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)
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 SrCl₂, Sr(NO₃)₂ and Sr(OH)₂ were used instead of Sr(CH₃COO)₂•1/2H₂O.

**Fig. S4** SEM images of products using different kinds of calcium salts as precursors, (a) using CaCl₂, (b) using Ca(NO₃)₂, (c) using Ca(OH)₂, (d) XRD pattern of hydrothermal products using CaCl₂ and GeO₂, and (e) XRD pattern of hydrothermal products using Ca(OH)₂ and GeO₂

**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 GeO₂ powders was not dissolved. At 180 °C, strontium acetate underwent slow hydrolysis to produce OH⁻. GeO₂ reacts with OH⁻ ions to form the soluble anion of HGO₃⁻. When the concentrations of the Sr²⁺ and HGO₃⁻ reach the supersaturation limit, small SrGe₄O₉ 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.

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\text{Fig. S6 Time-dependent XRD patterns of strontium germanate products}
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Time-dependent XRD pattern (Fig. S6) analyses confirm the evolution of the composition of products from GeO₂ to final SrGe₄O₉. A longer reaction time improves the crystalline degree of the hexagonal phase of SrGe₄O₉.
Fig. S7 SEM images of products using different kinds of strontium salts as precursors, (a) using Sr(NO₃)₂, (b) using SrCl₂, (c) using Sr(OH)₂, (d) XRD pattern of hydrothermal products using Sr(NO₃)₂ and GeO₂, and (e) XRD pattern of hydrothermal products using Sr(OH)₂ and GeO₂. 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 SrCl₂ or Sr(NO₃)₂ is used, large GeO₂ particles remained, indicating no reaction. While Sr(OH)₂ was used, similar SrGe₄O₉ nanowires are also obtained. Both SrCl₂ and Sr(NO₃)₂ were difficult to hydrolyze to produce enough OH⁻ ions, and GeO₂ cannot be transformed into HGO⁻. Sr(OH)₂ is able to provide enough OH⁻ and thus generates the same SrGe₄O₉ 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 SrGe₄O₉ nanowires can be delineated as following:

\[
\text{Sr(Ac)}_2 + 2 \text{H}_2\text{O} \leftrightarrow \text{Sr(OH)}_2 + 2 \text{HAc}; \\
\text{GeO}_2 + \text{OH}^- \leftrightarrow \text{HGeO}_3^-; \\
\text{Sr}^{2+} + 4\text{HGeO}_3^- \rightarrow \text{SrGe}_4\text{O}_9 + \text{H}_2\text{O} + 2\text{OH}^-.
\]

The whole reaction can be summarized in the following equation:

\[
\text{Sr(Ac)}_2 + 4\text{GeO}_2 + \text{H}_2\text{O} = \text{SrGe}_4\text{O}_9 + 2\text{HAc}.
\]

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 BaCl₂, Ba(NO₃)₂ and Ba(OH)₂ were used instead of Ba(CH₃COO)₂.
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 °C, barium acetate underwent slow hydrolysis to produce OH$^-$. GeO$_2$ reacts with OH$^-$ ions to form the soluble anion of HGO$_3^-$ . When the concentrations of the Ba$^{2+}$ and HGO$_3^-$ reach the supersaturation limit, small BaGe$_4$O$_9$ 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 GeO$_2$ to final BaGe$_4$O$_9$. A longer reaction time improves the crystalline degree of the hexagonal phase of BaGe$_4$O$_9$.

**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 Ca(OH)$_2$ as well as Sr(OH)$_2$, Ba(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 HGO$_3^-$. High concentrations of Ba$^{2+}$ and HGO$_3^-$ promote the reaction rate to produce large barium germanate crystals instantly. Based on above results, the growth mechanism of BaGe$_4$O$_9$ nanowires can be described as follows:

$$\text{Ba(Ac)}_2 + 2 \text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2 + 2 \text{HAc};$$

$$\text{GeO}_2 + \text{OH}^- \leftrightarrow \text{HGeO}_3^-;$$

$$\text{Ba}^{2+} + 4\text{HGeO}_3^- \rightarrow \text{BaGe}_4\text{O}_9 + \text{H}_2\text{O} + 2\text{OH}^-.$$

The whole reaction can be summarized in the following equation:

$$\text{Ba(Ac)}_2 + 4\text{GeO}_2 + \text{H}_2\text{O} = \text{BaGe}_4\text{O}_9 + 2\text{HAc}.$$

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 Ca$_2$Ge$_7$O$_{16}$ and BaGe$_4$O$_9$ nanowires between 0.02 and 3 V under a current density of 100 mA g$^{-1}$. 
Fig. S15 (a) SEM image of Ca$_2$Ge$_7$O$_{16}$ bulks prepared by a solid state reaction, (b) XRD pattern of Ca$_2$Ge$_7$O$_{16}$ bulks.

Fig. S16 (a) The initial three discharge/charge voltage profiles of Ca$_2$Ge$_7$O$_{16}$ bulks prepared by a solid state reaction under a current density of 100 mA g$^{-1}$, (b) Cycle performance of Ca$_2$Ge$_7$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 (Ca$_2$Ge$_7$O$_{16}$) electrode materials after 100 cycles; (c) SEM (d) TEM images of barium germanate (BaGe$_4$O$_9$) electrode materials after 100 cycles.