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ARTICLE TYPE

Preparation of porous nanostructured germanium from GeO₂ via “reduction-alloying-dealloying” approach

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We provide here controllable and affordable preparation of porous nanostructured germanium with interesting photo-responsive properties from GeO₂ powder through an electrochemical reduction-alloying-dealloying process in molten salt (reduction and alloying) and post zero-energy-consumption water etching (dealloying).

Over the past few decades, preparation and utilization of porous nanostructured germanium have raised enormous attention due to its unique physicochemical properties and promising applications in electronic, optical, electrochemical and biological devices. Several approaches were proposed for preparing nanoporous germanium such as electrochemically etching of Ge wafer, chemical vapor deposition, chemical reduction of porous GeO₂, liquid-crystals-templated chemical method and electrochemical deposition in room temperature ionic liquids. The widespread application of porous nanostructured germanium remains a challenge hitherto, to some extents due to the unsatisfactory economic competence (low space-time yield, intense investment in apparatus and labor, expensive feedstock and tedious procedures) and inferior environmental viability (toxic precursors and by-products) of the forenamed methods. In this sense, cost-affordable, environmentally sound and upscalable production of porous nanostructured germanium is of significant urgency and importance, aiming to fully exploiting its intriguing functionalities.

Recently, a generic approach for preparation of nanoporous materials by using initial electrochemical lithiation of matrix and following electrochemical delithiation of Li-rich matrix was proposed and confirmed. The reversibility in volume change with the maintenance in integrity of matrix during electrochemical lithiation-delithiation processes forms the scientific basis of generation of high-quality nanoporous materials. The extension of the aforementioned strategy to preparation of nanoporous metals/semimetals in group IV (e.g. Si, Ge and Sn) is however highly challenging due to inevitable vast change (higher than 300%) in volume of the above matrix upon electrochemical polarizations with cations (e.g. Li⁺) being electrochemically introduced/removed into/from the matrix (Si, Ge and Sn) via alloying/dealloying reactions. This results in destruction in architecture of matrix (so-called “pulverization”) and therefore inferior cycle performance of such materials used in Li and Na ion batteries.

Such a pulverization effect possesses the intrinsic barrier for

preparation of porous Ge via the above electrochemical lithiation-delithiation strategy, which, however, might be tackled by using etching strategy instead of electrochemical delithiation as the post step for removal of the previously alloyed components. The effectiveness of the etching strategy was well demonstrated in the successful preparation of porous germanium by chemically etching germanium alloys (Ge₄K₉) through ions exchanging and thermal decomposition reactions. The involved ions-exchanging and thermal-decomposition etching process of Ge₄K₉ for preparation of porous Ge can be further improved into a fascinating “zero-energy-consumption” etching method by using Ca-Ge as the precursor. In such a scenario, alloyed Ca can be chemically removed by reaction with water, creating voids in the Ge and generating porous Ge. This “zero-energy-consumption” etching strategy resembles to the method used in producing Raney nickel by selectively dissolving Al from NiAl intermetallic in alkaline solutions through the effective and generic chemical dealloying routes.

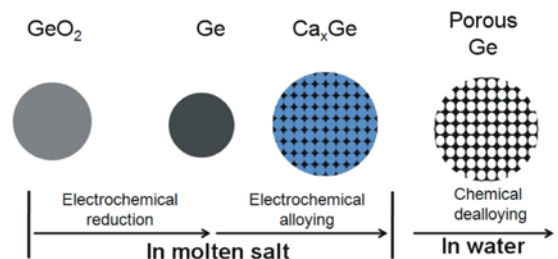


Fig. 1 Schematic illustration of porous Ge formation process.

Herein, for the first time, we propose a cost-affordable and environmentally sound strategy on producing porous nanostructured Ge from solid GeO₂ via a “reduction-alloying-dealloying” method. As schematically represented in Fig. 1, the first two steps occurring in molten CaCl₂-NaCl eutectics at 600 °C involve in electrochemical reduction of solid GeO₂ into nanostructured Ge (step I: “reduction”) and in-situ electrochemically intercalation (alloying) of cations from the melts into Ca-Ge alloys (step II: “alloying”) at more negative potentials. The above “reduction” and “alloying” occur in molten salts with the presence of cathodic polarizations, which occur in serials and/or in parallel. The electrolytic Ca-Ge is then subjected a “zero-energy-consumption” etching in water at room temperatures (step III: “dealloying”), with the maintenance of matrix and generation of nanoporous Ge after removal of Ca

species.

The merits of the proposed strategy for production of nanoporous Ge can be justified as follows. Firstly, as an analogue of the widely used silicon, Ge has higher dielectric constant, lower resistivity, higher electron/hole mobility and intriguing energy storage capabilities, promising the applications of Ge in electronic, optoelectronic and energy applications. However, its practical applications have been drastically hindered by the costly and high-risk extraction process based on chemical reduction of GeO_2 with hydrogen at 600 – 700 centigrade¹⁹. Secondly, GeO_2 powder is the most straightforward and favorite feedstock for Ge extraction due to its low cost and low toxicity. Thirdly, the relatively high temperature in molten salt electrolyzer enhances the kinetics of electrochemical alloying process (note the inevitably sluggish kinetics of solid diffusion process during alloying), facilitating the rapid preparation of massive Ca-Ge and therefore promising a high space-time yield. In addition, exothermic nature of alloying process not only further enhances reaction kinetics, and also helps to maintain high temperature of melts. Fourthly, “electrons” are employed as the green (considering the increasing installed capacity from renewable energy in grids) and no-trace (introducing no impurity) reductant here. More importantly, the activity of electrons can be easily tuned by just tailoring electrode potentials, promising controllable preparation of Ca-Ge (note that Ca and Ge can form binary solutions in any stoichiometries) in different stoichiometries and therefore generation of Ge in different porosity. Last but not the least, molten salt electrolysis of solid oxides (e.g. silica or GeO_2) was well addressed as an upscalable and controllable preparation of nanostructured (nanoparticles and nanowires) semiconductor (Si and Ge) powders.²⁰⁻²⁹ In this regard, the proposed method is upscalable and controllable. Molten salt electrolysis of solid oxides was well addressed to be an effective and environmentally friendly method for preparation of metals and alloys in recent years^{22, 26-29}. However, the preparation of nanoporous materials from molten salt electrolysis of solid oxides is absent in literature, which is for the first time reported here with the combination of molten salt electrolysis of solid oxides and facile etching process in water. In this regard, the method is of novelty and far-reaching impacts on preparation of porous materials.

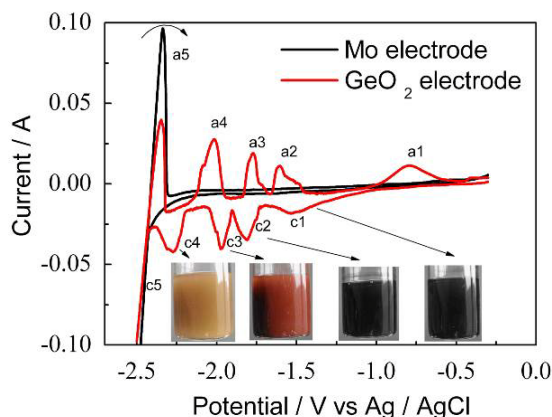
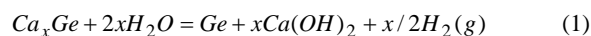


Fig. 2 CVs of the Mo and GeO_2 modified Mo cavity electrodes in CaCl_2 - NaCl melt at 600 °C at a scan rate of 20 mV s^{-1} . The insets are the digital pictures of the products (obtained at -1.35, -1.7, -1.9 and -2.1 V, respectively) dispersed in water.

Experimental details are provided in Electronic Supplementary Information (ESI). Electrochemical behaviors of solid GeO_2 were studied by cyclic voltammetry (CV) using a Mo cavity electrode filled with GeO_2 powder (Figure S1). As can be seen in Fig. 2, the first reduction peak starting at -0.9 V vs. Ag/AgCl (c1) is associated with the reduction of GeO_2 to Ge.²¹ Subsequently, three additional redox peak pairs consecutively appears at the potentials more negative than generation of Ge, followed by a redox peak pair assigned to electrodeposition/re-dissolution of liquid metals from melts near negative limits. The onsets of the three consecutive cathodic processes after Ge generation are -1.6, -1.8 and -2.0 V, corresponding to the three separate alloying processes. Such a scenario agrees well with the phase diagrams of the Ge-Ca and Ge-Na that indicates more than three alloys of Ge-Ca and Ge-Na³⁰⁻³¹. Upon the inverse anodic scan, three consecutive oxidation peaks correspond to three dealloying processes. The similar shape and integral charges between cathodic and the corresponding anodic peaks reveal the alloying/dealloying reactions are highly reversible. The above results suggest that the concentrations of Ca or Na in Ge can be controlled by adjusting the electrolysis potentials, promising the engineering of the microstructure and porosity of final products.

In order to specify the stoichiometries of electrolytic samples, potentiostatic electrolysis of GeO_2 filled Mo cavity electrodes was performed. Four electrodes were potentiostatically electrolyzed at -1.35, -1.7, -1.9 and -2.1V for 15 min, respectively. Since the products are stable in dimethyl sulfoxide (DMSO) which is able to dissolve residual salts, the obtained products washed with DMSO instead of aqueous solutions were analyzed by EDX (Figure S2) and XRD (Figure S3). Clearly, the product obtained at -1.35 V is pure Ge. While Ca is observed in the products obtained at the potentials more negative than -1.6 V. Na remains absent in all samples, indicating that Ca is the only alloying element in the electrochemical reduction process at the investigated potential range. CaO was found in the products obtained at -1.9 and -2.1V after treating by DMSO, further indicating the Ca was alloyed into Ge and the alloyed Ca can be oxidized in air (Figure S3)

Interestingly, the suspensions in water of the above electrolytic products show different colors (inset of Fig. 1). It should be noted that all of the electrolytic products are gray black without water rinse, indicating the water rinse procedure leads to the color change. The water suspensions of the electrolytic product obtained at -1.35 and -1.7 V remain gray black. It is observed that the product obtained at -1.35 V does not react with water. And a slight reaction between the water and product obtained at -1.7 V can be observed. While those obtained at -1.9 and 2.1 V changes to red and yellow, respectively. Moreover, the products obtained at -1.9 and -2.1V reacted with water rigorously along violent gas evolution, which can be expressed by equation (1):



According to the corresponding XRD patterns (Fig. S4), the products obtained at -1.35 and -1.7 V are crystalline Ge. While the red and yellow products are less crystalline, with the occurrence of two weak and broaden diffraction peaks. The thermodynamically spontaneous nature of Reaction 1 forms the scientific grounds of effective separation of Ge and Ca species,

which also facilitates the formation of porous Ge after rinse in water. In addition, the gas evolution is also beneficial to occurrence of pores. This process is quite similar to the process of producing porous Ni by etching Al from NiAl¹⁸.

After the products were washed with water, all products are pure Ge (Fig. S5), which further confirms the alloyed Ca can be removed by water etching. The SEM images of the products show the products obtained at -1.35 and -1.7 V were Ge nanowires (Figs. 3a and 3b). While the products obtained at potential of -1.9 and -2.1 V tend to agglomerate and look like coral and floccules, respectively (Figs. 3c and 3d). A trace amount of Ca and Cl was due to trace residual salt (Figs. S5c and S5d). To further investigate effects of electrolysis potentials on the morphology of products, products were characterized by TEM and HRTEM (Fig. 3). The diameter of the Ge nanowires obtained at -1.35 V is around 100 nm (Fig. 3a), and product obtained at -1.7 V are interconnected and no single nanowire can be observed (Fig. 3b), suggesting the inclusion of Ca affect the growth of Ge. At -1.9 V, the product turns to be prismatic particles (Fig. 3c) and, at -2.1 V, the product looks like cotton (Fig. 3d). As can be seen from the HRTEM shown in Figs. 3e and 3f, the products obtained at -1.9 and -2.1 V are in the form of porous structure. The decrease in crystalline after water rinse is also verified by HRTEM (Figure S6). Therefore, the porous Ge is successfully prepared by electrolysis of GeO₂ particles (Fig. S7) at -1.9V and -2.1 V and then via a water etching pathway. The BET surface area of the corresponded products presented in Fig. 3 indicates that the porous Ge has much larger surface area (~55 m² g⁻¹) than Ge nanowires (17 m² g⁻¹). Moreover, the BET surface area of product obtained at -1.7 V (30 m² g⁻¹) is larger than the product obtained at -1.35 V is also associated with the dealloying of Ca from Ge. CO₂ emission in graphite anode is acknowledged. The development of inert anodes to achieve zero carbon footprints deserves further research. However, the electrochemical method is of great advantage by adjusting the current density and/or potential to tailor the electrolytic products.

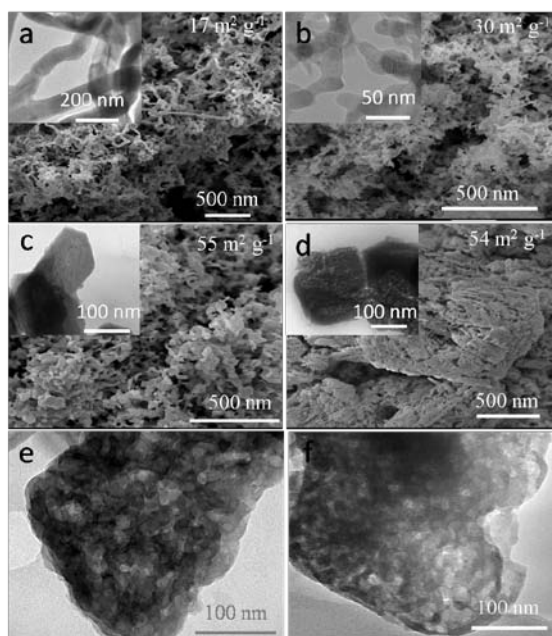


Fig. 3 SEM images of the Ge obtained at -1.35 V (a), -1.7 V (b), -1.9 V (c) and -2.1 V (d). The insets are their corresponding TEM images and the HRTEM image of Ge obtained at -1.9 V (e) and -2.1 V (f).

The obtained samples were further investigated by Raman (Figs. S8a and S8b) and FT-IR (Figs. S8c and S8d) spectroscopy. All the spectra confirm the formation of Ge. Some minor difference exists in the spectra between porous Ge (obtained at -1.90 and -2.1 V) and crystalline Ge (obtained at -1.35 and -1.7 V), indicating the optical properties can be tuned by changing the preparation parameters. Such difference in optical properties can also be reflected by the different color of the samples (Fig. 1), promising the application of the obtained sample in photoluminescence and photocatalysts. It is acknowledged that the research on optical properties is preliminary. The structure-optical properties relationship need further investigations in futures.

Conclusions

In summary, we provide the first proof-of-concept of controllable and affordable preparation of porous nanostructured germanium with interesting photo-responsive properties from GeO₂ powder through an electrochemical reduction-cum-alloying process in molten salt and post zero-energy-consumption water etching. Firstly, solid GeO₂ powder is electrochemically deoxygenated to Ge in CaCl₂-NaCl eutectics at 600 °C, at the same time, Ca²⁺ is electrochemically alloyed / intercalated into the pre-reduced Ge at a more negative potential. The obtained Ca_xGe is then dealloyed in aqueous solution generating porous germanium without the destruction of the original matrix integrity. The confirmed tunable nature of electrochemical alloying/dealloying between Ca and Ge species not only facilitates the preparation of nanostructured Ge with different pore characteristics, but also provides unprecedented opportunities to tune the optical properties of nanoporous Ge. In perspective, the high reversibility of the observed electrochemical alloying/dealloying of Ca into Ge promises the development of Ca ion rechargeable batteries in future.

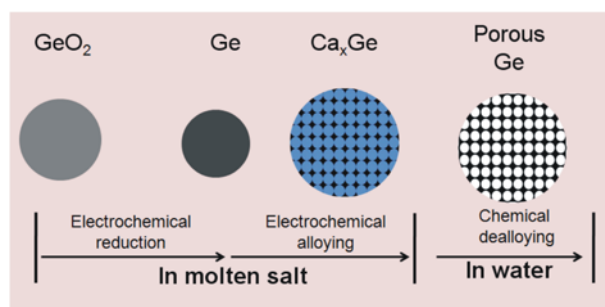
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- † Electronic Supplementary Information (ESI) available: [experimental details and more characterizations]. See DOI: 10.1039/b000000x/
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TOC:



Electrochemical reduction-cum-alloying in molten salt and post water-etching dealloying is controllable, affordable and environmentally friendly preparation of nanoporous germanium

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