Electronic Supplementary Information (ESI): Electrochemical Preparation of Silicon Nanowires from Nanometer Silica in Molten Calcium Chloride†

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Experiment Details

SiO_2 powder (99.98%, particle size:25-30nm) was manually pressed into a porous pellet (10 mm in diameter, 1mm in thickness, 0.081g in weight). The preformed pellets were dried at room temperature and in ambient atmosphere for 2 days and then sintered at 900°C in air for 2 hours. The sintered pellets were drilled and threaded onto a molybdenum wire (99.95%, 1.5mm diameter) to form Mo-SiO_2 contacting electrodes. All molten salt experiments were performed in a sealed stainless vessel that was continuously purged with argon gas (> 99.999%, O_2 < 2 ppm, H_2O < 1 ppm; 100ml min^{-1}) at 900°C. Pre-electrolysis for removing dissolved water and impurities from the molten salt was carried out at 1.5 V for 2 hours or longer, between the graphite crucible anode and a graphite rod cathode. Cyclic voltammetry and chronoamperometry (controlled potential electrolysis) were performed in the three- electrode manner in molten $CaCl_2$ with Mo-SiO_2 contacting electrode used as the working electrode. The graphite crucible was used as the container for the molten salt and also as a counter electrode. A platinum wire (99.95%, 1.5mm diameter) was used as a pseudo-reference electrode. A predetermined voltage (-1.2V) was applied for the electrochemical reduction of the SiO_2 pellet. After the electrolysis, the reduced pellet was raised from the molten salt and kept in the upper part of the reactor until the furnace temperature dropped to ambient temperature before removal for analysis. Any solidified salt that adhered to the surface of the reduced pellet was removed by washing in distilled water in an ultrasonic bath, a fulvous powder was collected. The obtained powder was dried under vacuum for analysis.

The synthesized powder was characterized by X-ray diffraction (XRD, X′Pert PRO MPD), field-emission scanning electron microscope (FESEM, Hitachi S4800), transmission electron microscopy and high-magnification transmission electron microscopy (HRTEM, FEI Tecnai F30), energy dispersive X-ray spectrum (EDS), and selected area electron diffraction (SAED). The room-temperature photoluminescence (PL) was recorded on a JY-HR800 Raman laser spectrometer with a 532nm emission line of Ai-ion laser

Additional Experimental Results

Cyclic Voltammetry Test

The cyclic voltammetry test result of the contacting electrode of the nano-SiO_2 powder in molten $CaCl_2$ at 900°C shows in figure S1. As generally observed from the Mo-SiO_2 contacting electrode, waves 2 and 3 were corresponding to the formation-deformation of Si-Ca alloy. Waves 1 and 4 were attributed to the reduction of SiO_2 and the oxidation of silicon, respectively. Clearly, the reduction of SiO_2 starts at the potentials at approximately -0.80V versus the platinum pseudo-reference electrode.

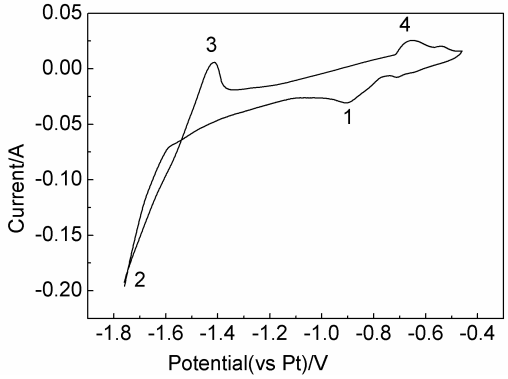

Fig. S1. Cyclic voltammogram of the contacting electrode of nano-SiO_2 powder in molten $CaCl_2$ at 900°C. The potential scan rate was 0.05V s^{-1}.

Influence of the potential on morphology of the electrolytic product

To clarify the influence of the potential on morphology of the electrolytic production, constant potential electrolysis was conducted in the range -0.8~ -1.5V. Figure S2a-S2d show the SEM images

of the cross-section of the specimen electrolyzed in molten $CaCl_2$ at 900°C for 30 minutes at -0.8V, -1.0V, -1.4V, -1.5V. The nanowires were observed only for the specimens obtained at -1.0 and -1.4V (Fig. S2b and S2c). At -1.5V, the Si particles were formed (Figure S2d). At -0.8V, the morphology didn't change in comparison with that for the pellet after immersing in molten $CaCl_2$ for 30 minutes and no reduction is observed.

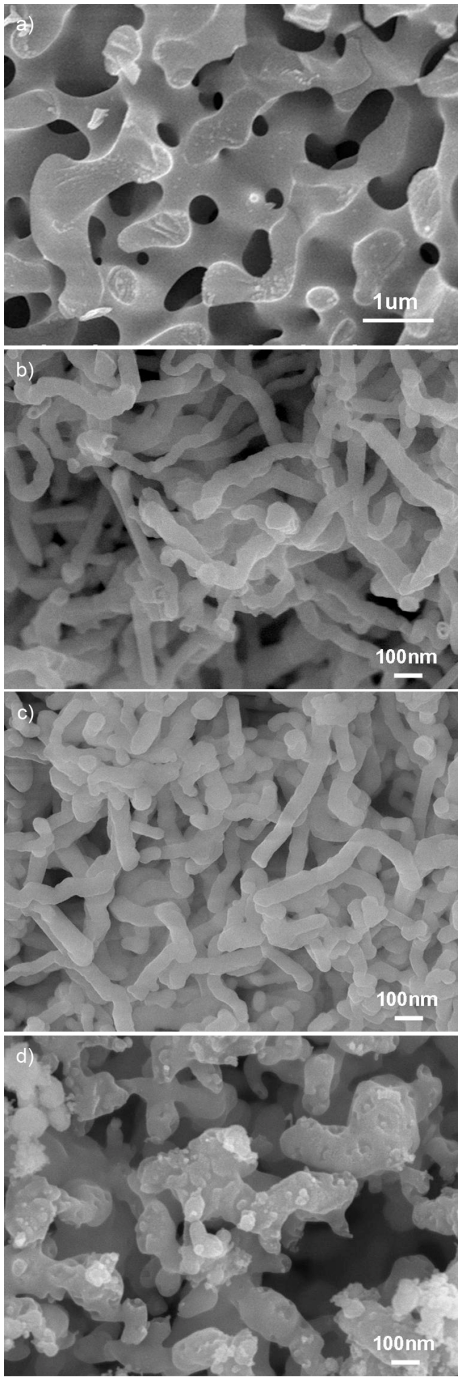

Fig. S2. SEM images of the cross-section of the specimen electrolyzed at different potentials in molten $CaCl_2$ at 900°C. (a) -0.8V. (b) -1.0V. (c) -1.4V. (d) -1.5V.

The appearance of the pellets after electrolysis for different time.

Fig. S3 shows the photographs of the washed pellets after electrolysis for different time. Apparently, the color near the area contacting with Mo wire changed to dark brown after electrolysis for 5min. Then, the color change proceeded even radically from the contacting point with the passage of time. This direct observation of the color change suggest that the electrolytic reduction started at the contacting point of SiO_2 pellets with Mo wire and the reaction might proceed through the propagation of the $Si/SiO_2/CaCl_2$ three phase interlines.

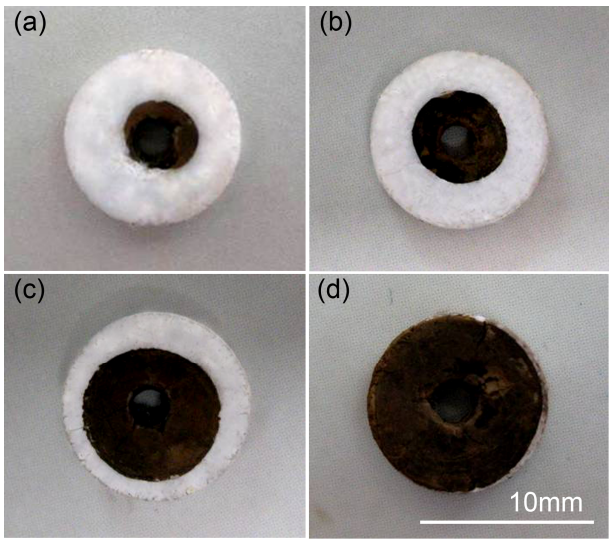

Fig. S3. Photographs of the contacting electrodes of nano-SiO_2 after electrolysis at -1.2V in molten $CaCl_2$ at 900□ for different time. (a) 5min. (b) 30min. (c) 60min. (d) 120min.