Self-templated Synthesis of Nickel Silicate Hydroxide/Reduced Graphene Oxide Composite Hollow Microspheres as Highly Stable Supercapacitor Electrode Material

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Abstract
Nickel silicate hydroxide/reduced graphene oxide (Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO) composite hollow microspheres were one-pot hydrothermally synthesized by employing graphene oxide (GO)-wrapped SiO$_2$ microspheres as the template and silicon source, which were prepared through sonication-assisted interfacial self-assembly of tiny GO sheets on positively charged SiO$_2$ substrate microspheres. The composition, morphology, structure, and phase of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres as well as their electrochemical properties were carefully studied. It was found that Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres featured distinct hierarchical porous morphology with hollow architecture and a large specific surface area as high as 67.6 m$^2$/g. When utilized as a supercapacitor electrode material, Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hollow microspheres released a maximum specific capacitance of 178.9 F g$^{-1}$ at the current density of 1 A g$^{-1}$, which was much higher than that of the contrastive bare Ni$_3$Si$_2$O$_5$(OH)$_4$ hollow microspheres and bare RGO material developed in this work, displaying enhanced supercapacitive behavior. Impressively, the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode exhibited outstanding rate capability and long-term cycling stability and durability with 97.6% retention of the initial capacitance after continuous charging/discharging for up to 5000 cycles at the current density of 6 A g$^{-1}$, which is superior or comparable to that of most of other reported nickel-based electrode materials, hence showing promising application potential in the energy storage area.

Keywords: Nickel silicate hydroxide, Graphene, Hollow structure, Supercapacitor, Self-template, Hydrothermal synthesis

Background
To ease the energy crisis and environmental problems, there is an important and urgent need to develop clean and sustainable power sources as well as advanced energy conversion and storage devices [1]. Supercapacitors, usually known as electrochemical capacitors, have attracted tremendous attention owing to their higher energy density than traditional dielectric capacitors, higher power density than batteries, rapid charge/discharge rate, and quite long cycle life [2]. The exploration of high-performance electrode materials is a crucial challenge for the construction and application of supercapacitors. Up to now, a large number of supercapacitor electrode materials with different components, morphologies, and architecture such as nanostructured carbonaceous matter (e.g., porous carbon, graphene network, carbon nanotubes), metal sulfides (e.g., MoS$_2$, Ni$_3$S$_2$, WS$_2$), metal oxides (e.g., MnO$_2$, RuO$_2$, CeO$_2$), metal hydroxides (e.g., Co(OH)$_2$, Ni(OH)$_2$), conducting polymers (e.g., polyaniline, polypyrrole), and their hybrid composites have been well fabricated [2–8]. Unfortunately, most of them suffer from one or more problems like high cost, complicated preparative process, limited specific capacitance, unsatisfactory cycling stability, and low rate capability. Among these disadvantages, the inferior cycling stability is particularly acute, which severely restricts their further practical applications in the supercapacitor field [9]. Consequently, it remains a challenging task to develop highly stable electrode materials with excellent supercapacitive behavior through facile and cost-effective strategies.

As a typical member of metal silicate hydroxides, nickel silicate hydroxide (Ni$_3$Si$_2$O$_5$(OH)$_4$) has a layered structure...
formed by outer octahedral Ni(II)O₆ sheets and inner tetrahedral SiO₄ sheets [10]. Thanks to the earth abundance and environmental friendliness, Ni₃Si₂O₅(OH)₄ has been widely utilized as adsorbents for heavy metal ions and organic dyes, carriers for drug release, molecular sieves, and catalyst supports [10–14]. However, its application as electroactive materials is quite limited because of its intrinsic poor electronic conductivity [10]. Despite this drawback, the layered structure of Ni₃Si₂O₅(OH)₄ still endows it with an appealing feature for electrochemical applications, since such structure could provide numerous well-defined multichannels for fast mass transfer, which is a critical factor during electrochemical reactions [10]. To improve the conductivity of Ni₃Si₂O₅(OH)₄-based materials, hybridization of Ni₃Si₂O₅(OH)₄ with a conductive matrix including reduced graphene oxide and carbon nanotubes has been recently achieved, and the resulting composites were successfully used in electrocatalytic water oxidation and lithium-ion batteries [10, 15–17]. Nevertheless, the report with respect to the application of Ni₃Si₂O₅(OH)₄-based materials in supercapacitor remains rare.

Graphene, a single layer of graphite, has been regarded as one of the most promising materials due to its attractive physicochemical properties and functions like light weight, exceptional electronic conductivity, and splendid chemical stability [17]. Accordingly, integration of graphene or reduced graphene oxide (RGO) with other inorganic species to boost electrochemical behavior has become an effective strategy, and a variety of graphene- or RGO-containing hybrids (e.g., hollow-structured MoS₂/RGO microspheres, RGO-wrapped polyaniline nanowires, nanocubic Co₃O₄/RGO composites) with reinforced supercapacitive performance have been explored as well [4, 18, 19]. Over the past few years, self-assembly of graphene oxide (GO) sheets on solid substrates via electrostatic interaction has been demonstrated to be a versatile way to prepare GO- and RGO-based composites [20]. By means of this methodology, we have pioneered the fabrication of highly water-dispersible GO-encapsulated SiO₂ microspheres (Fig. 1). The excellent aqueous dispersity of the resultant SiO₂/GO composite microspheres enabled them to be readily modified or treated for further functionalization [4, 21, 22]. Herein, we take advantage of this point and utilize them as the template and silicon source to prepare flower-like nickel silicate hydroxide/reduced graphene oxide (Ni₃Si₂O₅(OH)₄/RGO) composite hollow microspheres with a hierarchical porous structure in one pot. As illustrated in Fig. 1, SiO₂/GO microspheres underwent a hydrothermal process in the presence of polyvinylpyrrolidone, nickel nitrate, and urea, during which the SiO₂ inner core reacted with nickel cations to produce Ni₃Si₂O₅(OH)₄ in alkaline condition and its deposition, growth, and crystallization on substrate microspheres together with the reduction of GO to RGO were synchronously accomplished, giving rise to the final product of Ni₃Si₂O₅(OH)₄/RGO composite hollow microspheres. When employed as a supercapacitor electrode material, the synthesized Ni₃Si₂O₅(OH)₄/RGO microspheres released a maximum specific capacitance of 178.9 F g⁻¹ at the current density of 1 A g⁻¹ in a three-electrode system and maintained 97.6% of the initial capacitance after repetitive charging/discharging at the current of 6 A g⁻¹ over 5000 cycles, exhibiting outstanding long-term cycling stability and durability.

Methods

Materials and Reagents

Ammonium hydroxide (25 wt%), tetraethyl orthosilicate, poly(diallyldimethylammonium) chloride (PDDA), nickel nitrate hexahydrate, urea, polyvinylpyrrolidone (PVP) with an average molecular weight of 40,000, acetylene black, N-methyl-2-pyrrolidone (NMP), nickel foam, potassium hydroxide, and polyvinylidene fluoride (PVDF) were purchased from J&K Co., Ltd. (Shanghai, China). Commercial tiny GO sheets with the lateral size less than 200 nm were provided by Nanjing JCNANO Technology Co., Ltd. (Nanjing, China). All other chemicals were guaranteed reagents and directly used as received.
**Synthesis of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO Composite Hollow Microspheres**

Monodisperse colloidal SiO$_2$ microspheres with the diameter of ~300 nm were first prepared based on a modified Stöber method (see Additional file 1 for experimental details). Subsequently, GO-encapsulated SiO$_2$ microspheres (i.e., SiO$_2$/GO composite microspheres) were fabricated by sonication-assisted interfacial self-assembly of tiny GO sheets on cationic polyelectrolyte-decorated SiO$_2$ microspheres (i.e., PDDA-modified SiO$_2$ microspheres) through electrostatic interaction (see Additional file 1 for experimental details). Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hollow microspheres were one-step hydrothermally synthesized through a self-template route. Typically, 20 mg of SiO$_2$/GO microspheres were dispersed in 12 mL of water, followed by introduction of 8 mL of mixed aqueous solution containing 80 mg of nickel nitrate hexahydrate, 0.6 g of PVP, and 1 g of urea under sonication. The resulting reaction mixture was then poured into a stainless autoclave (50 mL of capacity) and sealed, which was subsequently allowed to undergo a hydrothermal reaction at 180 °C for 12 h. During the hydrothermal process, SiO$_2$ reacted with nickel ions and urea to yield Ni$_3$Si$_2$O$_5$(OH)$_4$, which was grown on the substrate microspheres. At the same time, the GO component was hydrothermally reduced to RGO, hence resulting in the generation of flower-like Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO composite hollow microspheres in one pot. After that, the product was separated and washed with abundant water, followed by drying and annealing at 600 °C for 2 h in Ar atmosphere. To demonstrate the role of PVP in the hydrothermal synthetic system, a Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hybrid material was similarly synthesized according to the above procedure but without the introduction of PVP. As control, contrastive bare Ni$_3$Si$_2$O$_5$(OH)$_4$ hollow microspheres were hydrothermally fabricated by using pure SiO$_2$ microspheres as the template, followed by the same annealing treatment. In addition, bare RGO material was also prepared through hydrothermal reduction of tiny GO sheets at 180 °C for 12 h.

**Characterizations**

Powder X-ray diffraction (XRD) patterns with the scanning range from 10° to 70° were obtained on a Bruker D8 ADVANCE diffractometer. Field emission scanning electron microscopy (FESEM) inspection was performed on a Hitachi SU8010 microscope working at the acceleration voltage of 3 kV. Transmission electron microscopy (TEM) observation was carried out on a JEOL JEM-2100F microscope operating at the acceleration voltage of 200 kV and equipped with an energy-dispersive spectroscopy (EDS) system. X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MARK II instrument. Raman spectra were collected from a HORIBA Scientific Raman spectrometer with the excitation source of 532-nm laser line. Nitrogen adsorption–desorption isotherms were recorded on a Micromeritics ASAP 2020 apparatus at −196 °C, and the specific surface area of the samples was calculated by the Brunauer–Emmett–Teller (BET) model.

**Electrochemical Measurements**

All the electrochemical tests were done on a CHI 760E electrochemical workstation (CH Instruments, Inc., Shanghai, China) with a three-electrode system by employing aqueous solution of 2 M KOH as the electrolyte. Hg/HgO electrode, platinum foil, and nickel foam substrate coated with active material were used as the reference electrode, counter electrode, and working electrode, respectively. To fabricate the working electrode, the active material was mixed with acetylene black and PVDF at the weight ratio of 80:10:10. Then, NMP was added into the mixture, followed by gentle grinding to generate a homogeneous slurry. After that, the resulting slurry was pasted onto a nickel foam current collector with the area of 1 cm × 1 cm, followed by drying at 60 °C overnight in a vacuum oven, and the loading amount of active material on the working electrode was ~2.5 mg. Cyclic voltammetry (CV) curves were recorded in the potential window between 0.15 and 0.65 V at various scanning rates. Galvanostatic charge/discharge (GCD) measurements were done in the potential range from 0.2 to 0.6 V at a series of current densities. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 0.01 to 100,000 Hz at open-circuit potential with an ac perturbation of 5 mV.

**Results and Discussion**

**Material Characterizations**

Figure 2a and Additional file 1: Figure S1a, b are the FESEM images of pure monodisperse SiO$_2$ microspheres with the diameter of ~300 nm and a perfect smooth surface, displaying white color (inset of Fig. 2a). Figure 2b and Additional file 1: Figure S1c, d present the FESEM images of SiO$_2$/GO microspheres, whose size seems to be unchanged as compared with SiO$_2$ microspheres while whose apparent color becomes yellow brown (inset of Fig. 2b). Also, the outer surface of SiO$_2$/GO microspheres seems to be slightly rougher and some twisted crumples can be identified (Fig 2b and Additional file 1: Figure S1d), which should arise from the encapsulation of tiny GO sheets on substrate microspheres. These results confirm the successful sonication-assisted interfacial self-assembly of tiny GO sheets on the positively charged SiO$_2$ microspheres by virtue of electrostatic interaction. Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO composite hollow microspheres were one-pot prepared by hydrothermal treatment of the SiO$_2$/GO microsphere template in the presence of nickel nitrate, urea, and PVP, and their morphology was carefully inspected. Compared with
the pristine SiO$_2$ and SiO$_2$/GO composite microspheres, Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres are bigger in size (~600 nm in diameter), and their external surface is composed of plenty of highly curved and wrinkled nanoflakes with the thickness of tens of nanometers (Fig. 2c, d), which should originate from the homogeneous deposition, coverage, and growth of Ni$_3$Si$_2$O$_5$(OH)$_4$ on the substrate microspheres, leading to the hierarchical porous architecture with a flower-like shape. Meanwhile, differing from the apparent colors of pristine SiO$_2$ and SiO$_2$/GO composite microspheres, Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres show a dark color (inset of Fig. 2c), and such deep color is owing to the presence of the RGO component within the sample. Figure 2d exhibits the FESEM image of a typical Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere with a broken shell, revealing the hollow structure, which was further verified by the following TEM and scanning TEM (STEM) examinations. As exhibited in Fig. 2e, f, an evident interior cavity with a uniform shell thickness of ~150 nm was found in each well-defined Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere, which is indicative of total removal of the SiO$_2$ template but without collapse of the hollow structure. The inset of Fig. 2e is a high-resolution TEM (HRTEM) image of an arbitrary Ni$_3$Si$_2$O$_5$(OH)$_4$ nanoflake anchored on a Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere, where the lattice fringes are visible and the interplanar spacing is calculated to be 0.74 nm, agreeing well with the (002) crystal plane of Ni$_3$Si$_2$O$_5$(OH)$_4$ [9, 16, 17]. The elemental distribution of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere presented in Fig. 2f was further analyzed by the corresponding EDS mappings. As can be clearly seen in Fig. 2g–j, all the Ni, Si, O, and C signals were detected and filled the microsphere area, demonstrating their homogeneous distribution in this sample. Notably, PVP plays an important role in the hydrothermal synthetic system. In the absence of PVP, although a Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hybrid material can be fabricated as well, such composite agglomerated seriously and its spherical morphology was rather inferior to that of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO composite hollow microspheres (Additional file 1: Figure S2). It is assumed that PVP favored the dispersion of substrate microspheres (i.e., the SiO$_2$/GO microspheres) and effectively alleviated the agglomeration of products during the hydrothermal process, leading to well-defined Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO composite hollow microspheres. Moreover, as a comparison, bare Ni$_3$Si$_2$O$_5$(OH)$_4$ hollow microspheres were hydrothermally fabricated by employing pure SiO$_2$ microspheres as the template, and the synthetic conditions were identical to those for preparation of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres. Obviously, their sphere-like shape, hierarchical morphology, and hollow structure are similar to those of the counterpart (Fig. 2k, l), whereas their apparent color shows bright green (inset of Fig. 2k).

Powder XRD technique was made to characterize the structure and phase information of the products. As shown in the XRD patterns of both Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres and bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microspheres (Fig. 3), six diffraction peaks are available at...
around $2\theta = 12.0^\circ$, $19.6^\circ$, $24.5^\circ$, $34.2^\circ$, $36.7^\circ$, and $60.5^\circ$, which are well indexed to the (002), (110), (004), (200), (202), and (060) crystal planes of pecoraite Ni$_3$Si$_2$O$_5$(OH)$_4$, respectively. These values are in accordance with previous reports and the standard XRD pattern (JCPDS no. 49-1859) as well [9, 10, 15, 17]. Commonly, RGO features a broad diffraction peak at $2\theta = 25^\circ$; nevertheless, in the XRD pattern of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres, it is likely to be overlapped by the peaks corresponding to the (110) and (004) crystal planes of the Ni$_3$Si$_2$O$_5$(OH)$_4$ component as a result of the low content and weak diffraction intensity of RGO within Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres [15, 17].

To verify the existence of the RGO component incorporated in Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres, the Raman spectra of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres and tiny GO sheets were characterized and depicted in Fig. 4. Obviously, there are a couple of bands at around $1350$ and $1590$ cm$^{-1}$ in both curves, which are ascribed to the characteristic D and G bands of graphene-based species [14, 15, 17]. Generally, the D band arises from the structural defects and edges that damage the symmetry, while the G band refers to the first-order scattering of $E_{2g}$ phonons [4, 14]. Especially, the peak intensity ratio of the D to the G band ($I_D/I_G$) is a useful measure to evaluate the graphitization degree of carbon matter [4, 14]. The $I_D/I_G$ value for Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres is $1.08$, which is higher than that for GO sheets ($0.88$), implying that the reduction of GO to RGO indeed occurred during the hydrothermal process, which was undoubtedly incorporated in the final product of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres [4, 14, 17].

X-ray photoelectron spectroscopy provides an effective tool for disclosing the surface composition and state of hybrid materials. Figure 5a gives the high-resolution XPS of C 1s of GO sheets. Figure 5b–e shows a set of high-resolution XPS of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres for the C 1s, Ni 2p, Si 2p, and O 1s regions, respectively. As envisioned, the detected signals suggest the presence of the four elements in the sample. Both of the C 1s spectra can be resolved into three Gaussian fitted peaks. The peak located at $284.6$ eV is attributed to the oxygen-free C=C and C–C bonding, whereas the other two peaks found around $285.6$ and $287.1$ eV are related to diverse oxygen-containing groups including C–OH, O=C, and C–O–C [23, 24]. The relative intensity of oxygen-containing groups in the C 1s spectrum of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres significantly decreased as compared with that in the C 1s spectrum of tiny GO sheets, once again indicating that the immobilized GO sheets wrapping on the substrate microspheres underwent a drastic loss of oxygen-containing groups during the hydrothermal reaction, leading to its reduction to the RGO component [4, 22, 23]. Figure 5c is the high-resolution XPS of Ni 2p of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres, where a pair of predominant peaks appear at $856.0$ and $873.5$ eV, corresponding to the binding energy (BE) of Ni 2p3/2 and Ni 2p1/2, respectively [10, 25]. Two shakeup satellite peaks (denoted as “Sat.” in Fig. 5c) close to the spin-orbit doublets are also visible at $862.0$ and $880.1$ eV with the BE separation of $18.1$ eV [10, 25]. All these data agree well with the reported ones and demonstrate the presence of Ni(II) in this sample [10, 25]. Besides, the high-resolution XPS of Si 2p and O 1s reveal strong peaks at $102.3$ and $531.3$ eV, respectively, which are typical BE values for metal silicate hydroxides as well and mainly derive from the Ni–Si and Si–O bonding [9, 10].

The porous feature of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO and bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microspheres was surveyed by BET measurements. As shown in their nitrogen adsorption–desorption isotherms (Fig. 6a), both of them can be classified into type IV isotherms with a typical hysteresis
loop ranging from 0.5 to 0.9 $P/P_0$ in each of them, suggesting the presence of mesopores in the two specimens [4, 26]. Based on the isotherms, the pore size distribution and specific area are deduced according to the Barrett–Joyner–Halenda model, and the corresponding plots are presented in Fig. 6b, which once again manifest the existence of well-developed porosity with an average pore size centered around 20 nm and a wide distribution from micropores to macropores in both samples [2, 26]. Such result is consistent with their FESEM and TEM observations as well (Fig. 2), and the pores are possibly formed by the complex intertwining and stacking among the nanoflakes [27]. Thanks to the hierarchical porous architecture, the specific surface area of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO and bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microspheres is as high as 67.6 and 61.6 m$^2$ g$^{-1}$, respectively. It is assumed that the larger specific surface area of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres would increase the contact area between the electrolyte and electrode material, facilitate the mass transport of charged ions, and provide more reactive sites during electrochemical reactions and thus bring about preferable supercapacitive performance [4, 28, 29].

**Electrochemical Investigation**

The electrochemical properties of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hollow microspheres, bare Ni$_3$Si$_2$O$_5$(OH)$_4$ hollow microspheres, and bare RGO material were evaluated by CV and GCD measurements in a three-electrode system employing aqueous solution of 2 M KOH as the electrolyte. Figure 7a displays their CV curves at the sweeping rate of 20 mV s$^{-1}$. There are a pair of redox peaks in both CV curves of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO and bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microspheres, which arise from the transition of nickel ions between different oxidation states [10, 27, 30]:

$$\text{Ni}^{II}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{OH}^- \leftrightarrow \text{Ni}^{III}_3\text{Si}_2\text{O}_5(\text{OH})_6 + 2\text{e}^-$$

implying their pseudocapacitive characteristics [27, 30], while there are no obvious redox peaks in the CV curve of bare RGO material, suggesting its electric double-layer capacitance nature [2, 4]. The peak current density...
and the integral area enclosed by the CV curve of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hollow microspheres are higher than those of bare Ni$_3$Si$_2$O$_5$(OH)$_4$ hollow microspheres and bare RGO material, indicating the best capacitance [4, 9]. Figure 7b is the CV curves of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hollow microspheres at varied scanning rates of 2–100 mV s$^{-1}$. With the elevating sweeping rates, the shape of the CV curves is not remarkably altered and the intensity of redox peaks gradually goes up with only a slight shift toward higher potential, demonstrating that fast electrochemical reactions take place at the interface between the electrolyte and active material and the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO hollow microsphere electrode possesses excellent rate capability [19, 31]. Figure 7c depicts the GCD curves of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO, bare Ni$_3$Si$_2$O$_5$(OH)$_4$, and bare RGO electrodes in the potential range of 0.2–0.6 V tested at the current density of 1 A g$^{-1}$. It is not hard to see that the discharge time of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode is the longest. Such result is consistent with the CV measurements displayed in Fig. 7a and further confirms its superior supercapacitive behavior. The specific capacitance of a single electrode is able to be obtained on the basis of the equation described as follows:

$$C = i \cdot \Delta t / \Delta V \cdot m$$

where $C$ (F g$^{-1}$) stands for the specific capacitance, $i$ (A) represents the constant current, $t$ (s) is the discharge time, $\Delta V$ (V) is the potential window, and $m$ (g) is the mass of active material [4, 9, 27]. Therefore, the $C$ of Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres at the current density 1 A g$^{-1}$ is deduced to be 178.9 F g$^{-1}$, which is clearly higher than that of bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microspheres (138.4 F g$^{-1}$) and bare RGO material (12.2 F g$^{-1}$). Figure 7d gives its GCD curves at a group of different current densities, based on which the $C$ of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode is calculated to be 178.9, 166.5, 150.8, 138.9, 132.5, 126.8, 120.1, and 114.4 F g$^{-1}$ at the current density of 1, 2, 3, 4, 5, 6, 8, and 10 A g$^{-1}$, respectively. The change in its $C$ as a function of current density is also plotted in Fig. 7e. Obviously, the $C$ of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode gradually drops with increasing current density. It is inferred that both the outer and inner pores and reactive sites would contribute to the electrochemical reactions at low current densities, giving rise to high $C$ values, while only the external surface of the electrode material is involved in the charge/discharge processes at high current densities, thus resulting in the diminishment of the $C$ value [4, 29]. Compared with its maximum $C$ at the current density of 1 A g$^{-1}$, its $C$ at 5 and 10 A g$^{-1}$ maintains as high as 74.1 and 63.9% of the initial one, respectively, indicating prominent rate capability. However, for the bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microsphere electrode, the $C$ at 5 and 10 A g$^{-1}$ decreases to only 57.2 and 47.2% of that at 1 A g$^{-1}$, respectively, exhibiting inferior rate capability (Additional file 1: Figure S3). It is assumed that two reasons are responsible for the capacitance enhancement and rate capability improvement of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode. On the one hand, Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microspheres feature a porous hollow structure with a high-level hierarchy and larger specific surface area, which is quite favorable for the rapid transport and adsorption of electrolyte ions inside the electrode material. On the other hand, benefiting from the hybridization of Ni$_3$Si$_2$O$_5$(OH)$_4$ with RGO, the electronic conductivity is significantly improved, thus facilitating more effective electron transport within the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode.

To further interpret the enhanced electrochemical behavior of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode, EIS measurements on Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO and bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microsphere electrodes were conducted, and the corresponding Nyquist plots are
presented in Fig. 7f. Both of them show a depressed semicircle in the high-frequency region together with a straight line in the low-frequency region. In the high-frequency region, the intercept at the real axis and the diameter of the semicircle represent the equivalent series resistance ($R_s$) of the electrode and the charge transfer resistance ($R_{ct}$) at the electrode/electrolyte interface, respectively [32–34]. Apparently, compared with the bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microsphere electrode, the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode possesses much smaller $R_s$ and $R_{ct}$ values, which are indeed indicative of its better electronic conductivity and allow for faster electron transport within the electrode matrix [32–34]. In the low-frequency region, the straight line reflects the Warburg impedance, which can be used to describe the diffusive resistance of electrolyte ions [32–34]. The Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode shows a higher slope than the bare Ni$_3$Si$_2$O$_5$(OH)$_4$ microsphere electrode in the linear part, suggesting more rapid ion diffusion inside it [32–34]. These EIS findings further support and verify the abovementioned analyses on the excellent electrochemical performances of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode.

Cycle life plays a key role in the application of electrode materials in supercapacitors, since little change in their capacitance would make the supercapacitors work steadily and safely [27]. The cyclic performance of the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode was determined by repetitive GCD measurements for up to 5000 cycles at the current density of 6 A g$^{-1}$ (Fig. 8a, b). As continuous charging/discharging proceeds, the
capacitance decays quite slowly (Fig. 8a), and the shape of the GCD curve for the last 10 cycles remains good enough (Fig. 8b). The capacitance retention of the electrode even reaches up to 97.6% after the whole tests, which is preferable or comparable to a number of nickel-based supercapacitor electrode materials reported previously (Table 1). Besides, the Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO microsphere electrode after such tests was subjected to FESEM examinations as well, which disclosed the hierarchical porous architecture with spherical morphology freed from significant collapse and deformation (Fig. 8c, d). The structural integrity during the repetitive charging/discharging process largely contributes to the capacitance retention and convincingly demonstrates the

Table 1 Comparison of cycling stability between Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO composite hollow microspheres and some of other reported nickel-based electrode materials. All these data were obtained in three-electrode systems.

| Electrode materials                        | Current density (A g$^{-1}$) | Number of cycles | Capacitance retention (%) | Ref. |
|-------------------------------------------|------------------------------|------------------|---------------------------|------|
| Ni$_3$Si$_2$O$_5$(OH)$_4$/RGO composite hollow microspheres | 6                            | 5000             | 97.6                      | This work |
| NiO nanoparticles                         | 2                            | 1000             | 60.6                      | [35] |
| NiO nanosheet hollow spheres              | 3                            | 1000             | 91                        | [36] |
| Nanoporous Ni(OH)$_2$                    | 1                            | 2000             | 92.3                      | [37] |
| Porous Ni(OH)$_2$/NiOOH composite film   | 2                            | 1000             | 81                        | [38] |
| Doughnut-like Ni(OH)$_2$–Co(OH)$_2$ composites | 5                            | 1000             | 84.7                      | [39] |
| Ni(OH)$_2$–Ni nanohybrids                | 5                            | 2000             | 98.4                      | [40] |
| Mesoporous NiCo$_2$O$_4$ nanosheets       | 2                            | 2400             | 94                        | [41] |
| Urchin-like NiCo$_2$O$_4$ nanostructures  | 8                            | 2000             | 90.8                      | [42] |
| Mesoporous Ni$_3$Co$_2$O$_7$O$_4$ hierarchical structures | 0.625 | 3000 | 98.1 | [43] |
| RGO/NiCo$_2$O$_4$ nanoflake composites    | 4                            | 2000             | 90.8                      | [44] |
| NiCo$_2$S$_4$ ball-in-ball hollow spheres | 5                            | 2000             | 87                        | [45] |
splendid cycling stability, durability, and application potential in practical supercapacitors.

Conclusions
In summary, GO-encapsulated SiO₂ microspheres were prepared by sonication-assisted interfacial self-assembly of tiny GO sheets on positively charged SiO₂ microspheres. By employing the resulting SiO₂/GO composite microspheres as the template and silicon source, Ni₃Si₂O₅(OH)₄/RGO composite hollow microspheres were one-pot hydrothermally synthesized, which possessed unique hierarchical porous architecture with a large surface area. When used as a supercapacitor electrode material, Ni₃Si₂O₅(OH)₄/RGO composite hollow microspheres delivered a maximum specific capacitance of 178.9 F g⁻¹ at the current density of 1 A g⁻¹, which was better than that of currently developed contrastive bare Ni₃Si₂O₅(OH)₄ hollow microspheres and bare RGO material, exhibiting enhanced supercapacitive property. Of note, the Ni₃Si₂O₅(OH)₄/RGO microspheres had salient rate capability and long-term cycling stability, which maintained 97.6% of the initial capacitance after continuous charge/discharge for up to 5000 cycles, displaying a remarkably supercapacitive advantage over lots of other reported nickel-based materials. These results testify that Ni₃Si₂O₅(OH)₄/RGO composite hollow microspheres are a promising candidate for high-performance energy storage devices and systems. Moreover, we also anticipate that the present self-template synthetic strategy would be adopted to develop more and more other metal silicate-based materials with distinct morphologies and structures for important applications in various fields.

Additional file

Additional file 1: The experimental details for synthesis of SiO₂ microspheres and SiO₂/GO composite microspheres. Figure S1 (a, b) FESEM images of pristine SiO₂ microspheres at low and high magnifications, respectively. (c, d) FESEM images of SiO₂/GO composite microspheres at low and high magnifications, respectively. Figure S2: FESEM images of Ni₃Si₂O₅(OH)₄/RGO hybrid material synthesized in the absence of PVP. Figure S3 (a) GCD curves of bare Ni₃Si₂O₅(OH)₄ hollow microspheres measured at a set of varied current densities. (b) Specific capacitance of bare Ni₃Si₂O₅(OH)₄ hollow microsphere electrode deduced from the GCD curves depicted in (a) as a function of current density. (DOCX 5399 kb)

Abbreviations
BE: Binding energy; BET: Brunauer–Emmett–Teller; CV: Cyclic voltammetry; EDS: Energy-dispersive spectroscopy; EIS: Electrochemical impedance spectroscopy; FESEM: Field emission scanning electron microscopy; GCD: Galvanostatic charge/discharge; GO: Graphene oxide; HRTEM: High-resolution transmission electron microscopy; NMP: N-Methyl-2-pyrrolidone; PDDA: Poly(diallyldimethylammonium) chloride; PVD: Polyvinylidene fluoride; PVP: Polyvinylpyrrolidone; RGO: Reduced graphene oxide; STEM: Scanning TEM; TEM: Transmission electron microscopy; XPS: X-ray photoelectron spectra; XRD: X-ray diffraction

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Authors’ Contributions
WX conceived this research and revised the manuscript. LT designed the experimental strategy. YZ, WZ, and HY carried out most of the experiments. TF, YP, and HL analyzed the data and drafted this paper. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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References
1. Wang Y, Song Y, Xia Y (2016) Electrochemical capacitors: mechanism, materials, systems, characterization and applications. Chem Soc Rev 45:5925–5950
2. Yi H, Wang H, Jing Y, Peng T, Wang Y, Guo J, He Q, Guo Z, Wang X (2015) Advanced asymmetric supercapacitors based on CNF@Ni(OH)₂ core–shell composites and 3D graphene networks. J Mater Chem A 3:19545–19555
3. Liu Y, Shi Z, Gao Y, An W, Gao Z, Liu J (2016) Biomass-swelling assisted synthesis of hierarchical porous carbon fiber for supercapacitor electrodes. ACS Appl Mater Interfaces, 8:28283–28290
4. Xiao W, Zhou W, Feng T, Zhang Y, Liu H, Tian L (2016) Simple synthesis of molybdenum disulfide/reduced graphene oxide composite hollow microspheres as supercapacitor electrode material. Materials 9:783
5. Zang X, Dai Z, Yang J, Zhang Y, Huang W, Dong X (2016) Template-assisted synthesis of nickel sulfide nanowires: tuning the compositions for supercapacitors with improved electrochemical stability. ACS Appl Mater Interfaces 8:24645–24651
6. Zhu SJ, Jia JQ, Wang T, Zhao D, Yang J, Dong F, Guo Z, Shang ZG, Zhang YX (2015) Rational design of octahedron and nanowire CeO₂@MoO₃ core–shell heterostructures with outstanding rate capability for asymmetric supercapacitors. Chem Commun 51:4840–4843
7. Liu Y, Wang W, Huang H, Gu L, Wang Y, Peng X (2014) The highly enhanced performance of lamellar WS₂ nanosheet electrodes upon intercalation of single-walled carbon nanotubes for supercapacitors and lithium ions batteries. Chem Commun 50:4848–4848
8. Yu Z, Tetard L, Zhai L, Thomas J (2015) Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. Energy Environ Sci 8:702–730
9. Rong Q, Long L-L, Zhang X, Huang Y-X, Yu H-Q (2015) Layered cobalt nickel silicate hollow spheres as a highly-stable supercapacitor material. Appl Energy 153:63–69
10. Qiu C, Jiang J, Ai L (2016) When layered nickel-coalite silicate hydroxide nanosheets meet carbon nanotubes: a synergetic coaxial nanocable structure for enhanced electrocatalytic water oxidation. ACS Appl Mater Interfaces 8:945–951
11. Zhang S, Gao H, Li J, Huang Y, Alsaeed A, Hayat T, Xu X, Wang X (2017) Rice husks as a sustainable silica source for hierarchical flower-like metal silicate architectures assembled into ultrathin nanosheets for adsorption and catalysis. J Hazard Mater 321:92–102
12. Kuzmič SM, Bell VA, Nair S, Hillhouse HW, Jacobinis RM, Braambart CH, Toby BH, Tsapatsis M (2001) A titanosilicate molecular sieve with adjustable structure for enhanced electrocatalytic water oxidation. Adv Funct Mater 21:1902–1909

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14. Gui C-X, Wang Q-Q, Hao S-M, Qu J, Huang P-P, Cao C-Y, Song W-G, Yu Z-Z (2014) Sandwichlike magnesium silicate/reduced graphene oxide nanocomposite for enhanced PbO2 and methylene blue adsorption. ACS Appl Mater Interfaces 6:14653–14659
15. Tang C, Sheng J, Xu C, Kajrhbashi SMB, Wang X, Hu P, Wei X, Wei Q, Zhou L, Mal L (2015) Facile synthesis of reduced graphene oxide wrapped nickel silicate hierarchical hollow spheres for long-life lithium-ion batteries. J Mater Chem A 3:19427–19432
16. Gui C-X, Hao S-M, Liu Y, Qu J, Yang C, Yu Y, Wang Q-Q, Yu Z-Z (2015) Carbon nanotube@layered nickel silicate coaxial nanocables as excellent anode materials for lithium and sodium storage. J Mater Chem A 3:16551–16559
17. Wang Q-Q, Qu J, Liu Y, Gui C-X, Hao S-M, Yu Y, Yu Z-Z (2015) Growth of nickel silicate nanosheets on reduced graphene oxide as layered nanocomposites for highly reversible lithium storage. Nanoscale 7: 16805–16811
18. Yu P, Li Y, Zhao X, Wu L, Zhang Q (2014) Graphene-wrapped polyaniline nanowire arrays on nitrogen-doped carbon fabric as novel flexible hybrid electrode materials for high-performance supercapacitor. Langmuir 30:5306–5313
19. Numan A, Duraisamy N, Omar FS, Mahipal YK, Ramesh K, Ramesh S (2016) Enhanced electrochemical performance of cobalt oxide nanostructure intercalated reduced graphene oxide for supercapacitor application. RSC Adv 6:34894–34902
20. Lee T, Min SH, Gu M, Jung YK, Lee WJ, Lee JU, Seong DG, Kim BS (2015) Layer-by-layer assembly for graphene-based multilayer nanocomposites: synthesis and applications. Chem Mater 27:3785–3796
21. Xiao W, Zhang Y, Liu B (2015) Raspberrylike SiO2/reduced graphene oxide@AgNP composite microspheres with high aqueous dispersity and excellent catalytic activity. ACS Appl Mater Interfaces 7:6041–6046
22. Xiao W, Zhang Y, Tian L, Liu H, Liu B, Pu Y (2016) Facile synthesis of reduced graphene oxide/titania composite hollow microspheres based on sonication-assisted interfacial self-assembly of tiny graphene oxide sheets and the photocatalytic property. J Alloys Compd 665:21–30
23. Zhang Z, Xiao F, Guo Y, Wang S, Liu Y (2013) One-pot self-assembled three-dimensional TiO2-graphene hydrogel with improved adsorption capacities and photocatalytic and electrochemical activities. ACS Appl Mater Interfaces 5:2227–2233
24. Cao J, Liu Q, Han D, Yang S, Yang J, Wang T, Niu H (2014) Highly enhanced photocatalytic properties of ZnS nanowires–graphene nanocomposites. RSC Adv 4:30798–30806
25. Niu H, Zhou D, Yang X, Li X, Wang Q, Qu F (2015) Towards three-dimensional hierarchical ZnO nanofiber@Ni(OH)2 nanoflake core–shell heterostructures for high-performance asymmetric supercapacitors. J Mater Chem A 3:18413–18421
26. Zhu Y, Ji X, Wu Z, Liu Y (2015) NiCo2S4 hollow microspheres decorated by acetylene black for high-performance asymmetric supercapacitors. Electrochim Acta 186:562–571
27. Zhao J, Zhang Y, Wang T, Li P, Wei C, Pang H (2015) Reed leaves as a sustainable silica source for 3D mesoporous nickel (cobalt) sicate architectures assembled into ultrathin nanoflakes for high-performance supercapacitors. Adv Mater Interfaces 2:1400377
28. Thangappan R, Kalaiselvam S, Elayaperumal A, Jayavel R, Arivanandhan M, Karthikeyan R, Hayakawa Y (2016) Graphene decorated with MoS2 nanosheets: a synergetic energy storage composite electrode for supercapacitor applications. Dalton Trans 45:26337–2646
29. Wang L, Ma Y, Yang M, Qi Y (2015) Hierarchical hollow MoS2 nanospheres with enhanced electrochemical properties used as an electrode in supercapacitor. Electrochim Acta 186:391–396
30. Duraiyami N, Numan A, Ramesh K, Choi K-H, Ramesh S, Ramesh S (2015) Investigation on structural and electrochemical properties of binder free nanostructured nickel oxide thin film. Mater Lett 161:694–697
31. Ji H, Liu C, Wang T, Chen J, Mao Z, Zhao J, Hou W, Yang G (2015) Porous hybrid composites of few-layer MoS2 nanosheets embedded in a carbon matrix with an excellent supercapacitor electrode performance. Small 11:6480–6490
32. Shi D, Zhang L, Yin X, Huang TJ, Gong H (2016) A one step processed advanced interwoven architecture of Ni(OH)2 and Cu nanosheets with ultrahigh supercapacitor performance. J Mater Chem A 4:12144–12151
33. Zhang Y, Sun W, Rui X, Li B, Tan HT, Guo G, Madhavi S, Zong Y, Yan Q (2015) One-pot synthesis of tunable crystalline Ni3S4@amorphous MoS2 core/shell nanospheres for high-performance supercapacitors. Small 11:3694–3702
34. Numan A, Duraisamy N, Choi K-H, Ramesh S, Ramesh S (2015) Influence of particle size on performance of a nickel oxide nanoparticle-based supercapacitor. RSC Adv 5:14010–14019
35. Ding S, Zhu T, Chen JS, Wang Z, Yuan C, Lou XW (2011) Controlled synthesis of hierarchical NiO nanosheet hollow spheres with enhanced supercapacitive performance. J Mater Chem 21:6602–6606
36. Hu G, Li C, Gong H (2010) Capacitance decay of nanoporous nickel hydroxide. J Power Sources 195:6977–6981
37. Yuan YF, Xia XH, Wu JB, Yang JL, Chen YB, Guo SY (2011) Nickel foam-supported porous Ni(OH)2/NiO composite film as advanced pseudocapacitor material. Electrochim Acta 56:2627–2632
38. Li J, Yang M, Wei J, Zhou Z (2012) Preparation and electrochemical performances of doughnut-like Ni(OH)2–Co(OH)2 composites as pseudocapacitor materials. Nanoscale 4:4498–4503
39. Zhao J, He J, Sun M, Qu M, Pang H (2015) Nickel hydroxide–nickel nanohybrids indirectly from coordination microfibers of high-performance supercapacitor electrodes. Inorg Chem Front 2:129–135
40. Yuan C, Li J, Hou L, Zhang X, Chen D, Shen G (2012) Morphology evolution of urchin-like NiCo2O4 nanostuctures and their applications as pseudocapacitors and photoelectrochemical cells. J Mater Chem 22:21647–21653
41. Wu HB, Pang H, Lou XW (2013) Facile synthesis of mesoporous Ni0.3Co2.7O4 hierarchical structures for high-performance supercapacitors. Energy Environ Sci 6:3619–3626
42. Wang L, Wang X, Xiao X, Xu F, Sun Y, Li Z (2013) Reduced graphene oxide/nickel cobaltite nanoflake composites for high speciation capacitance supercapacitors. Electrochim Acta 111:937–945
43. Shen L, Yu L, Wu HB, Yu X-Y, Zhang X, Lou XW (2015) Formation of nickel cobalt sulfide ball-in-ball hollow spheres with enhanced electrochemical pseudocapacitive properties. Nat Commun 6:6694

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