Hollow sandwich-structured N-doped carbon-silica-carbon nanocomposite anode materials for Li ion batteries

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Abstract. Silica has attracted much attention as a promising anode material for lithium ion batteries (LIBs), however, the low conductivity and unstable solid electrolyte interface (SEI) film limit its applications. In this paper, hollow sandwich-structured N-doped carbon-silica-carbon (CSC) nanoparticles was designed and prepared as anode materials for LIBs. The combination of polymer template approach and dopamine self-oxidation polymerization results in the conformal coatings on the surface of silica, which enhances the conductivity and stability of the composite materials. The hollow sandwich-structured material displays a high reversible capacity of 480 mA h g⁻¹ at current density of 1.0 A g⁻¹ and excellent rate performance, which can be attributed to the synergetic effect of the unique structure of hollow silica and N-doped carbon conformal coatings. The hollow sandwich-structured N-doped carbon-silica-carbon composite materials can be promising anode materials for LIBs.

1. Introduction
Silica as one of the most abundant materials on the earth, has been considered as a promising anode material for lithium ion batteries (LIBs) due to its remarkable advantages such as high theoretical specific capacity (1965 mA h g⁻¹) [1] and low discharge potentials [2]. However, bulk silica shows little electrochemical activity towards Li due to the sluggish Li⁺ diffusivity and poor intrinsic electrical conductivity [3], which limits its potential applications.

Designing fine-sized particles, as an effective strategy, can effectively shorten the Li⁺ diffusion length and enhance the electrochemical activity of silica [4,5]. Hollow structured materials with hollow cavities for volume variation Li⁺ accommodation and thin shells for diffusion represent a promising category of electrode architecture [6,7] and various hollow structured silica such as hollow spheres, hollow cubes, hollow nanobelts, and nanotubes have been explored in lithium storage [8-10]. Nakashima et al. synthesized silica hollow nanospheres with a uniform size of 30 nm using the triblock copolymer PS-P2VP-PEO as template, and the obtained silica hollow nanospheres delivered a capacity of 242 mA h g⁻¹ after 300 cycles [8]. Chen et al. fabricated hollow silica nanocubes by a hard template, and the nanospheres exhibit a stable discharge capacity of 334 mA h g⁻¹ after 500 cycles [10].

On the other hand, many efforts have been dedicated to improving the conductivity of silica by coupling with carbon, which can enhance the electrical conductivity and buffer the volume fluctuation of silica [11,12]. Recently, porous silica/carbon composites have drawn considerable attention [13-15]. The porous structure not only provides free space for the volume expansion of silica upon lithiation...
but also enables rapid Li\(^+\) diffusion. As a result, both the cycling stability and rate capability can be enhanced. Wu et al. constructed a porous silica/carbon nanocomposite, in which the continuous silica framework provided abundant active sites for lithium storage, the carbon wired the whole composite and enhanced the integrated structure, and the nanopores effectively accommodated the volume expansion of silica and enabled the rapid diffusion of Li\(^+\). The porous silica/carbon composite displayed a capacity of 560 mA h g\(^{-1}\) after 30 cycles [13]. Wang et al. prepared a mesoporous silica/C composite with a reversible capacity of 670 mA h g\(^{-1}\) [15]. Zhao et al. designed a silica/C composite anode by coating ordered mesoporous silica with carbon, which demonstrated a high specific capacity of 780 mA h g\(^{-1}\) after 350 cycles [16]. A carbon core@mesoporous silica@carbon shell three-layer structure designed by Cao et al. delivered a capacity of 1055 mA h g\(^{-1}\) after 150 cycles [17].

Combining the advantages of both hollow structures and carbon coating, hollow structured silica/carbon composites have been explored by several groups [18-20]. Zhang et al. prepared silica/carbon mesoporous hollow spheres, which delivered a capacity of 441 mA h g\(^{-1}\) after 500 cycles at 500 mA g\(^{-1}\) and a specific capacity of 695 mA h g\(^{-1}\) at a lower current density of 100 mA g\(^{-1}\) [18]. Wang et al. prepared a hollow core–shell structured silica/carbon composite with a high specific capacity of 670 mA h g\(^{-1}\) after 100 cycles [20]. Further structural designing and compositional optimization of anode materials can be expected to possess excellent electrochemical performance.

In this paper, hollow sandwich-structured N-doped carbon-silica-carbon (CSC) nanoparticles was prepared as anode materials for LIBs. The integration of polymer template approach and dopamine self-oxidation polymerization results in the conformal coatings on the surface of silica, which enhances the conductivity and stability of the composite materials.

2. Experimental section

2.1. Materials
Poly(vinylpyrrolidone) (PVP-10, Aldrich), dodecylamine (DDA, Aldrich), dopamine hydrochloride (Aladdin), and tetraethyl orthosilicate (TEOS, Aladdin) were used as received.

2.2. Preparation of hollow sandwich-structured N-doped carbon-silica-carbon nanoparticles
The preparation of target product followed the procedure reported previously and modified as follows [21]. PVP-10 (0.5 g) was dissolved in a mixture of ethanol (20.0 mL) and water (80.0 mL) under stirring for 30 min. DDA (1.17 g) and TEOS (3.5 mL) were then added into the solution and the mixture was stirred for 24 h at room temperature. The dopamine hydrochloride (0.1 g) was dissolved in above-mentioned system, and the resultant mixture was stirred for another 24 h at ambient temperature. The precipitate was collected by centrifugation, washing and drying at 70 °C for 3 h. The product was annealed at 650 °C for 3 h at the rate of 3 °C min\(^{-1}\) under Ar atmosphere to obtain CSC composite nanoparticles.

2.3. Characterization
The morphology, structure, and composition of hollow sandwich-structured nanoparticle was determined by field-emission scanning electron microscopy (SEM, Nova Nano450), transmission electron microscopy (TEM, FEI Titan 60-300 Cs). Phase structures of the synthesized samples were characterized by X-ray diffraction (XRD) on a Rigaku diffractometer using Cu K\(\alpha\) radiation under working current of 40 mA, working voltage of 40 kV, scanning angle of 10-90° with a step size of 0.03°.

2.4. Electrochemical measurements
Electrodes were prepared by mixing 70 wt% of the active materials (CSC), 20 wt% of super P as the conducting agent, and 10 wt% of polyvinylidene fluoride (PVDF) as the binder. First, a certain amount of PVDF mixed with NMP was stirred magnetically until it was completely dissolved. The super P and the active material were uniformly ground in a mortar, which was added to the NMP solution of
PVDF, and stirring continued until a uniform slurry was formed. The slurry was spread onto a Cu foil and then dried in vacuum at 60 °C overnight, then it was pressed and punched into electrode. The electrode was evaluated via LIR2032-type coin cells assembled in a glove box with Li foil as counter electrode. The electrolyte was 1 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) and the separator is Celgard 2400 membrane. The charging and discharging profiles were conducted on a battery tester, with a voltage cut-off between 0.1 and 3.0 V. Cyclic voltammetry (CV) was conducted on the CHI 1000C electrochemical workstation at a scan rate of 0.1 mV⁻¹ in a potential range from 0.01 to 3.0 V and electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI 760E electrochemical workstation.

3. Results and discussion
The preparation process of hollow sandwich-structured carbon-silica-carbon nanocomposite is illustrated in figure 1. Firstly, PVP-10 and DDA as co-template form core-shell micelles in ethanol-water mixture. Deposition of silica precursors on the surface of the co-template results in core-shell structured aggregates with PVP-10 as the core and silica as the shell, and hollow structured silica form. Then the aggregates are embedded and conformally coated by polydopamine through the self-oxidation polymerization of dopamine, resulting in composite aggregates with core-shell structure. After annealing the composite product in Ar atmosphere, the PVP-10 and DDA derived N-doping carbon is tightly adhered on the internal surface of silica, and the PDA derived N-doping carbon is adhered on the external surface of silica. Accordingly, the hollow sandwich-structured nanocomposite was constructed.

The XRD patterns of CSC composite is shown in figure 2. A broad peak around 23° suggests that the structure of hollow silica is amorphous, and another wide peak at 43° in XRD pattern is characteristic of the amorphous carbon in carbon-silica-carbon composites. SEM and TEM images of the resultant composite materials are shown in figure 3. It can be seen that the composite materials are characterized by hollow sphere, well-dispersed, and uniform with a diameter of less than 100 nm.

![Figure 1. Schematic preparation of hollow sandwich-structured CSC nanocomposite.](image-url)
The electrochemical reaction mechanisms of silica with Li-ion have been conducted and confirmed by equations as follows \cite{22,23}: (1) SiO$_2$ + 4Li + 4e$^-$ → Li$_4$SiO$_4$ + Si; (2) SiO$_2$ + 4Li + 4e$^-$ → Li$_2$Si$_2$O$_5$ + Si; (3) SiO$_2$ + 4Li + 4e$^-$ → Li$_2$O$_2$ + Si; (4) Si + xLi + xe$^-$ → Li$_x$Si. Figure 4a shows the typical CV curves of CSC nanocomposites in the voltage window from 0.01 to 3.0 V at a scanning rate of 0.1 mV s$^{-1}$. There are two remarkable reduction peaks located at 0.75 and 0.2 V, the former is due to the irreversible reactions between the electrode and electrolyte (Eqs (1) and (3)) and continued formation of SEI films \cite{24}. The lowest peak at 0.2 V is associated with the reversible alloy-dealloy reaction of silicon with Li ions (Eqs (4)), which would contribute to lithium storage capacity. The CV curves of carbon-silica-carbon composite are almost overlapped indicating of highly reversible behavior.

The discharge and charge voltage profiles of different cycles at a current density of 1.0 A g$^{-1}$ in the voltage range of 0.01-3.0 V (figure 4b) are in good agreement with the CV measurements. A plateau at 0.7 V can be observed in the first discharge voltage profile, which can be attributed to SEI forming and irreversible reaction of silica electrode and electrolyte. The discharge and charge capacities of the first cycle are 1080 and 450 mA h g$^{-1}$ at 1.0 A g$^{-1}$ with an initial CE of 42%. At 1.5 A g$^{-1}$, they are 950 and 470 mA h g$^{-1}$ with an initial CE of 50%. The long-term cycle performance of carbon-silica-carbon were tested at a current density of 1.0 A g$^{-1}$, indicating a reversible capacity of 500 mA h g$^{-1}$ even after 700 cycles with high CE approaching 100%. The excellent electrochemical can be attributed to the unique sandwich structure, which plays an important role in achieving superior structural stability and cycling stability. The hollow void and the protective silica interlayer can synergistically
accommodate the huge volume change upon lithiation/delithiation, and stabilize the whole structure by preventing the pulverization of silica. Firstly, the conformal coating carbon on silica nanoparticles as the mechanical backbone and networks can effectively endure volume expansion during alloying-dealloying cycle process and inhibit the destruction of the hollow structure [25]. Secondly, the conformal carbon coating forms a three dimensional conductive network to contact with silica nanoparticles closely, bring out high electrochemical activity. Carbon coating on the surface of silica hollow spheres cannot relieve the huge expansion effectively and even lose contact with anode material during many cycles which can lower the ability to stabilize the shell structure and increase the resistance of ion and electron diffusion to anode material [18]. Finally, forming more stable and thinner SEI film on the external surface of hollow silica can be beneficial to avoid the direct contact of high active silica and electrolyte.

![Graphs](image)

**Figure 4.** Typical CV curves of the CSC electrodes at a potential sweep rates of 0.1 mV s\(^{-1}\) (a); charging/discharging profiles at current of 1.0 A g\(^{-1}\) (b) and 1.5 A g\(^{-1}\) (c), long cycle at 1.0 A g\(^{-1}\) (d).

4. Conclusions

In summary, a facile preparation method to obtain hollow sandwich N-doped carbon-silica-carbon has been demonstrated. The unique nanostructure can effectively tune the huge volume change, shorten the electron/Li\(^+\)-ion transport distances, and provide fast electron transport in the interconnected hollow structure. As an anode material for LIBs, this material shows high reversible capacity, superior rate capability, and durable long term cyclability. The hollow sandwich nanostructure design may be extended to other high-capacity electrodes in the development of high performance energy storage systems.

5. References
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