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Facile synthesis of freestanding Si nanowire arrays by one-step template-free electro-deoxidation of SiO_2 in a molten salt†

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This communication presents a novel kind of silicon nanomaterial: freestanding Si nanowire arrays (Si NWAs), which are synthesized facilely by one-step template-free electro-deoxidation of SiO_2 in molten $CaCl_2$. The self-assembling growth process of this material is also investigated preliminarily.

Owing to the integrated feature of silicon nanowires and the facility for device assembly, silicon nanowire arrays (Si NWAs), which consist of well-ordered silicon nanowires, have been studied recently in many emerging technologies, such as lithium-ion batteries,[1] solar cells,[2] sensors[3] and thermoelectric modules,[4] *etc.* Several methods have been developed to prepare Si NWAs, such as etching of silicon wafers,[2–4] template-assisted or catalyst-assisted growth,[1] lithography techniques, *etc.* To date the Si nanowire arrays prepared by these methods have all been supported on some dense substrates to maintain the morphology. The aligned Si NWAs are not retained when the substrate is removed. The reliance on the substrate of Si NWAs not only limits the variety of preparation, but also hampers the performance in applications. For example, both well-designed Si substrate films[5,6] and freestanding nanostructured Si[7,8] produce better anode performance than Si NWAs in Li-ion batteries because of the features of a lightweight substrate or freestanding structure. The dense substrate could also hinder the mass transfer in the fluid phase when the Si NWAs serve as antibacterial materials or sensors.[9,10] Generally, if freestanding Si NWAs could be prepared, devices assembled with some accommodative substrates or without any substrate would be viable, and a better performance would be expected in the applications aforementioned.

The electro-deoxidation process in a molten salt for silicon preparation, also called the FFC-Cambridge process of SiO_2 or the electro(chemical)-reduction process of SiO_2, is considered to be a green process to prepare Si from SiO_2 because of the limited or even zero emission of CO_2.[11] In spite of the fact that some silicon materials have been prepared by this process, preparation of well aligned nanostructured silicon, especially Si nanowire arrays by this method remains a challenge.[12,13]

In this communication, we introduce a kind of novel nanostructured silicon material – freestanding Si nanowire arrays (Si NWAs), which have been synthesized from quartz glass by a one step and template-free electro-deoxidation process in molten $CaCl_2$ at 850 °C. Also, the growth of the Si NWAs has been investigated preliminarily and new experimental insight into the process of electro-deoxidation of SiO_2 is discussed.

In general, the electro-deoxidation of SiO_2 reaction occurs at the conductor–SiO_2–electrolyte three-phase interfaces where solid SiO_2 is electrochemically deoxidized to silicon, and O^{2-} dissolves in the electrolyte, transfers to the anode and reacts with anode carbon, as shown in Fig. 1a. In a typical synthesis, analytical $CaCl_2$ was used as a molten salt and a graphite crucible was used to host the reaction and also worked as an anode. The working electrode was in a sandwich structure, which was composed of a SiO_2 glass plate and 2 pieces of nickel net (Fig. S1, ESI†). Samples were prepared by

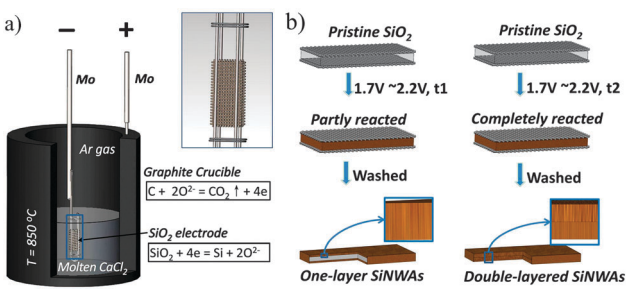

Fig. 1 Schematic diagram of (a) the electro-deoxidation system and the quartz glass electrode and (b) synthesis procedures for the Si NWAs: one-layer freestanding Si NWAs and double-layered freestanding Si NWAs.

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electro-deoxidation at a constant cell voltage in an Ar atmosphere at 850 °C, and then collected and washed (see ESI† for more experimental details). The nanowires grew from the outer surface towards the inside and aligned vertically to the surface. As shown in Fig. 1b, two pieces of one-layer freestanding Si NWAs could be synthesized when the quartz glass was not completely consumed (Fig. S2, ESI†). When a quartz glass plate of 0.5 mm thick was used as a reactant and made to react completely, double-layered freestanding Si NWAs could be produced. The double-layered freestanding Si NWAs are generally firmer than the one-layered Si NWAs.

Typical SEM images of double-layered freestanding Si NWAs are shown in Fig. 2a–c. These freestanding Si NWAs are composed of two layers. Each layer contains more than 200 micron thick aligned nanowires, as shown in Fig. 2a. The side view SEM image (Fig. 2b and the inset of Fig. 2b) shows that the nanowires are aligned in the same direction and distributed almost uniformly but not in perfect order. The wires exhibit diameters of 50–200 nm and length ranging from less than 1 micron to tens of microns (except for the top part of each layer which will be demonstrated hereafter). The top view of the Si NWAs (Fig. 2c) is very similar to that of the Si NWAs grown on the Si plate by the etching method.[14] EDS (inset of Fig. 2c) confirms that the nanowire arrays are composed of pure silicon. The small amount of oxygen observed in EDS analysis could be attributed to the surface oxide layer, which usually exists in the silicon nanomaterial. The XRD pattern in Fig. 2d shows that the nanowires are highly crystalline silicon with impurities undetectable. All the peaks can be indexed to a cubic phase Si (JCPDS 27-1402) with a = 5.431 Å. Using Scherrer analysis from the three strongest lines, an average silicon crystallite size is estimated to be ~32 nm.

As indicated by the TEM image, the nanowires have a rough surface and imperfect cylindrical shape (Fig. 3a). The TEM image also reveals that one wire is connected interlaced with the wires nearby (Fig. 3a and Fig. S2, ESI†). These connections are so strong that the morphology is still maintained even after the ultrasonic dispersion for TEM characterization. This feature is different from those of all the Si NWAs synthesized by other methods before in which little interconnections exist.[1–4,14] It can be deduced that these connections provide the structure strength of the arrays so that the as-synthesized Si NWAs could be freestanding. Spotty rings are shown in the SAED pattern of a part of one nanowire (inset of Fig. 3a), revealing that the nanowire is polycrystalline. Numerous crystalline grains with different orientations and sizes can be clearly seen on one nanowire in the HRTEM image (Fig. 3c), confirming that the nanowires are composed of crystalline grains which are of no primarily crystallographic orientation. In the survey scan of XPS analysis, only Si, O and C (contamination) elements can be detected primarily. The peak at 103.5 eV corresponds to the Si^{4+} of SiO_2, and the peak at 99.4 eV is assigned to Si^0 of elemental Si in the inspection of the Si 2p region (Fig. 3b). No other oxidation state of Si can be detected confirming that the surface layer is only SiO_2. Considering the investigation depth of X-rays and with reference to Xun's method,[15] the thickness of the surface oxide layer is estimated to be ~3 nm, which matches well the HRTEM observation.

The structure of these freestanding Si NWAs is different from the Si in micron-size columns which are synthesized *via* a similar electrochemical process in previous reports.[16,17] In this synthesis, it is found that the electrode structure plays an important role in the growth of Si NWAs. The nickel nets in the sandwich structure of the electrode (Fig. S1, ESI†) not only provided good and uniform electrical conduction contact, but also facilitated the transfer of oxygen ions from the silica to the bulk molten salt phase through the holes in the net. This was also a suitable construction to protect the structure of the product. After removing the salts and Ni nets, the Si product could almost maintain the original plate structure (Fig. S4, ESI†). Interestingly, the freestanding Si NWAs could form not only in plane shape. Cone-shaped Si NWAs were obtained when cylindrical quartz and Ni nets surrounding the outer cylindrical surface were used as electrodes (Fig. S5, ESI†). However it has been confirmed in our results that the Si NWAs do not grow on Ni nets directly. A layer of disordered silicon is in direct contact with the Ni net, which is easy to remove during the washing process in most

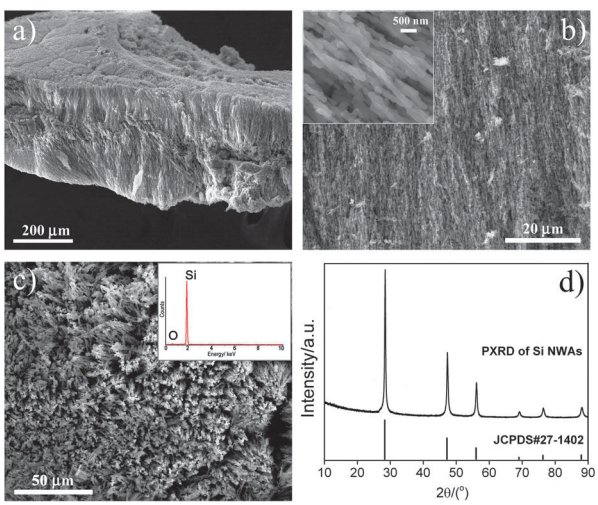

Fig. 2 SEM images of the freestanding Si NWAs in (a) low magnification oblique view, (b) side view, and (c) top view. (d) Powder XRD patterns of the Si NMAs. The inset in panel b shows a higher magnification side view SEM image of the Si NWAs. The inset in panel c shows the EDX spectrum of the Si NWAs obtained in SEM investigation.

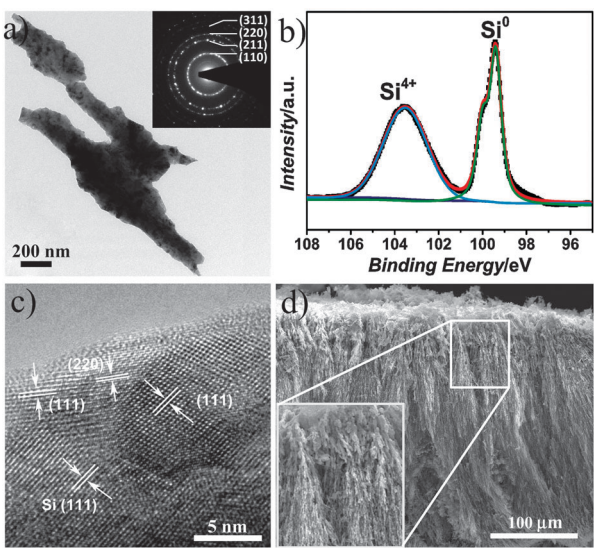

Fig. 3 (a) TEM image of a part of the Si NWAs. The inset in panel b shows the SAED pattern of part of one nanowire. (b) Si 2p region XPS spectrum of the Si NWAs. (c) HRTEM image of part of one Si nanowire. (d) SEM image of Si NWAs in side view showing the wheatear-like structure on the growth-starting side of the Si NWAs.

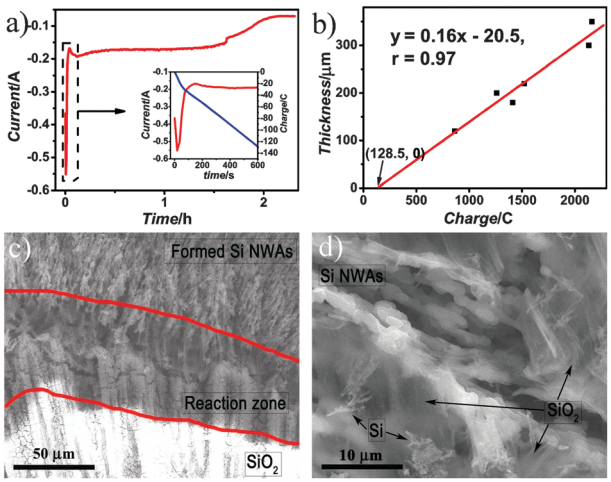

Fig. 4 (a) A typical plot of current against time from a double-layered Si NWAs synthesis. The inset in panel (a) shows the *i*–*t* curve (in red) and *Q*–*t* curve (in blue) for the first 10 minutes in the reaction. (b) Plots of thickness of the Si NWAs against electric quantity and a linear fitting curve. (c) SEM image of the reaction zone in side view. (d) Higher magnification SEM image of the reaction zone, showing the growing Si NWAs, the Si nanoparticles and the thin-silk-like SiO_2.

cases (Fig. S3, ESI†). A wheatear-like structure at the starting points of the nanowire arrays below the disordered silicon layer can be identified in the side-view of the SEM image (Fig. 3d).

The typical chronoamperometric plot of one Si NWA sample is shown in Fig 4a. The reaction current dropped drastically in the first 10 minutes, and then remained almost constant until all the SiO_2 was consumed. The first stage of high current may be caused by the surface SiO_2 consumption,[18] and may also correspond to the formation of the disordered silicon layer. To analyse the growth process, six samples were prepared in different batches and a linear fitting could be gained on the thickness of nanowire arrays *versus* the consumed electric quantity. This confirms the constant growth rate of Si NWAs. From the fitting, it can be concluded that the initial charge which may correspond to the growth of disordered Si layer is 128.5 C. And the growth of 1 μm Si NWAs per unit area (1 cm^2) needs a charge of 1.56 C, which is a power of ~3.43 J if the cell voltage of 2.2 V used in the electro-deoxidation is considered.

To clarify the growth mechanism of Si NWAs, samples were taken out from the reaction in progress and inspected using SEM and EDS after washing with hydrochloric acid. A reaction region was found between the as formed Si NWAs and unreacted SiO_2, where the elements in this region are only Si and O using the EDS test and the O : Si atom ratio is changed gradually from 2 to 0 from unreacted SiO_2 to the produced Si NWAs (Fig. 4c). In the reaction region, besides the growing nanowires, one thin-silk-like nanostructure and one kind of nanoparticles could be identified, as shown in Fig. 4c and d. From EDS analysis, it is found that the thin-silk-like substance composed of SiO_2, while the nanoparticles which are similar to but smaller in shape than the nanowires are Si. Generally, the growth of Si NWAs is likely a self-assembling process. As shown in Fig. 4d, it can be speculated that pieces of thin-silk-like SiO_2 move to the Si nanowires and are rolled up during the reaction to form new nanowires. The small Si particles are wrapped by the thin-silk-like SiO_2 and connect onto the nanowires to become part of the wires. It has been suggested in a previous report that the nano-SiO_2 may have mobility in the reaction.[12] Recently $CaSiO_3$ has been illustrated as a solute medium in the reduction process, which shows another mechanism of mobility of the Si source.[19] Because quartz glass is composed of amorphous SiO_2 and has a relaxing bonding structure, when the solid-to-solid electro-deoxidation occurs and silicon nanoparticles are generated, the surface of quartz glass may become loose and porous, which may result in the movable thin-silk-like SiO_2. To date the mechanism of this process has not been very clear and needs more exploration. From these observations it is clear that the Si NWAs are not formed entirely by the reduction of pristine SiO_2 with which they are in direct contact.

In summary, a novel silicon nanostructured material: freestanding silicon nanowire arrays have been prepared *via* electro-deoxidation of quartz glass in molten $CaCl_2$. The nanowire arrays are composed of interlaced connected polycrystalline silicon nanowires which range from 50–200 nm in diameter and can be as thick as several hundreds of micrometres. The growth of the Si NWAs may experience a self-assembling process of the electrochemical reaction. These free-standing Si NWAs would be promising for applications, such as lithium-ion batteries.[20]

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