Fig. S4A), the utilization of Si drastically decreases with cycles due to the instable SEI and the loss of structural support from SiC@C (see Figure S10 and Fig. 5A). The charge–discharge performances of C@SiC@Si@SiC@C and pure Si are further compared, using the differential capacity as a function of voltage and the corresponding charge–discharge profiles under different current density. In Fig. 5B, as for the C@SiC@Si@SiC@C sample during the 7th cycle at 0.2 C, two pairs

of redox peaks are observed. The first cathodic peak c_1 is located at 0.19 V, attributed to the reduction of Si and the generation of a Li-Si alloy phase; the corresponding anodic peak a_1 at 0.50 V is related to the extraction of Li ions from the Si host. The second cathodic peak c_2 at 0.04 V and the anodic peak a_2 at 0.29 V suggest the further reduction of the Li-Si alloy and the partial decomposition of the Li-Si alloy, respectively. It reflects that the lithiation mechanism is the gradual reduction process of Si, and the delithiation is the gradual oxidation of the Li_xSi alloy. Besides, after running under various current rates, the two pairs of redox peaks are both maintained at the 26th cycle. In contrast, these redox peaks for the pure Si electrode become too flat to be observed after cycling (Figure S11A). In the charge–discharge profiles of Fig. 5C, the C@SiC@Si@SiC@C anode exhibits the specific electrochemical platforms of silicon in the voltage range of 0.0–0.2 V, echoed by the cathodic lithiation peaks c_1 and c_2 in Fig. 5B. Furthermore, there is almost no change among discharge curves from the 7th cycle to the 26th – 28th cycle. As far as the hollow porous pure Si anode is concerned, the characteristic plateau of silicon dramatically shortens (Figure S11B). Based on the above, such extreme utilization of Si in the composite electrode and highly reversible capacity values of C@SiC@Si@SiC@C could be attributed to the following reasons: i) thanks to the three-dimensional carbon coating, the electronic conductivity is enhanced compared to the pure Si material; ii) nanosized Si greatly shortens the pathways of electrons and Li^+ in the active materials of the composite electrodes, in which the thickness of Si layer is ultrathin compared to some previously reported Si-based materials (Table S1); iii) the formation of a stable SEI and the robust structure from SiC@C further improves the stability of the composite electrode. The formation of a stable SEI is also confirmed by SEM characterization of electrodes after cycling (Figure S12). The electrode of C@SiC@Si@SiC@C displays smooth and uniform surface, as well as the highly intact morphology of nanospheres after running. On the contrary, the surface of hollow porous Si electrode is uneven and coarse with obvious cracks, resulting from the volumetric change of bare Si without robust coating during cycles. In addition, the original

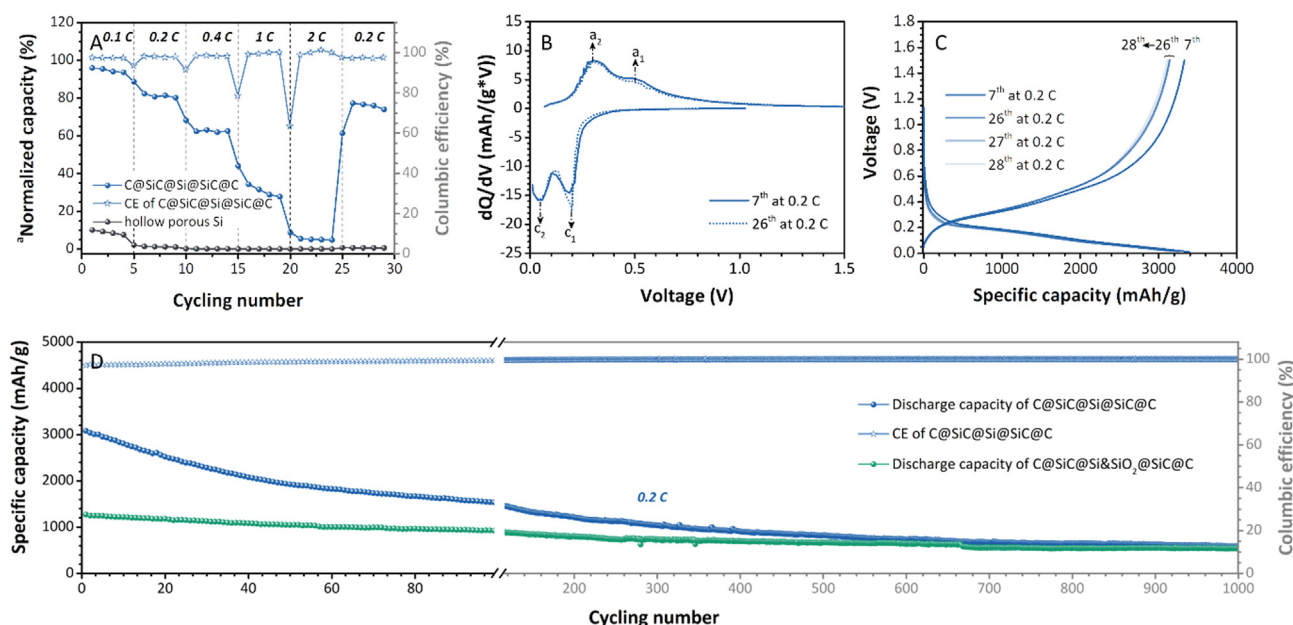


Fig. 5. (A) Cycling performance of C@SiC@Si@SiC@C electrode and hollow porous pure Si reference electrode at various rate from 0.1C to 2C. (B) The differential capacity as a function of voltage (dQ/dV vs V) for C@SiC@Si@SiC@C measured at the 7th cycle and the 26th cycle with a rate of 0.2C between 0 and 1.5 V. (C) Charge/discharge curves of C@SiC@Si@SiC@C at the 7th cycle and the 26th – 28th cycle with a rate of 0.2C. (D) Long-term cycling performance of C@SiC@Si@SiC@C electrode and C@SiC@Si@SiO₂@SiC@C electrode at the current rate of 0.2C. ^a Normalized capacity is calculated by dividing experimental data by the theoretical capacity of Si (4200 mAh g^{-1}).

spherical shape of the nanoparticles is lost since they become aggregated when covered by a thick SEI film.

The long-term cycling performance of the C@SiC@Si@SiC@C electrode has been tested at 0.2C after the rate capacity measurement. As shown in Fig. 5D, despite having been cycled under different current densities, the composite electrode still exhibits a capacity as high as 3200 mAh g⁻¹ (based on the content of Si) at the beginning of the long cycling. After 1000 cycles, the reversible capacity of the C@SiC@Si@SiC@C electrode remains more than 600 mAh g⁻¹ and the CE maintains at around 100 % for the entire measurement. Moreover, there is only 0.8 % loss of capacity per cycle for the electrode during the whole cycling and, if only the last 900 cycles are considered, such value is further improved to 0.7 %. The long-term cyclability of C@SiC@Si@SiC@C electrodes could be related to two features: i) the robust SiC@C layer efficiently prevents the inner Si material from pulverization [30,49,50], ensuring the stability of the SEI and improving the conductivity of the composite electrode; ii) the nanoscale size of silicon is responsible for superior stability when lithium repeatedly inserts and extracts compared to the large size particles [8], and allows a better utilization of Si. Nevertheless, the capacity shows a more obvious degradation for the first 100 cycles (decay rate of 0.5 % per cycle at 0.2C). This may be due to the gradual inactivation of part of the Si component. Because of the complex hierarchical nanostructure and the small size of different components in the nanoparticles, the step of removing unreduced SiO₂ may cause the breakage of small parts of particles (see Fig. 1E), resulting in the exposure of Si to the electrolyte. Hence the exposed Si would become gradually inactive. To test this hypothesis, another reference sample has been synthesized in which the residual SiO₂ component is retained by suppressing the HF acid washing step, denoted as C@SiC@Si&SiO₂@SiC@C (synthetic process shown in Supporting Information). Hence, the structural integrity of the particles is improved and prevented from breakage (SEM image and XRD pattern are shown in Figure S13). The rate capacity performance of C@SiC@Si&SiO₂@SiC@C is inferior than that of the C@SiC@Si@SiC@C sample (59.0 % at 0.01C, 50.0 % at 0.05C, 40.9 % at 0.1 C, 31.2 % at 0.2C, 16.4 % at 0.5 C, and 7.0 % at 1 C), which could be attributed to the lower conductivity of the C@SiC@Si&SiO₂@SiC@C particles (Figure S14). However, C@SiC@Si&SiO₂@SiC@C particles display higher stability at long-term cycling (decay rate of 0.6 % at 0.2C for 1000 cycles and 0.5 % per cycle at 0.2C during last 900 cycles). It could be inferred that the structural integrity of the C@SiC@Si&SiO₂@SiC@C particles is beneficial to the cycling stability.

4. Conclusion

The polymer-templated one-pot synthesis strategy detailed in this contribution innovatively takes advantage of the intrinsic swelling property of PTMPM in ethanol, successfully allowing the formation of a sandwiched structure in which a silica porous capsule is uniformly wrapped on both sides by polymer layers. Remarkably, those precursor structures are not only employed as template agents for the formation of two distinct types of pores, but can also be *in-situ* transformed into a well-defined SiC@C 3D coating surrounding the porous silicon layer after high temperature and reduction treatments, hence preventing the waste of organic components and the post-introduction of foreign carbon sources. The nano-size of the accordingly formed Si crystals guarantees the stability of Si during lithiation and improves its utilization at different current densities. This is because their size is far less than the critical breaking dimension reported for lithium insertion and the diffusion paths of Li ions and electrons through the Si active material are quite short. Lastly, the accordingly

formed carbon species could admirably improve the electrical conductivity and the conformal coating provided by carbon and silicon carbide contributes strongly to the robustness of the C@SiC@Si@SiC@C nanospheres, not only providing strong structural support, but also favoring the formation of a stable SEI. This unique design contributes strongly to the ultrahigh capacity (3200 mAh g⁻¹), the high coulombic efficiency (64.0 % of ICE of Si-in-C@SiC@Si@SiC@C, above 90 % from the second cycle, and almost 100 % during cycling), and the excellent long-term cycling stability (0.7 % per cycle decay rate) of the C@SiC@Si@SiC@C anodes. Clearly, the polymer templated approach presented in the present study discloses an original design of composite Si-based hollow nanoparticles exhibiting a unique combination of C, SiC and Si materials with a well-defined 3D structure. Furthermore, those newly designed materials demonstrate outstanding electrochemical performance when used as anodes in Li-ion batteries.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2023.111624>.

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