

Copper Silicate Hydrate Hollow Spheres Constructed by Nanotubes Encapsulated in Reduced Graphene Oxide as Long-Life Lithium-Ion Battery Anode

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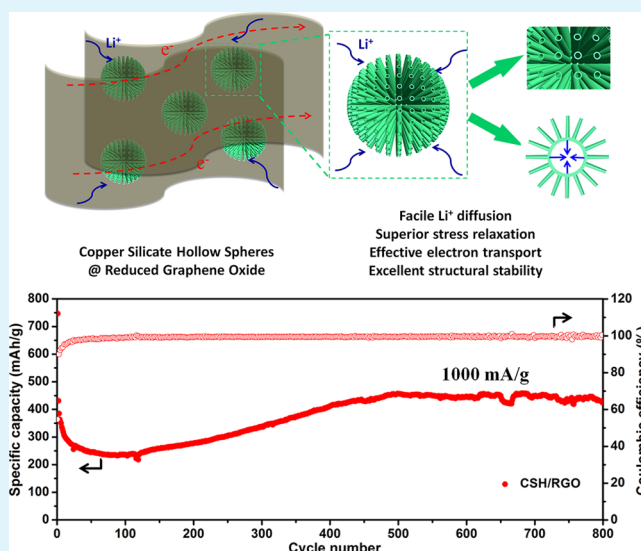
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Supporting Information

ABSTRACT: Hierarchical copper silicate hydrate hollow spheres-reduced graphene oxide (RGO) composite is successfully fabricated by a facile hydrothermal method using silica as *in situ* sacrificing template. The electrochemical performance of the composite as lithium-ion battery anode was studied for the first time. Benefiting from the synergistic effect of the hierarchical hollow structure and conductive RGO matrix, the composite exhibits excellent long-life performance and rate capability. A capacity of 890 mAh/g is achieved after 200 cycles at 200 mA/g and a capacity of 429 mAh/g is retained after 800 cycles at 1000 mA/g. The results indicate that the strategy of combining hierarchical hollow structures with conductive RGO holds the potential in addressing the volume expansion issue of high capacity anode materials.

KEYWORDS: hierarchical hollow spheres, copper silicate hydrate, reduced graphene oxide, lithium-ion battery, long cycling performance



INTRODUCTION

As a well-known energy storage device, lithium-ion batteries (LIBs) have drawn great attention in portable electronics due to their high energy density and environmental benignity.¹ To meet the rapid development of portable electronics and electric vehicles, novel anode materials with high capacity and long cycle life are needed.^{2,3} Therefore, anode materials with higher specific capacity than that of commercial graphite, such as pure elements (e.g., Si, Sn, Sb) and metal oxides (e.g., Co₃O₄, SnO₂, Fe₂O₃) have attracted considerable attention.^{4–9} Among them, silicon has been considered as the most attractive candidate because of its extremely high theoretical capacity (~4200 mAh/g).¹⁰ However, silicon based electrode suffers from rapid capacity fading caused by large volume variation (>300%) during Li⁺ insertion/extraction.¹¹ Various silicon nanostructures, such as porous particle,¹² nanowire,¹³ and silicon/carbon composite¹⁴ have been explored to overcome this problem. Although improved cycling performance has been achieved, the high cost of synthesizing silicon nanostructures hinders the industrial

applications. Therefore, exploring alternative anode materials with low cost and abundant sources is required.

Silicates have attracted increasing interests in energy storage, catalysts, and adsorption due to its abundance, stability, and nontoxicity.^{15–17} Among them, Li₂MSiO₄ (M = Fe, Mn, and Co) have been widely studied as cathodes.¹⁸ Recently, silicates have also been considered as promising anode materials for LIBs.^{19–22} Compared to metals or metal oxides, silicate has lower cost and more abundant sources than Sn, SnO₂, Ge, etc. In addition, the synthesis of silicate is much easier than that of Si and Ge. Both factors make the silicate very promising for large scale production and industrial applications. Unfortunately, the silicates possess low electronic and ionic conductivity, leading to poor electrochemical performance. One possible strategy to address this issue is constructing composites with carbonaceous matrix,

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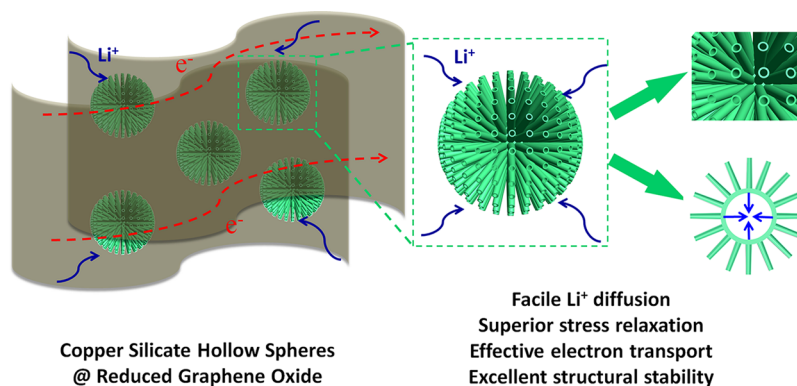


Figure 1. Schematic illustration of the CSH/RGO composite with facile Li^+ diffusion, superior stress relaxation, effective electron transport, and excellent structural stability during Li^+ insertion/extraction.

which enhances the electronic conductivity and buffers the volume expansion.^{23–26} Due to its intrinsically high electrical conductivity, excellent mechanical flexibility, and high surface area,^{27,28} graphene has been widely studied in LIBs^{29–33} and capacitors.^{34,35} For example, Zou et al. produced NiO-graphene nanohybrids, which show improved lithium storage properties.³² Another way to solve this problem is to design hierarchical hollow structures, which provides an enhanced surface area and reduced length for lithium ion transportation.^{36–42} Meanwhile, the hierarchical hollow structure is able to accommodate the volume expansion/contraction and thus enhances the cycling performance. It is expected that the combination of hollow architecture with graphene may integrate the advantages from both components, realizing high electrochemical performance.

Herein, we present a simple templating method for fabricating hierarchical copper silicate hydrate (CSH) hollow spheres encapsulated in reduced graphene oxide (RGO) and study the electrochemical performance of CSH/RGO as LIBs anode for the first time. In this constructed structure (Figure 1), the CSH hollow spheres with void space accommodate the volume change and enhance the lithium ion diffusion, while the RGO facilitates the electron transport and improves the structural stability. Benefiting from the synergistic effect of hierarchical hollow spheres and conductive RGO matrix, the CSH/RGO composite exhibits excellent cycling stability and rate capability.

EXPERIMENTAL SECTION

Material Synthesis. *Synthesis of CSH/RGO.* First, the SiO_2 spheres were synthesized via the modified Stöber method.⁴³ Graphene oxide (GO) was synthesized by the modified Hummer's method.⁴⁴ The concentration of the obtained GO suspension was ~ 2.3 g/L. The as-prepared SiO_2 spheres (0.1 g) and GO aqueous dispersion (5 mL) were dispersed into 38 mL of distilled water and sonicated for 40 min. After that, 1 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added into the above solution and stirred for 5 min. Then, 10 mmol of NH_4Cl was added into the solution under stirring. After that, 1 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added into the solution drop by drop. After 10 min, the suspension was transferred into the Teflon-lined stainless steel autoclave and kept at 140°C for 20 h. The precipitate was collected by centrifugation, washed with distilled water and ethanol, and dried at 70°C for 12 h under vacuum. Pure CSH spheres were synthesized by the same procedure except that no GO was introduced.

Material Characterization. X-ray diffraction (XRD) measurement was performed to investigate the crystallographic information using a D8 Advance X-ray diffractometer with a nonmonochromated Cu K α X-ray source. The carbon content analysis was determined by Vario EL cube CHNSO elemental analyzer. TGA was performed using a Netzsch STA 449F3 simultaneous thermal analyzer at a heating rate of

$10^\circ\text{C}/\text{min}$ in air. Brunauer-Emmet-Teller (BET) surface areas were measured using a Tristar II 3020 instrument. Raman spectra were obtained using a Renishaw IN VIA micro-Raman spectroscopy system. X-ray photoelectron spectroscopy (XPS) analysis was done on a VG Multilab 2000. Field emission scanning electron microscopic (FESEM) images and energy dispersive spectra (EDS) were collected using a JEOL-7100F microscope. Transmission electron microscopy (TEM) images were recorded by a JEM-2100F microscope.

Electrochemical Measurements. 2016 coin cells were assembled in a glovebox filled with pure argon. Lithium chips were used as the counter electrode and the reference electrode. The working electrode was obtained by mixing the as-prepared materials, acetylene black, and carboxyl methyl cellulose (CMC) at a weight ratio of 70:25:5. The slurry was casted on copper foil, dried at 70°C for 12 h, and heated at 120°C for 2 h in a vacuum oven. The active material loaded on the copper foil was $1.5\text{--}2.0$ mg/ cm^2 . The electrolyte consisted of 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio of 1:1. Before the electrochemical performance, the cell was aged at room temperature for at least 4 h. Galvanostatic charge/discharge measurements were performed at a potential range of 0.01–3 V vs Li^+/Li using a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested by an electrochemical workstation (CHI600D and Autolab Potentiostat Galvanostat 302N). All of the measurements were carried out at room temperature.

RESULTS AND DISCUSSION

The morphology and structure of the obtained CSH/RGO composite is characterized by FESEM and TEM, as shown in Figure 2. Uniform copper silicate spheres embedded in RGO nanosheets can be seen in the low magnification SEM image (Figure 2a). The low magnification TEM image (Figure 2b) shows that the prepared copper silicate spheres possess a hollow cavity at the center. It is clearly observed in the high magnification TEM image (Figure 2c) that the hollow spheres encapsulated in RGO matrix are constructed by radially aligned nanotubes. The size of the hollow spheres is in the range of 400–500 nm. Figure 2d further confirms that the hierarchical hollow spheres are assembled by radially aligned nanotubes with a diameter of about 5 nm. The morphology of the pristine CSH without RGO was also investigated by FESEM (Figure S1). The pristine CSH shows a similar urchin-like structure to that of CSH in the composite.

Time-dependent experiments were also carried out to investigate the formation process of CSH hollow spheres. Figures S2 and S3 show the morphologies of SiO_2 template and CSH hollow spheres at different stages during the synthesis process. The SiO_2 template shows a uniform spherical morphology with an average size of ~ 400 nm (Figure S2). When the reaction time is 1 h,

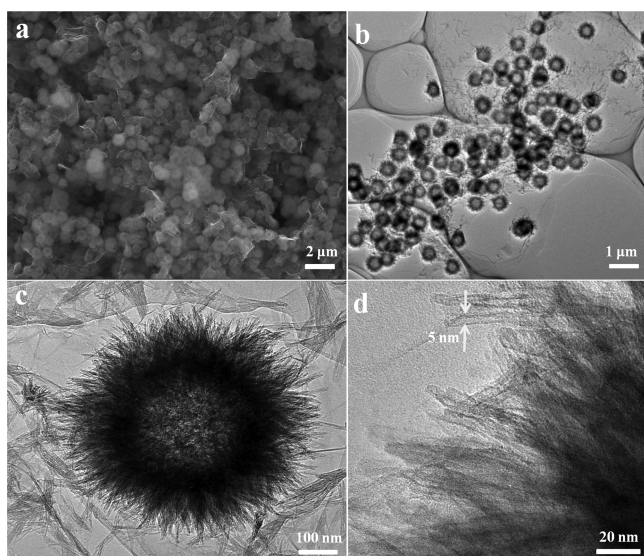


Figure 2. (a) FESEM image and (b) the low and (c, d) high magnification TEM images of CSH/RGO composite.

the surface of SiO_2 spheres becomes rough and some nanoparticles are generated on the surface. After a 3 h reaction, the core–shell structure is formed, indicating that the outer part of the SiO_2 spheres is consumed and copper silicate is formed on the surface of SiO_2 spheres. As the reaction time increases to 16 h, the copper silicate shell becomes thicker and the nanotube building blocks can be clearly discerned. On the basis of the time-dependent experiments, the formation mechanism of CSH spheres is proposed and illustrated in Figure 3. The SiO_2 Stöber

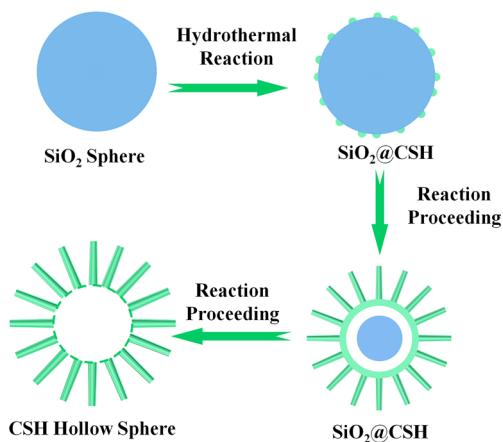


Figure 3. Schematic illustration of CSH hollow spheres in the fabrication process.

spheres act as the sacrificing template for the formation of CSH spheres. Under hydrothermal treatment, the SiO_2 spheres react with $\text{NH}_3 \cdot \text{H}_2\text{O}$ slowly, releasing SiO_3^{2-} . The *in situ* generated SiO_3^{2-} reacts with the Cu^{2+} nearby, forming a copper silicate hydrate shell on the surface of SiO_2 spheres. With the reaction time increasing, the outer part of SiO_2 spheres is consumed and the copper silicate hydrate shell grows thicker. As a result, a gap between the SiO_2 core and copper silicate shell is formed. Further extension of the reaction time leads to complete consumption of the SiO_2 core, resulting in the hierarchical CSH hollow spheres.

The crystallographic structure and phase of the CSH/RGO and CSH spheres were characterized by XRD. Figure 4a shows

the XRD pattern of as-prepared CSH/RGO, which matches well with the chrysocolla copper silicate hydrate ($\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$, JCPDS card No. 00-003-1152). No impure peaks can be observed. EDS analysis of the as-prepared CSH/RGO shows the presence of Cu, Si, and O with a Cu/Si atomic ratio of 1:1 (Figure S4). The XRD pattern of the pristine CSH can be indexed to the same chrysocolla copper silicate hydrate phase (Figure S5). The EDS spectrum of CSH indicates that its chemical composition is same as that of copper silicate hydrate (Figure S6).

Raman spectrum of as-prepared CSH/RGO was tested to clarify the existence of RGO, as shown in Figure 4b. The bands in the range of 1200–1450 and 1500–1650 cm^{-1} are attributed to the D-band and G-band of graphene,⁴⁵ respectively. The content of RGO in the CSH/RGO composite was determined by the CHNSO elemental analyzer and TGA (Table S1 and Figure S7). A mass loss was observed below 150 °C in both CSH and CSH/RGO, corresponding to the evaporation of adsorbed water. The weight loss at 200–600 °C is attributed to the loss of hydrated water and combustion of RGO. On the basis of the TGA result, the RGO content is estimated to be 5 wt % and the number of hydrated water is determined to be 0.5, which is consistent with the CHNSO analysis (Table S1). The porous structures of CSH/RGO and CSH were characterized by nitrogen sorption (Figures 4c,d and S8). The CSH/RGO composite exhibits a high BET surface area of 465.6 m^2/g and a high pore volume of 0.9 cm^3/g . For bare CSH, the BET surface area and pore volume are 395.4 m^2/g and 0.6 cm^3/g , respectively. The CSH/RGO and CSH show similar nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distributions. The pore size is centered at around 3 nm for both samples.

The electrochemical performances of the as-prepared materials were investigated. Figures 5a and S9 show the cycling performance of CSH/RGO composite, CSH, and RGO at the current density of 200 mA/g. It is clear that the CSH/RGO composite exhibits higher capacity and better cycling stability than those of the pristine CSH and RGO. The capacity of CSH/RGO decreases in the first 20 cycles and then levels off. Interestingly, the capacity begins to increase after 100 cycles. After 200 cycles, a capacity of 890 mAh/g can be obtained. To study the structural stability of CSH/RGO during cycling, the coin cells after 100 cycles at 200 mA/g have been disassembled for TEM characterization. The hierarchical hollow spherical structure of CSH/RGO can be well preserved, indicating the good structural stability (Figure S10).

The charge–discharge profiles (1st, 3rd, 30th, and 50th cycles) of the CSH/RGO composite at 200 mA/g are shown in Figure 5b. A potential plateau at about 1.5 V can be observed in the first discharge curve. However, the plateau disappears in the subsequent cycles, which is in agreement with most of the alloy type and conversion reaction type anode materials.^{46,47} An irreversible capacity loss occurred in the first cycle, which may be attributed to the formation of SEI film.⁴⁸ Although the initial Coulombic efficiency (45.5%) is not satisfactory, it can be significantly improved by applying a prelithiation strategy.⁴⁹ The CV of CSH/RGO composite was performed in the potential window of 0.01–3 V at a sweeping rate of 0.1 mV/s to characterize the charge and discharge process (Figure S11). A strong peak appears at about 1.3 V in the first cathodic sweep, which is consistent with the plateau in the first cycle discharge curve (Figure 5b). For comparison, the CV curves and charge–discharge profiles of CSH are shown in Figure S12.

The rate performances of the CSH/RGO composite and CSH were investigated by varying the current densities from

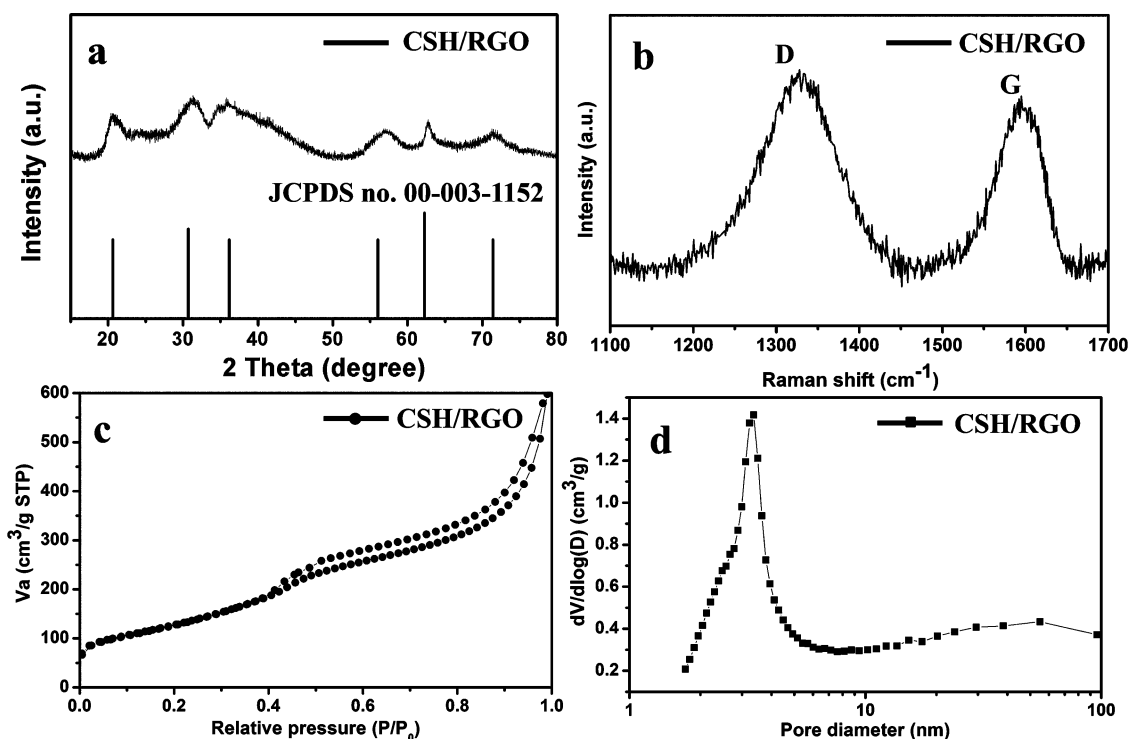


Figure 4. (a) XRD pattern of CSH/RGO composite, (b) Raman spectroscopy, (c) N_2 adsorption and desorption isotherms, and (d) pore size distribution of CSH/RGO composite.

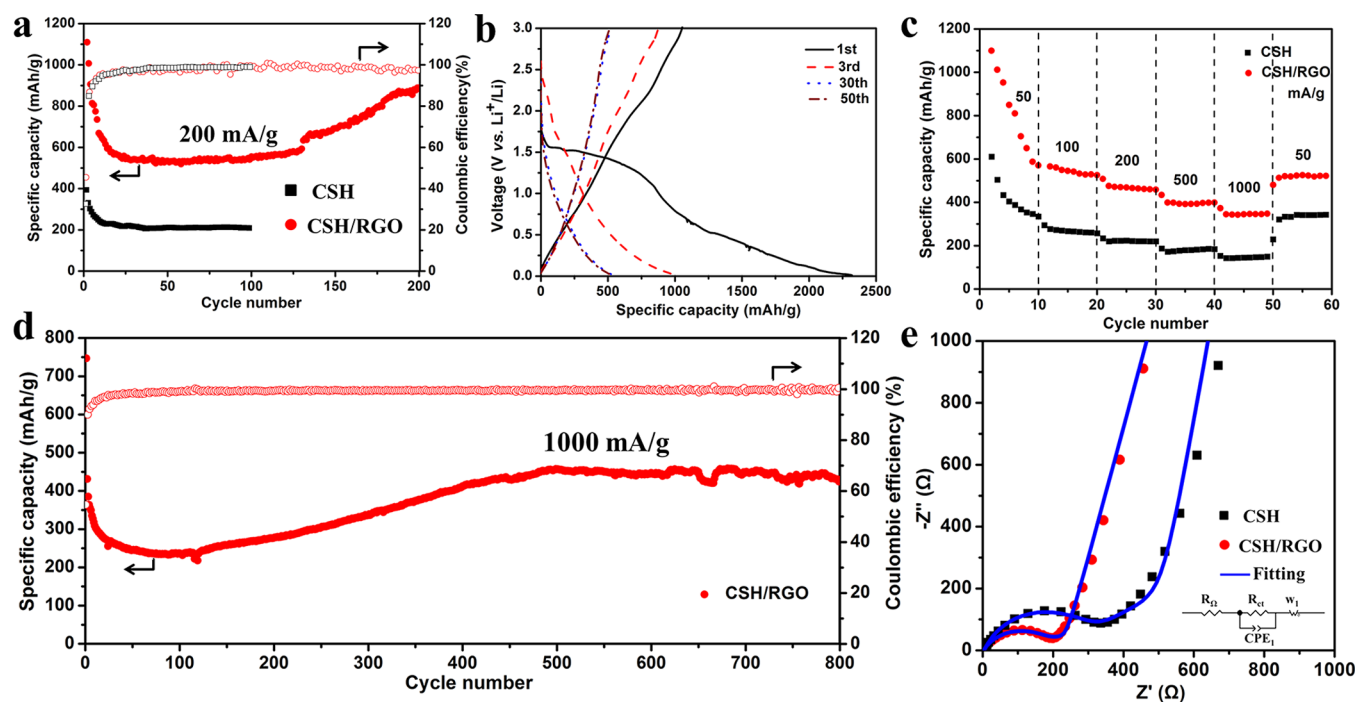


Figure 5. (a) Cycling performance of CSH spheres and CSH/RGO composite at the current density of 200 mA/g, (b) galvanostatic charge and discharge curves of CSH/RGO at the current density of 200 mA/g, (c) rate cycling performance of CSH and CSH/RGO, (d) long-life cycling performance of CSH/RGO at 1000 mA/g, and (e) AC-impedance plots of CSH and CSH/RGO.

50 to 1000 mA/g (Figure 5c). The CSH/RGO composite exhibits much better rate performance than bare CSH. The capacities of CSH/RGO composite are 571, 522, 460, 398, and 357 mAh/g at the current densities of 50, 100, 200, 500, and 1000 mA/g, respectively. When the current density is reduced to 50 mA/g, a capacity of 531 mAh/g is recovered. However,

the capacities of bare CSH are only 332, 255, 218, 182, and 148 mAh/g at the different current densities of 50, 100, 200, 500, and 1000 mA/g, respectively.

The long-life cycling performance of CSH/RGO composite was further evaluated at a high current density of 1000 mA/g (Figure 5d). The first and second cycle capacities of CSH/RGO

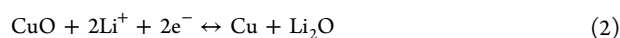
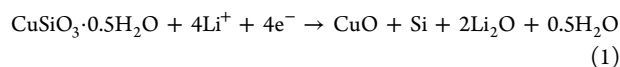
composite are 747 and 431 mAh/g. The capacity remains 429 mAh/g after 800 cycles, corresponding to a capacity retention of 99.5% (compared to the capacity of the second cycle). It is worthy to note that the capacity begins to increase after 100 cycles and stabilizes after 500 cycles. A similar lithiation-induced reactivation phenomenon has also been observed in metal oxide based anode materials.^{36,50}

To further demonstrate the advantageous design of CSH/RGO, the high temperature cycling performance at 60 °C is investigated. As shown in Figure S13, the CSH/RGO composite exhibits excellent high temperature cycling performance. A capacity of 791 mAh/g can be retained after 150 cycles at 200 mA/g.

To understand the enhanced performances of the CSH/RGO composite, electrochemical impedance spectra (EIS) were measured (Figure 5e). It can be seen that the charge transfer resistance of CSH/RGO composite in the high frequency region (178 Ω) is smaller than that of bare CSH (269 Ω), indicating the faster kinetics of CSH/RGO composite.^{51,52} The EIS results indicate that the introduction of conductive RGO matrix, which improves the electronic conductivity, is the underlying reason for the superior electrochemical performances of CSH/RGO.

The AC-impedance plots and SEM images of the CSH/RGO composite after 100 and 200 cycles are shown in Figures S14 and S15, respectively. The EIS results show that the charge transfer resistance of the CSH/RGO first increases with cycling and then decreases (Figure S14 and Table S2). SEM images show that the CSH/RGO composite after 100 cycles has thicker SEI layer formation on the surface than that after 200 cycles (Figure S15). Both the EIS results and *ex situ* SEM observations are highly consistent with the cycling behavior of CSH/RGO (Figure 5a).³⁶

To study the electrochemical reaction mechanism of copper silicate hydrate, XPS (Figure S16) and *ex situ* XRD (Figure S17) are carried out. In the initial state, the binding energy for Cu 2p_{3/2} appears at 935.4 eV, corresponding to Cu²⁺.⁵³ After the first discharge, the XPS spectrum shows a broad Cu 2p_{3/2} peak with the binding energy of 933.0 eV, demonstrating the presence of the metallic Cu.⁵⁴ That is to say, the Cu²⁺ is reduced to Cu⁰ during the first discharge process. *Ex situ* XRD results indicate that severe structure amorphization occurs during the initial discharge, and the copper silicate hydrate phase cannot be recovered after charge. In combination of the XPS and *ex situ* XRD results, the possibility of intercalation/deintercalation reaction can be ruled out. In consideration of the high reversible capacity of CSH/RGO (1109 mAh/g), it is speculated that the copper silicate hydrate stores lithium through the combination of alloying/dealloying and conversion reaction. The possible reaction mechanism is tentatively proposed as follows:



On the basis of the above results, the excellent electrochemical performances of hierarchical CSH/RGO composite can be credited to the synergistic effect of the hierarchical hollow structure and interconnected conductive network, as illustrated in Figure 1. First, the hierarchical hollow structure constructed by radially aligned nanotubes possesses large free space for volume variation accommodation and open channels for lithium ion diffusion.⁵⁵ Second, the RGO matrix with high electronic

conductivity and superior mechanical flexibility not only provides a 3D conductive network but also improves the structural stability.^{30,56,57} The combination of hierarchical hollow spheres and conductive RGO matrix effectively integrates the advantages of both components, resulting in highly improved cycling performance and rate capability.

CONCLUSIONS

The CSH/RGO composite composed of hierarchical copper silicate hydrate hollow spheres and conductive RGO matrix has been successfully fabricated via a facile, low-cost hydrothermal method. Benefiting from the synergistic effect of the hierarchical hollow spheres and conductive RGO matrix, the composite exhibits excellent long-life cycling performance and good rate capability. The superior electrochemical performances of CSH/RGO make it a promising anode material for LIBs. The strategy of combining hierarchical hollow structures with conductive RGO holds the potential in addressing the volume expansion issue of high capacity anode materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07863.

SEM images of CSH and SiO₂ spheres; SEM images of CSH obtained at different times; EDS spectrum of CSH/RGO; XRD pattern and EDS spectrum of CSH; TGA curves of CSH/RGO and CSH; N₂ sorption results of CSH; cycling performance of RGO; TEM images of CSH/RGO after 100 cycles; CV curves of CSH/RGO; CV curves and charge–discharge profiles of CSH; cycling performance of CSH/RGO at 60 °C; AC-impedance plots and SEM images of CSH/RGO after 100 and 200 cycles; XPS spectra of CSH before and after the first discharge process; XRD patterns of CSH after the first discharge and charge process; CHNSO results of CSH/RGO; charge transfer resistances of CSH/RGO at initial state, after 100 cycles, and after 200 cycles (PDF)

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Notes

The authors declare no competing financial interest.

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