

Electronic Supplementary Information

Low-cost and large-scale synthesis of alkaline earth metal germanate nanowires as a new class of lithium ion battery anode materials

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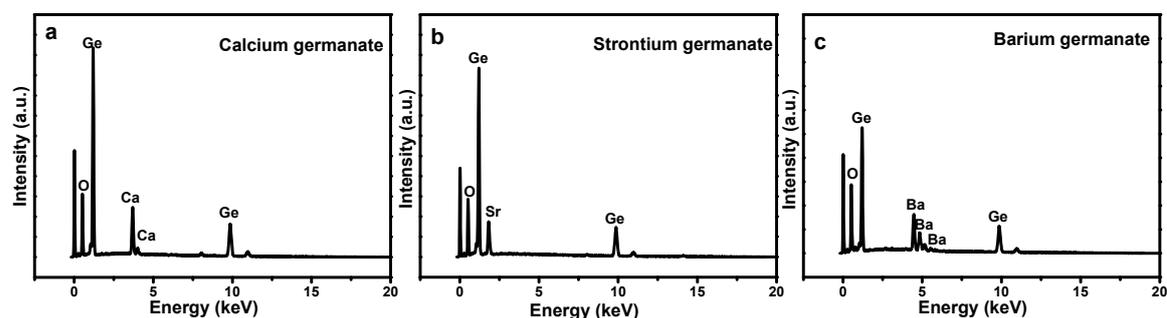


Fig. S1 EDX spectra of (a) calcium germanate nanowires, (b) strontium germanate nanowires and (c) barium germanate nanowires.

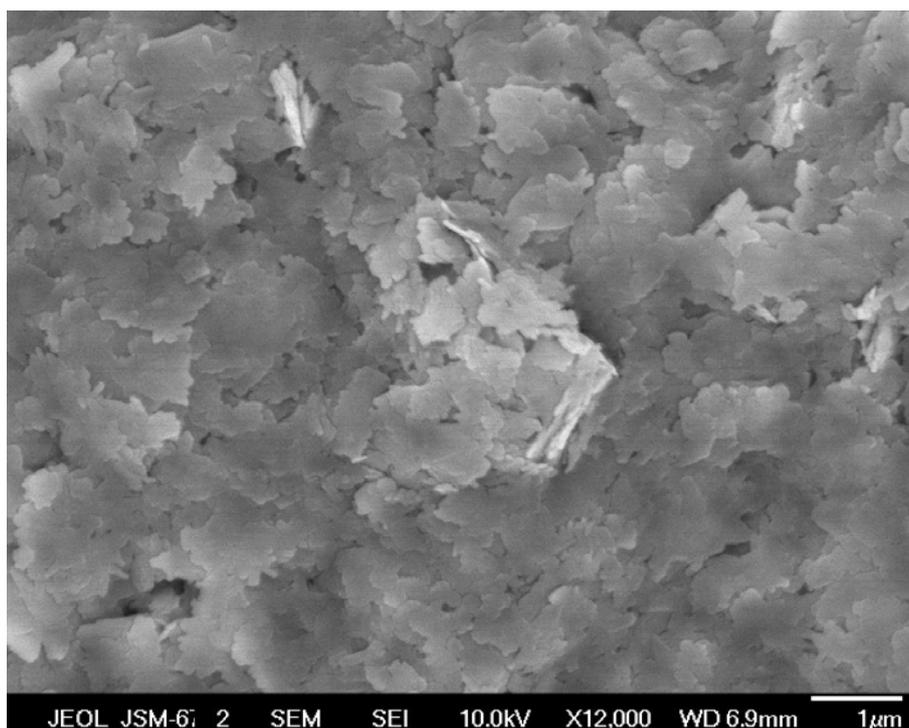


Fig. S2 SEM image of magnesium germanate microsheets synthesized by the similar hydrothermal method.

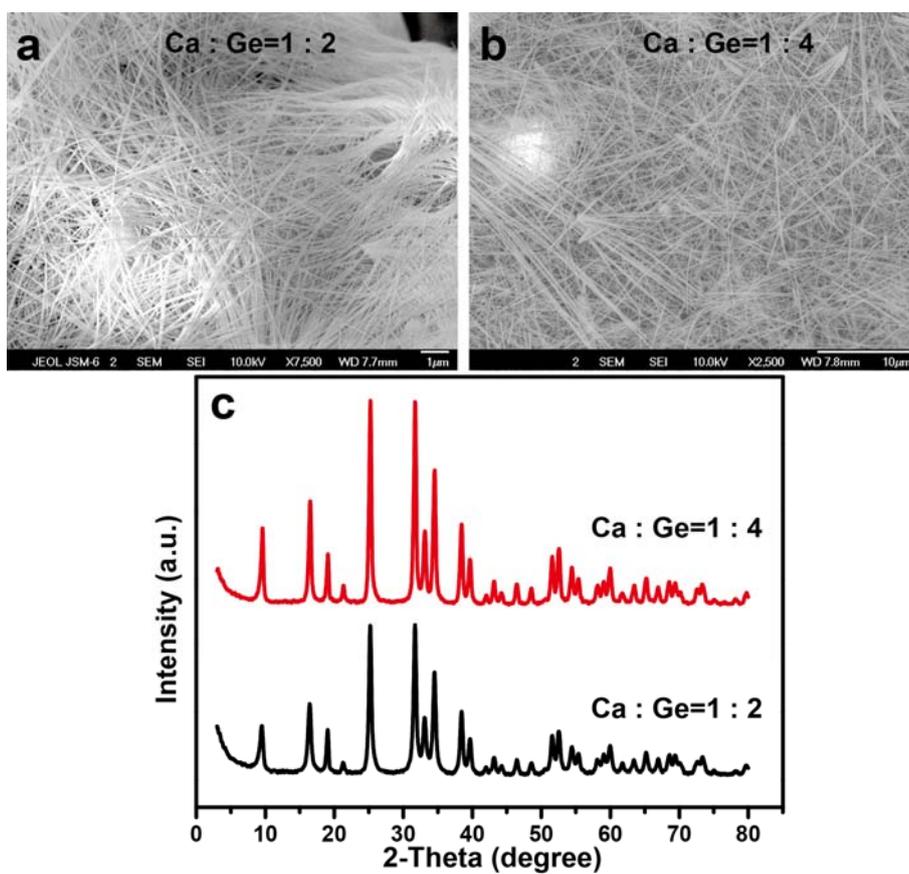


Fig. S3 (a) SEM image of calcium germanate nanowires using the raw materials with a molar ratio of Ca : Ge = 1 : 2, (b) SEM image of calcium germanate nanowires using the raw materials with a molar ratio of Ca : Ge = 1 : 4, and (c) XRD patterns of (a) and (b)

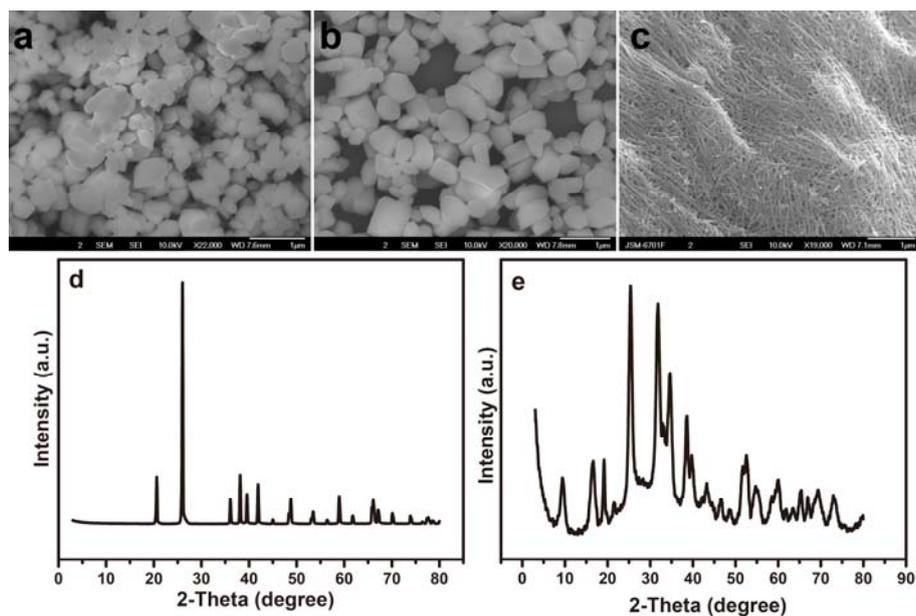


Fig. S4 SEM images of products using different kinds of calcium salts as precursors, (a) using CaCl_2 , (b) using $\text{Ca}(\text{NO}_3)_2$, (c) using $\text{Ca}(\text{OH})_2$, (d) XRD pattern of hydrothermal products using CaCl_2 and GeO_2 , and (e) XRD pattern of hydrothermal products using $\text{Ca}(\text{OH})_2$ and GeO_2

In order to investigate the possible growth mechanism of strontium germanate nanowires, the hydrothermal synthesis was also carried out under varying conditions. The reaction time ranged from 5 min to 24 h. Other kinds of strontium precursor salts such as SrCl_2 , $\text{Sr}(\text{NO}_3)_2$ and $\text{Sr}(\text{OH})_2$ were used instead of $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$.

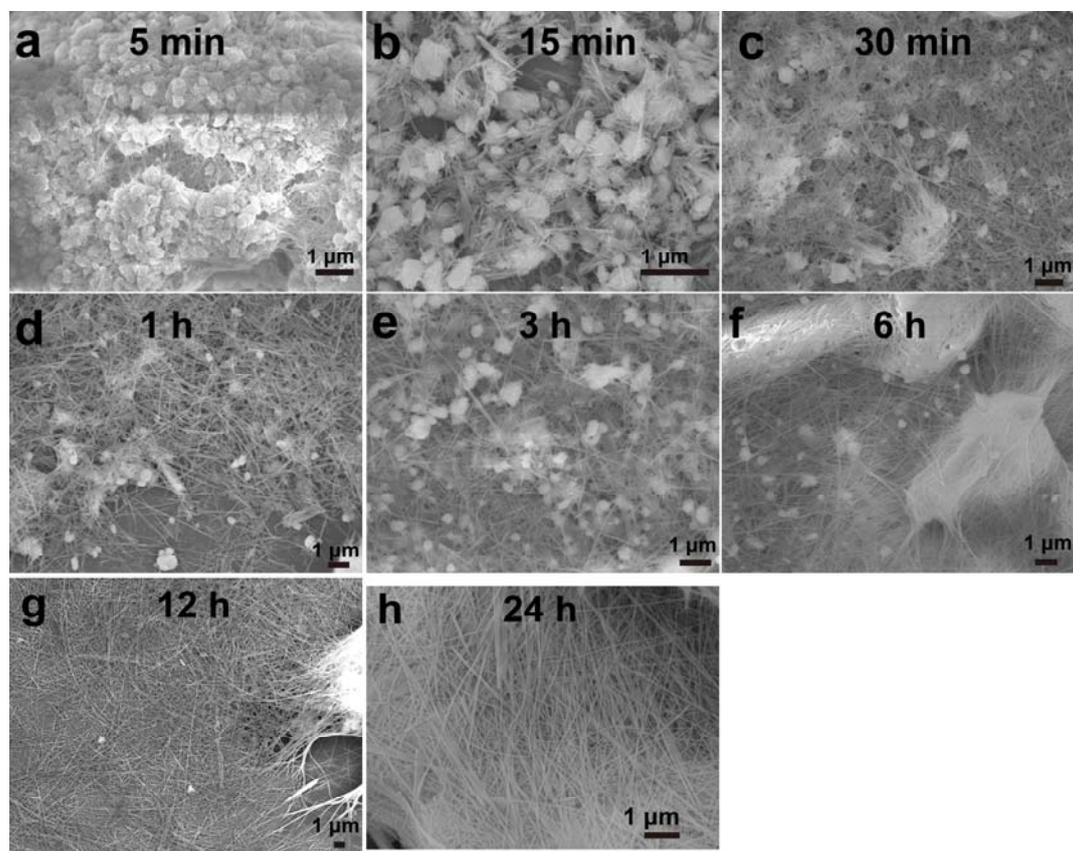


Fig. S5 (a)-(h) SEM images of strontium germanate products synthesized for different time

ranging from 5 min to 24 h.

Fig. S5 shows the evolution of strontium germanate nanowires with increasing hydrothermal time. At the beginning, strontium acetate dissolved readily in the water while most of GeO_2 powders was not dissolved. At 180 °C, strontium acetate underwent slow hydrolysis to produce OH^- . GeO_2 reacts with OH^- ions to form the soluble anion of HGeO_3^- . When the concentrations of the Sr^{2+} and HGeO_3^- reach the supersaturation limit, small SrGe_4O_9 nuclei is generated and undergoes Ostwald ripening process to grow into nanowires. During the hydrothermal process, the pH value of the mixture solution decreased from 8.09 to 4.32.

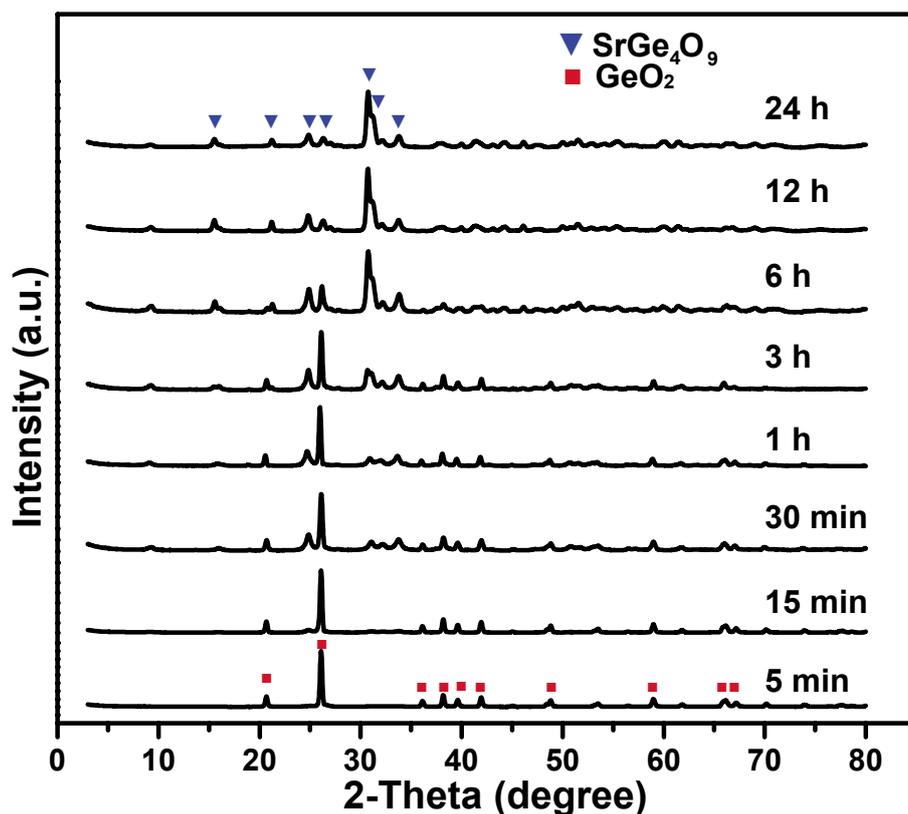


Fig. S6 Time-dependent XRD patterns of strontium germanate products

Time-dependent XRD pattern (Fig. S6) analyses confirm the evolution of the composition of products from GeO_2 to final SrGe_4O_9 . A longer reaction time improves the crystalline degree of the hexagonal phase of SrGe_4O_9 .

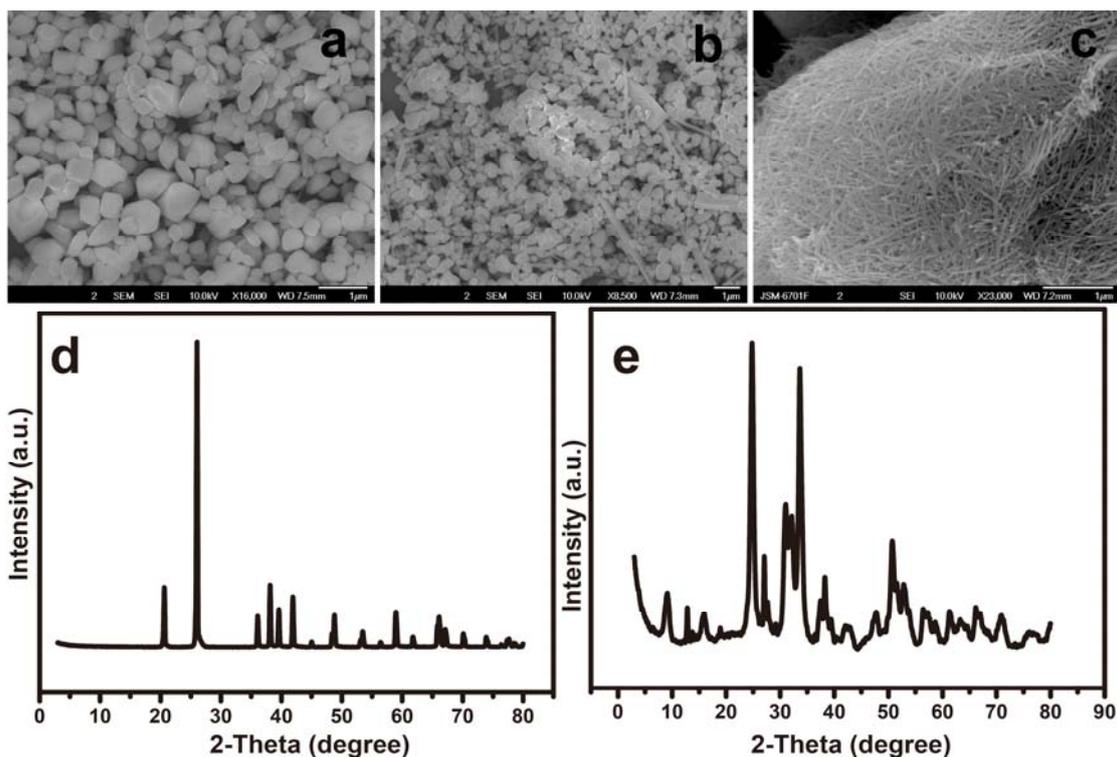
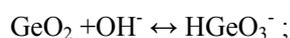


Fig. S7 SEM images of products using different kinds of strontium salts as precursors, (a) using $\text{Sr}(\text{NO}_3)_2$, (b) using SrCl_2 , (c) using $\text{Sr}(\text{OH})_2$, (d) XRD pattern of hydrothermal products using $\text{Sr}(\text{NO}_3)_2$ and GeO_2 , and (e) XRD pattern of hydrothermal products using $\text{Sr}(\text{OH})_2$ and GeO_2 . The kind of strontium salts also influenced the morphology and composition of products. Fig. S7 showed the SEM images and XRD patterns of products using other kinds of strontium salts instead of strontium acetate as precursors. When SrCl_2 or $\text{Sr}(\text{NO}_3)_2$ is used, large GeO_2 particles remained, indicating no reaction. While $\text{Sr}(\text{OH})_2$ was used, similar SrGe_4O_9 nanowires are also obtained. Both SrCl_2 and $\text{Sr}(\text{NO}_3)_2$ were difficult to hydrolyze to produce enough OH^- ions, and GeO_2 cannot be transformed into HGeO_3^- . $\text{Sr}(\text{OH})_2$ is able to provide enough OH^- and thus generates the same SrGe_4O_9 nanowires. During this hydrothermal process, the pH value of the mixture solution decreased from 12.88 to 6.72.

Based on above results, the formation mechanism of SrGe_4O_9 nanowires can be delineated as following:



The whole reaction can be summarized in the following equation:



In order to investigate the possible growth mechanism of barium germanate nanowires, the hydrothermal synthesis was also carried out under varying conditions. The reaction time ranged from 5 min to 24 h. The Ba/Ge feeding ratio was changed. Other kinds of barium precursor salts such as BaCl_2 , $\text{Ba}(\text{NO}_3)_2$ and $\text{Ba}(\text{OH})_2$ were used instead of $\text{Ba}(\text{CH}_3\text{COO})_2$.

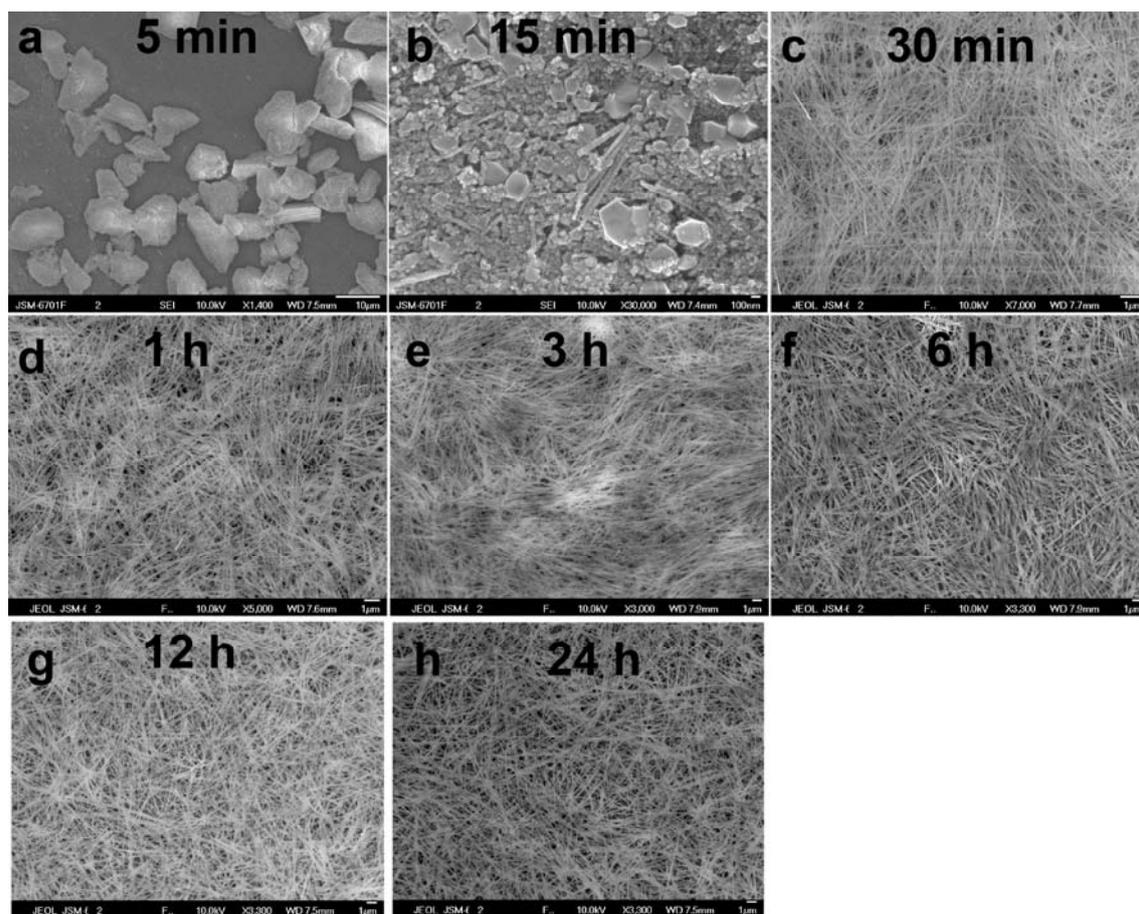


Fig. S8 (a)-(h) SEM images of barium germanate products synthesized for different time ranging from 5 min to 24 h

Fig. S8 shows the evolution of barium germanate nanowires with increasing hydrothermal time. At the beginning, barium acetate dissolved readily in the water while most of GeO_2 powders was not dissolved. At $180\text{ }^\circ\text{C}$, barium acetate underwent slow hydrolysis to produce OH^- . GeO_2 reacts with OH^- ions to form the soluble anion of HGeO_3^- . When the concentrations of the Ba^{2+} and HGeO_3^- reach the supersaturation limit, small BaGe_4O_9 nuclei is generated and undergoes Ostwald ripening process to grow into nanowires. During the hydrothermal process, the pH value of the mixture solution decreased from 8.40 to 5.80.

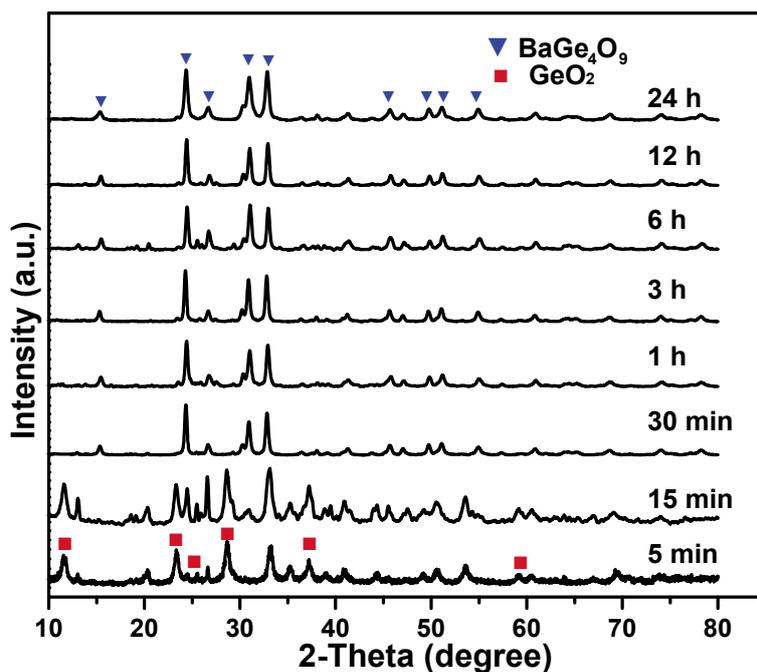


Fig. S9 Time-dependent XRD patterns of barium germanate products

Time-dependent XRD pattern (Fig. S9) analyses confirm the evolution of the composition of products from GeO₂ to final BaGe₄O₉. A longer reaction time improves the crystalline degree of the hexagonal phase of BaGe₄O₉.

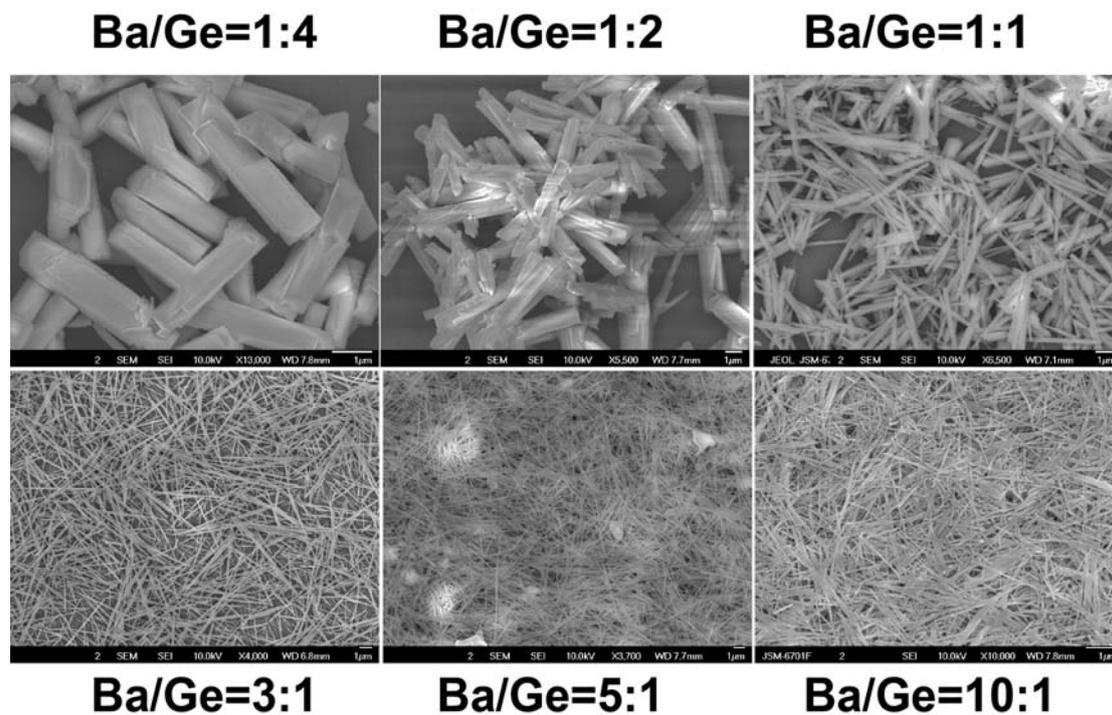


Fig. S10 SEM images of products using raw materials with different molar ratio of Ba : Ge ranging from 1/4 to 10/1.

As shown in Fig. S10, the Ba/Ge molar ratio plays a critical role in the morphology of as-obtained products. With the increasing Ba/Ge atomic ratio, the length-to-diameter ratio of barium germanate rises. The morphology evolves from micro-size rod to long nanowires.

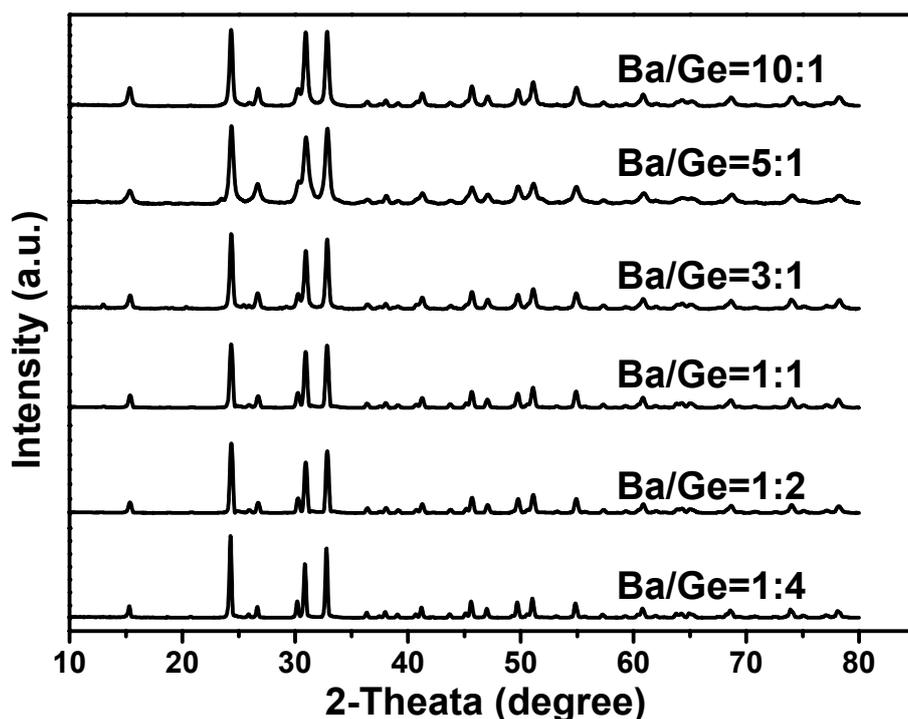


Fig. S11 XRD patterns of products using raw materials with different molar ratio of Ba : Ge. All the as-obtained products from different initial Ba/Ge molar ratios are the hexagonal phase of BaGe₄O₉. The barium component in excess still remains in the solution in the form of soluble Ba²⁺ ions after the hydrothermal reaction.

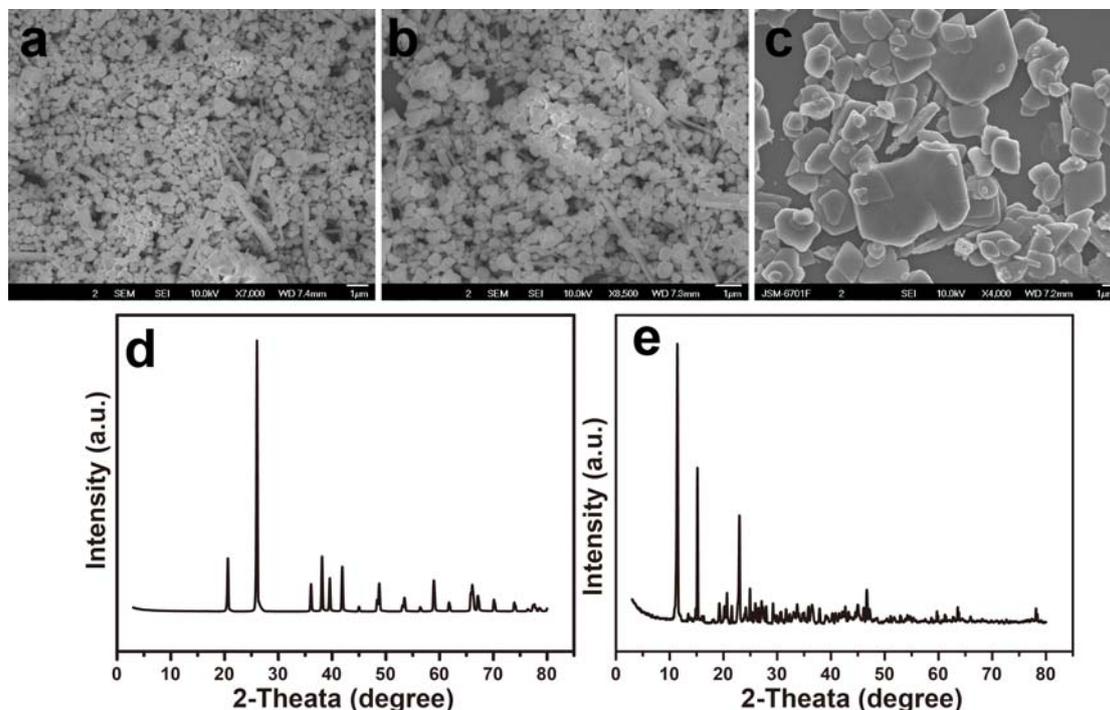
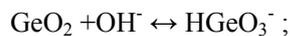


Fig. S12 SEM images of products using different kinds of barium salts as precursors, (a) using BaCl₂, (b) using Ba(NO₃)₂, (c) using Ba(OH)₂, (d) XRD pattern of hydrothermal products using BaCl₂ and GeO₂, and (e) XRD pattern of hydrothermal products using Ba(OH)₂ and GeO₂. BaGe₄O₉ nanowires cannot be produced when Ba(OH)₂ is used instead of barium acetate, as

illustrated in Fig. S12. Because it has much higher solubility and basicity than $\text{Ca}(\text{OH})_2$ as well as $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ can provide large amounts of OH^- in the system. As a result, GeO_2 may be dissolved quickly to generate large numbers of HGeO_3^- . High concentrations of Ba^{2+} and HGeO_3^- promote the reaction rate to produce large barium germanate crystals instantly.

Based on above results, the growth mechanism of BaGe_4O_9 nanowires can be described as follows:



The whole reaction can be summarized in the following equation:

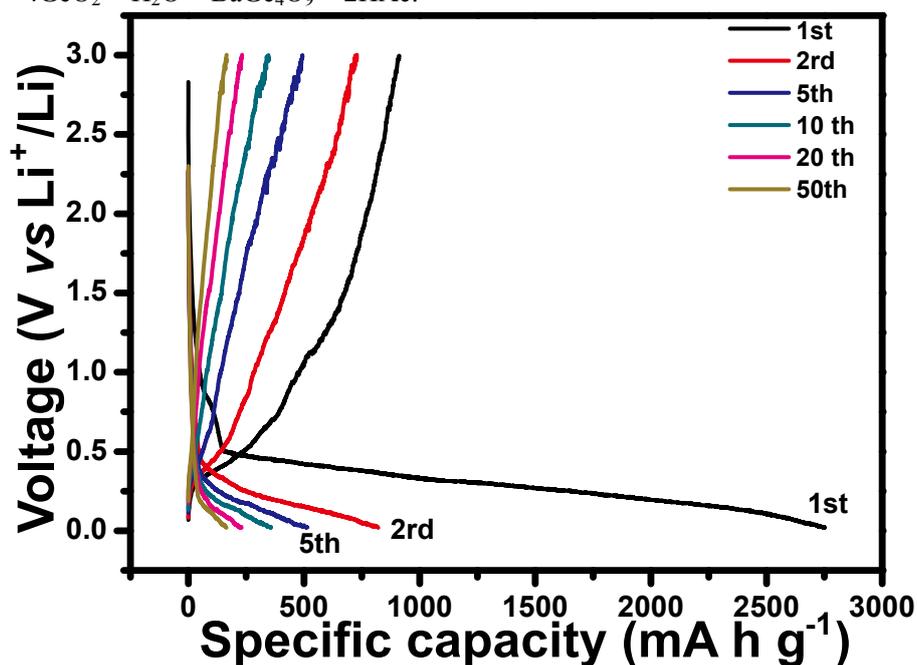


Fig. S13 The discharge/charge voltage profiles of commercial GeO_2 under a current density of 100 mA g^{-1} .

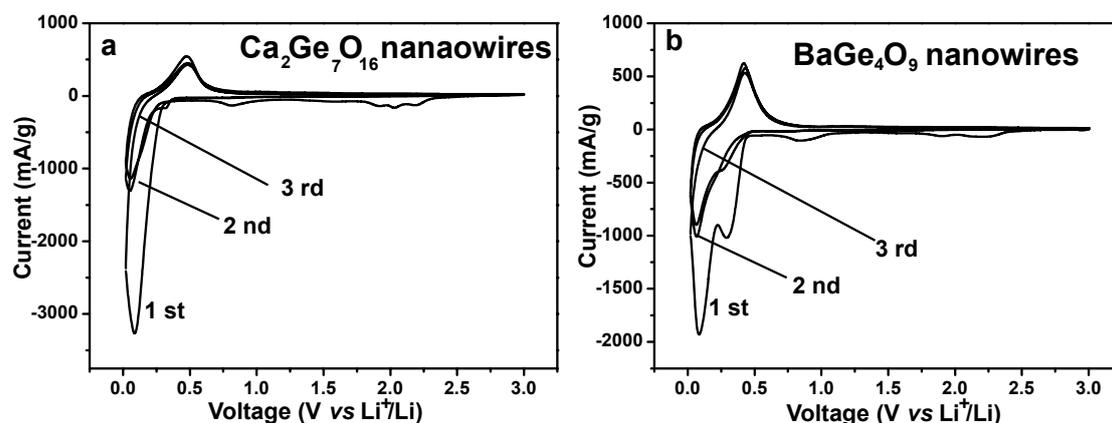


Fig. S14 The initial three cyclic voltammogram (CV) profiles of $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ and BaGe_4O_9 nanowires between 0.02 and 3 V under a current density of 100 mA g^{-1} .

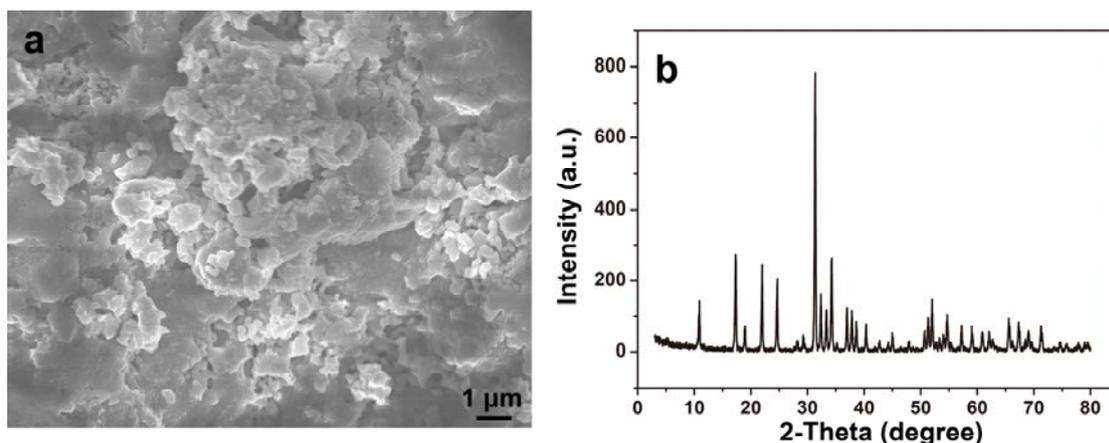


Fig. S15 (a) SEM image of $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ bulks prepared by a solid state reaction, (b) XRD pattern of $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ bulks.

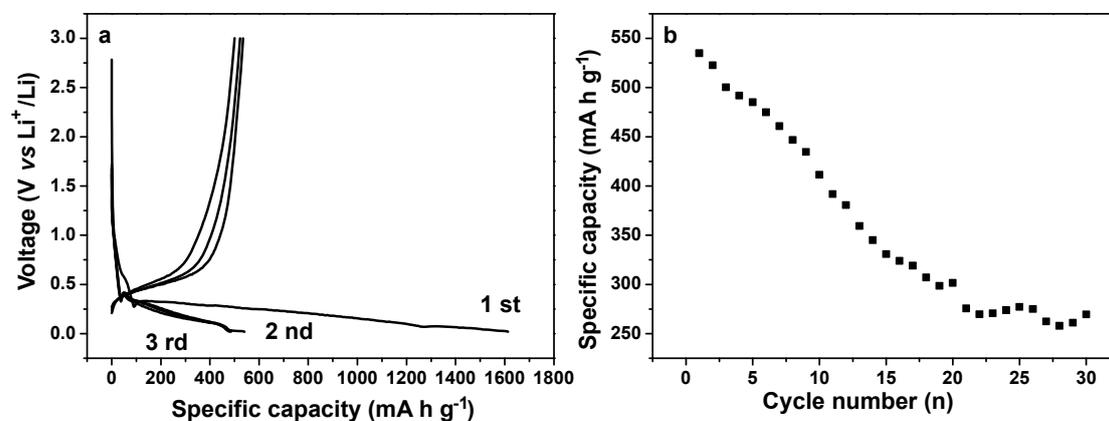


Fig. S16 (a) The initial three discharge/charge voltage profiles of $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ bulks prepared by a solid state reaction under a current density of 100 mA g^{-1} , (b) Cycle performance of $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ bulks under a current density of 100 mA g^{-1} in the voltage range of 0.02–3.0 V.

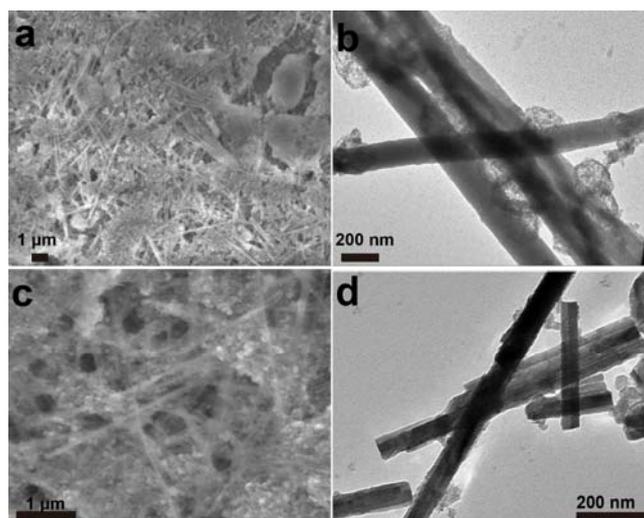


Fig. S17 (a) SEM and (b) TEM images of calcium germanate ($\text{Ca}_2\text{Ge}_7\text{O}_{16}$) electrode materials after 100 cycles; (c) SEM (d) TEM images of barium germanate (BaGe_4O_9) electrode materials after 100 cycles.