Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Preparation of porous nanostructured germanium from GeO_2 via "reduction-alloying-dealloying" approach

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Experimental

1. Cyclic voltammetry

Cyclic voltammetry was performed by using a three-electrode system controlled by an electrochemical workstation (CHI 1140, Shanghai Chenhua). A home-made GeO_2 powder modified molybdenum cavity electrode , [1] pyres-glass sealed Ag/AgCl (LiCl-KCl melt with 2 wt% AgCl), and a graphite rod were used as working electrode, reference electrode and counter electrode, respectively. About 500 g anhydrous $CaCl_2$-NaCl (Ca:Na = 1 : 1, molar fraction) mixed salts contained in an alumina crucible (inner diameter: 8cm, height: 15cm) sealed in an stainless steel (SS) reactor was used as electrolyte. The SS reactor was heated by a tube furnace. Firstly, the salts were dried at 250 ^oC in the air for more than 48 hours, and then the SS reactor was flushed by continuous argon flow. Afterward, temperature was raised to 600 ^oC to melt the salt. Pre-electrolysis was performed between a nickel plate cathode and a graphite anode under constant cell voltage of 2.6V for 8 hours to further remove the moisture and impurities of the melt.

2. Potentiostatic electrolysis and chemical etching

Electrochemical potentiostatic electrolysis of solid GeO_2 was performed in $CaCl_2$-NaCl melt at 600 ^oC. All of the experimental setups and pre-treating procedures were the same as mentioned above. The porous GeO_2 pellet cathode was fabricated by slipcasting and die-pressing of GeO_2 power under 6 MPa followed by sintering at 700 ^oC for 2h to ensure a certain mechanical strength. A GeO_2 pellet (diameter: 10 mm, thickness: 2 mm, ~0.3 g GeO_2 powder) attached to a molybdenum wire was used as working electrode (cathode). The reference and counter electrode are the same depicted in the CV test. Potentiostatic electrolysis was performed by applying four different potentials corresponding to the four reduction peaks recorded from CVs. After the electrolysis terminated, the working electrode was lift out of the melt and cooled down in headspace of the SS reactor protected by argon.

The chemical etching process was conducted by rinsing the electrolytic products in water. After the products were washed with de-ionized water for several times, they were centrifugated and dried under vacuum at 80 ^oC for 12 hours. In order to test the alloying elements (Ca or Na), the GeO_2 powder filled Mo cavity electrode was used as working electrode and potentiostatic-electrolyzed at the same potentials used for the pellet cathode. Differently from the pellet GeO_2 electrode, the products in cavity electrodes were rinsed with dimethyl sulfoxide (DMSO) instead of water to remove the salt within the products.

3. Materials characterization

The precursory GeO_2 powder and the obtained products were characterized by X-ray diffraction spectroscopy (XRD, Shimadzu X-ray 6000 with Cu Kα1 radiation at λ =1.5405Å), scanning electron microscopy (SEM, FEI Sirion field emission gun), transmission electron microscopy (TEM, JEM2010-HT), High-resolution TEM (JEM 2010-FEF), energy-dispersive X-ray (EDAX GENESIS 7000), Brunauer–Emmett–

Teller (BET) surface area analyzer (Gemini V 5331, Micromeritic), Raman and Fourier-transform infrared (FT-IR) spectroscopy analysis.

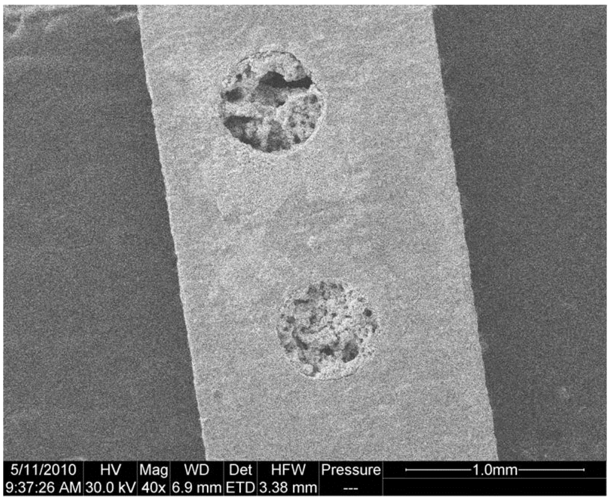

Figure S1. Digital image of Mo cavity electrode filled with electrolytic germanium.

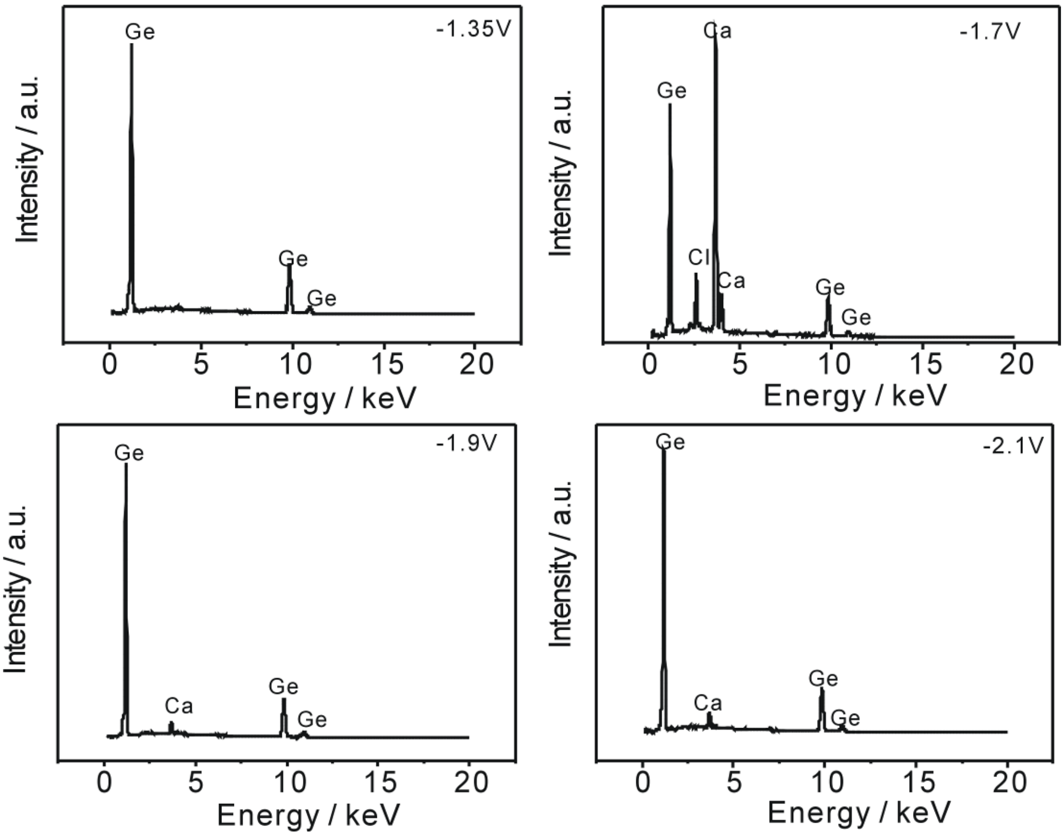

Figure S2 EDX spectra of the Ge produced at the indicated potentials using Mo cavity electrode, and the salt within the products were washed with DMSO.

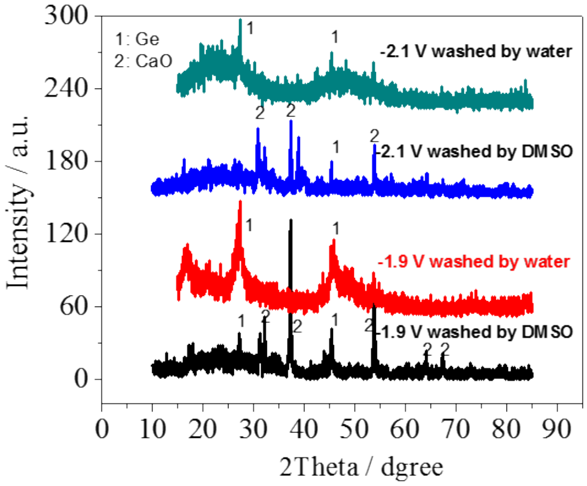

Figure S3. XRD patterns of the products obtained at -1.9V and -2.1V and the products were treated in water and DMSO, respectively.

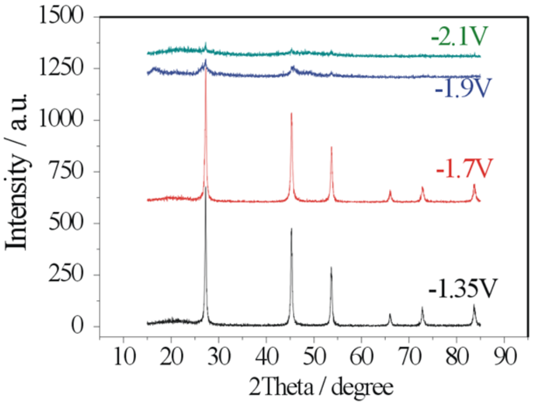

Figure S4. XRD patterns of the products obtained by potentiosticly electrolyzing GeO_2 pellets at the indicated potentials.

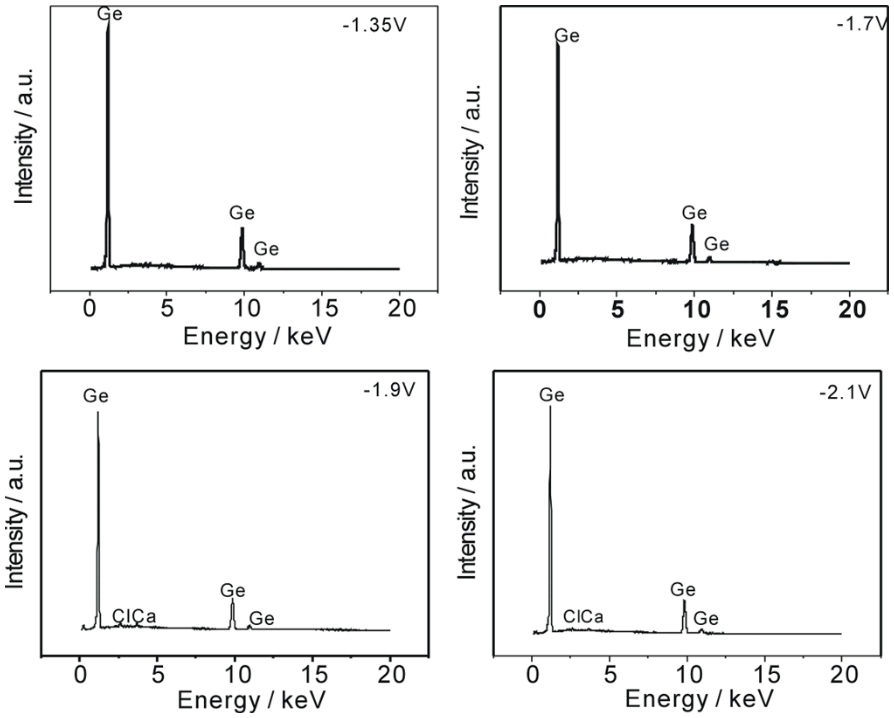

Figure S5. EDX spectra of the Ge produced at the indicated potentials, and the salt within the products were washed with water.

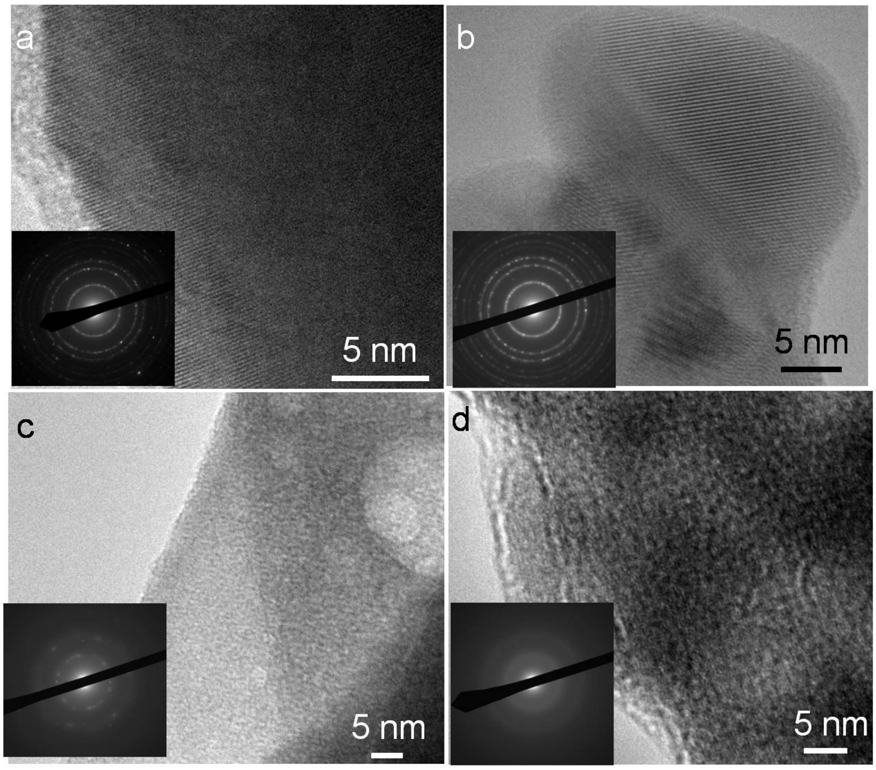

Figure S6. HR-TEM images of the electrolytic Ge obtained at -1.35 V (a), -1.7 V (b), -1.9V (c) and -2.1V (d) for 12h, the insets display the corresponding SEAD pattern.

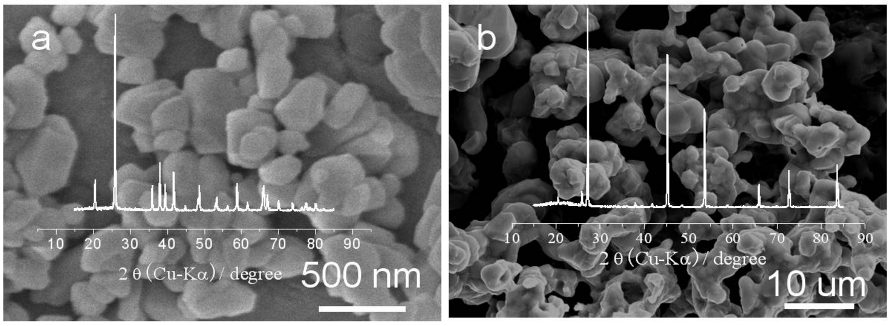

Figure S7. SEM images of the GeO_2 precursor (a) and commercial Ge (b), the insets are their corresponding XRD patterns.

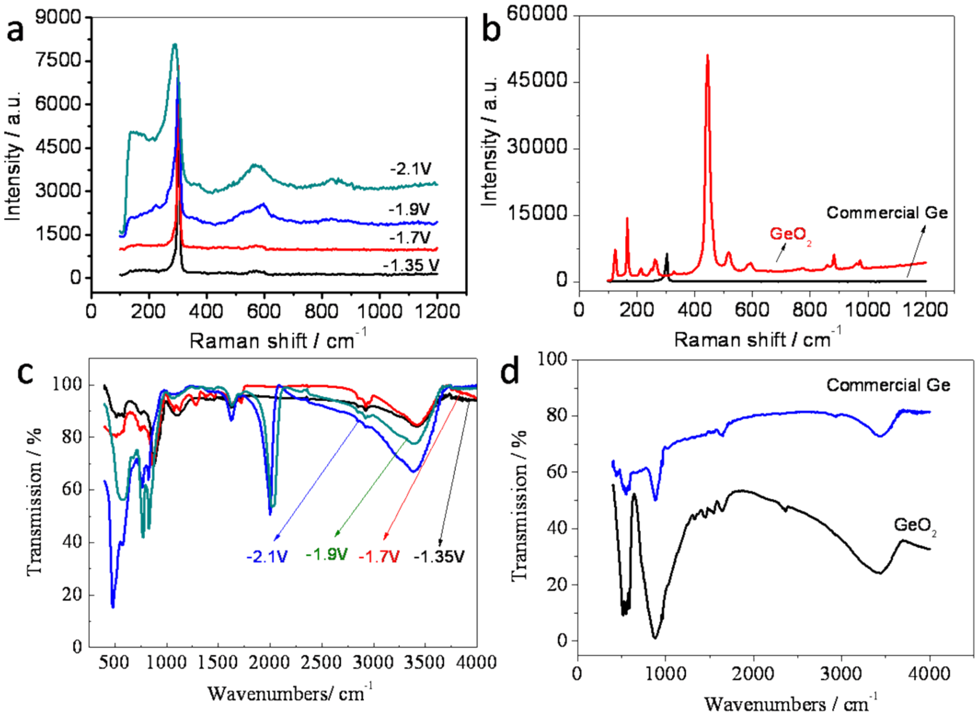

Figure S8. Raman spectra (a, b) and FT-IR spectra (c, d) of the electrolytic Ge and the commercial Ge and GeO_2 powder.

A typical Ge-Ge optical phono-vibration at 302 cm^{-1} can be observed from the Raman spectra of the electrolytic products (Figure S7a). The peaks of crystalline Ge (obtained at -1.35V and -1.7V) are sharp and symmetrical, and the porous Ge (obtained at -1.90 and -2.1V) have much stronger and broad peaks with a small shoulder corresponding to the small nano-structured pores. [2] A weak peak around 600 cm^{-1} may be due to some functional groups on the surface of Ge, such as Ge-O and Ge-H_x. As a comparison, the Raman spectra of commercial crystalline Ge with diameter around 10μm (Figure S6b) and GeO_2 was displayed in Figure S7b. Ge is a good candidate for the IR optical element because it has good transmission in the wavelength range of 500 cm^{-1} - 4000 cm^{-1} [3, 4] The crystalline Ge obtained at -1.35V and -1.7 V perfectly meet the requirement (Figure S7c). An absorption at 2000 cm^{-1} may arise from the Ge-H$_x$, [4, 5] and the peaks at 3400 cm^{-1} and below 1000 cm^{-1} are ascribed to the Ge-O, which is verified by the standard spectrum of GeO$_2$ (Figure 7d). It shows the electrolytic Ge nanowire has better transmission than the commercial Ge with diameter of ~10 μm. Because GeO$_2$ is soluble in water, the Ge-O bond in all of the products is due to the oxidation of surface of Ge in the air preventing the inner Ge being further oxidized. Note that the Ge-H$_x$ on the surface of the porous Ge is very stable which will passivate the surface of Ge in the chemical etching process. [5] Therefore, the in situ generated Ge-H$_x$ is essential for the chemical dealloying process preventing the porous Ge being oxidized.

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