



# A convenient way of manufacturing silicon nanotubes on a silicon substrate



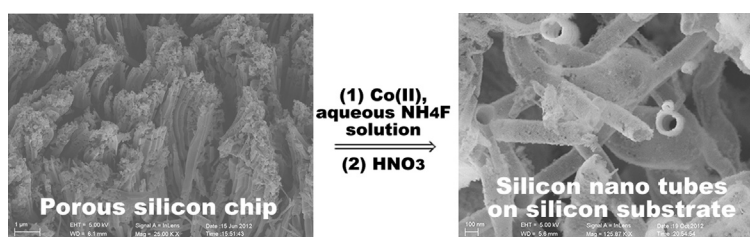
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## HIGHLIGHTS

- A facile approach of preparing silicon nano tubes was invented.
- The experimental results demonstrated the strong reducibility of Si-H<sub>x</sub> species.
- It provided a new way of manufacturing silicon-contained hybrids.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A convenient approach of preparing silicon nanotubes (SiNTs) on a silicon substrate is described in this work in detail. Firstly, a porous silicon (PSi) slice is prepared by a galvanic displacement reaction. Then it is put into aqueous solutions of 20% (w%) ammonium fluoride and 2.5 mM cobalt nitrate for a pre-determined time. The cobalt ions are reduced and the resulted cobalt particles are deposited on the PSi slice. After the cobalt particles are removed with 5 M nitric acid a plenty of SiNTs come out and exhibit disorderly on the silicon substrate, which are illustrated by scanning electron microscopy (SEM). The compositions of the SiNTs are examined by energy-dispersive X-ray spectroscopy. Based on the SEM images, a suggested mechanism is put forward to explain the generation of the SiNTs on the PSi substrate.

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## 1. Introduction

Nano silicon (Si) material attracted extensive interests for their potential and practical applications on account of its rich resources, convenient chemical modifications [1,2] and different forms of Si nanoparticles (NPs) [3–7]. For instance, silicon quantum dots have the promises to be used in labeling biomolecules [5]. Silicon nanowires (SiNWs) arrays on a silicon substrate were applied in depositing metallic NPs to improve the sensitivity of some analytic techniques [6,7]. Many routes of preparing SiNWs arrays [6,8–11]

on a silicon substrate were described in previous reports. In these reports, nano Ag [10,12], Au [13,14] Co [15] or Cu [16] was firstly deposited on a wafer. Then the wafer was put into aqueous solutions of hydrofluoric acids (HF) and hydrogen peroxides (H<sub>2</sub>O<sub>2</sub>) for a predetermined time to prepare SiNWs on a silicon substrate.

Compared with SiNWs, the forming of silicon nanotubes (SiNTs) are relatively difficult. According to the previous reports the processes of preparing SiNTs were rather complicate. Chemical vapor deposition (CVD) in nano channels of an aluminium oxide substrate was a candidate to prepare SiNTs [17,18]. Silane, hydrogen and argon gasses were mixed at a chamber under a defined pressure and temperature for a predetermined time. The decomposition of the silane gasses resulted in the deposition of silicon atom on the walls of shaped nano channels until the accomplishment of SiNTs.

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Molecular beam epitaxy [19] (MBE) was another way of synthesizing SiNTs. SiNTs grew on surface of nano channels of a porous aluminium oxide template under high vacuum and a high temperature. The silicon atoms were supplied by an electron-beam evaporator with a growth rate of  $0.07 \text{ \AA s}^{-1}$ . Patolsky [20,21] reported an innovative method of preparing SiNTs with well-controlled inner diameter and wall thickness using single-crystalline germanium-core nanowires as a sacrificial base for the epitaxial growth of SiNTs. The germanium nanowires template, obtained by an ultrahigh-vacuum CVD system, could be dissolved ultimately by wet-chemical etching. Such nanostructures of silicon were utilized in making photocathodes for water reduction [22–24]. Porous Si nanowires, as anode materials, had prospective applications in manufacturing next generation lithium ion battery [25].

Herein, we report a facile route of preparing SiNTs on a silicon substrate without requirements of highly purified reagents and harsh conditions of high vacuum and high temperature. Also there is no need for the expensive equipments. To do so, a porous silicon (PSi) slice was first obtained via electroless chemical etching aided by the deposited Ag NPs through galvanic displacement reaction. Then the SiNTs were formed on the silicon substrate by putting the PSi slice in a solution of cobalt ions ( $\text{Co}^{2+}$ ) and ammonium fluorides ( $\text{NH}_4\text{F}$ ) at a defined temperature for a defined time.

## 2. Experimental

### 2.1. Materials

Silver nitrate ( $\text{AgNO}_3$ ,  $\geq 99.8\%$ ),  $\text{H}_2\text{O}_2$  (30% in water), HF (40%), Cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ) and  $\text{NH}_4\text{F}$  (98%) were purchased from Aladdin (Shanghai) Reagent Company and were used as received without any further purification. Doubly distilled water was used throughout the work. Double-side polished silicon slice (p-type, boron doped, electrical resistivity:  $8\text{--}10 \text{ \Omega cm}$ ) with a size of  $10 \text{ mm} \times 5 \text{ mm}$  was chosen to prepare the PSi and the SiNTs.

### 2.2. SiNTs preparation on a silicon substrate and characterization techniques

A Si(111) slice was cleaned with piranha solution containing 98% concentrated sulfuric acid and 30%  $\text{H}_2\text{O}_2$  with a volume ratio of 3:1 at  $150 \text{ }^\circ\text{C}$  for at least 2 h to remove any surface fouling. Then it was washed with copious water for at least three times. The cleaned slice was put into a solution containing 5 mM  $\text{AgNO}_3$  and 5.0 M HF for 20 s at  $50 \text{ }^\circ\text{C}$  to deposit Ag NPs [12,26]. Subsequently, it was immersed in etching solution of 5.0 M HF and 0.6 M  $\text{H}_2\text{O}_2$  at  $50 \text{ }^\circ\text{C}$  for 1 h to prepare a PSi slice via galvanic displacement reaction. Then the deposited Ag NPs were removed with 5 M  $\text{HNO}_3$  for about half an hour at room temperature. Successively, the resultant PSi slice was put into a solution of 20%  $\text{NH}_4\text{F}$  and 2.5 mM  $\text{Co}(\text{NO}_3)_2$  to deposit Co at  $50 \text{ }^\circ\text{C}$  for a predetermined time. The SiNTs on a silicon substrate were obtained by removing the deposited Co with 5 M  $\text{HNO}_3$  for 20 min.

The PSi and Co-covered slice as well as the resulted SiNTs on a silicon substrate were examined by scanning electron microscopy (SEM). And the elemental compositions of the SiNTs were investigated by energy dispersive X-ray spectroscopy (EDS, Nano SEM 430, FEI Company).

## 3. Results and discussion

### 3.1. Preparation of the PSi slice

When a cleaned silicon slice was immersed in aqueous solution of HF and  $\text{AgNO}_3$ , surface  $\text{Si-H}_x$  ( $x = 1, 2$  or  $3$ ) species [27] are produced instantly. The silver ions are reduced by the set  $\text{Si-H}_x$  species producing Ag NPs-decorated silicon slice [28] according to the reactions of  $2\equiv\text{Si-H} + 12\text{F}^- \rightarrow 2[\text{SiF}_6]^{2-} + \text{H}_2 + 2\text{e}$  and  $2\text{Ag}^+ + 2\text{e} \rightarrow 2\text{Ag}$  (herein, the monohydride of  $\text{Si-H}$  species are chosen as an example). The surface Ag NPs are shown in the insert of Fig. 1(a). Surface Si elements are consumed giving  $[\text{SiF}_6]^{2-}$  according to the reactions, which demonstrated by the surface holes in the inset of Fig. 1(a). In previous reports, NPs of Au [29,30], Ni [31] and Bi [32] could also be obtained readily by the reduction of corresponding precursors with surface  $\text{Si-H}_x$  species, which illustrated the powerful reducibility of the surface silicon hydrides. Although most of Ag NPs merge together forming a big nano-sized block within such a short time of 20 s there are some separated Ag NPs sized at 20–30 nm, which can be observed clearly in the inset of Fig. 1(a). When such a silicon slice is put into the solution of HF and  $\text{H}_2\text{O}_2$ , the decomposition of  $\text{H}_2\text{O}_2$  is accelerated because of the catalysis of the deposited Ag NPs. The adjacent silicon atoms near the Ag NPs are oxidized into silicon dioxides ( $\text{SiO}_2$ ) by the liberated oxygen and are quickly removed by HF giving  $[\text{SiF}_6]^{2-}$ . This generates shallow holes at the initial stage. As the reaction goes on the holes become deep and deep [28]. The Ag NPs will precipitate into the silicon slice leading to the porous structures. The top and cross-sectional views of a PSi slice are shown in the SEM image of Fig. 1(a) and (b). The porous structures are full of the entire silicon substrate, which resulted from electroless chemical etching catalyzed by the nano-sized blocks of Ag. A large amount of micro holes (marked with arrows in Fig. 1(a)) can be seen on the surfaces of PSi, as are also shown in the sectional image of Fig. 1(b). The morphologies of the porous silicon obtained by such a technique are quite different from the electrical chemical etching with an intensive etching of galvanization [33], which gave numerous crossing cracks on the silicon substrate. The porous structures also differ from the reported SiNWs array on a silicon substrate [34]. We can not observe SiNWs on the silicon substrate in Fig. 1(a) and (b). Imaginably, if the Ag NPs are very tiny in this case the diameters of the resulted holes are accordingly small. Such tiny holes may provide an optimized condition of manufacturing SiNTs on a silicon substrate.

### 3.2. Deposition of cobalt particles on a silicon substrate

The porous structure improves the surface specific areas of the silicon slice. Hence density of the produced  $\text{Si-H}_x$  [35] species is enhanced greatly when the slice is immersed in  $\text{NH}_4\text{F}$  solutions. As a result, the reducibility of the  $\text{Si-H}_x$  species will be enhanced extraordinarily so that  $\text{Co}^{2+}$  ions may be reduced on the PSi slice. We once tried to put a PSi slice in solutions of  $\text{Co}^{2+}$  and 10%  $\text{NH}_4\text{F}$  the reduction reaction of  $\text{Co}^{2+}$  did not occur at all. When the concentration of  $\text{NH}_4\text{F}$  was raised to 20% the reaction proceeded violently accompanied by large amounts of  $\text{H}_2$  and deposition of the metallic Co on the silicon surface. The reduction of  $\text{Co}^{2+}$  also reflects the strong reducibility of the surface  $\text{Si-H}_x$  species and the key role of the high concentration of  $\text{F}^-$  ( $[\text{F}^-]$ ). The PSi images covered by cobalt particles are exhibited in Fig. 2(a) and (b) respectively.

Fig. 2(a) displays that Co particles cover entire surface of PSi like toy building blocks. The following redox reactions of (a–d) may explain the production of Co particles on the silicon substrate.

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