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A Polyoxometalate-Assisted Electrochemical Method for Silicon Nanostructures Preparation: From Quantum Dots to Nanowires

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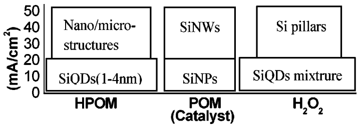
Silicon (Si) and carbon nanostructures are of great interest to many areas of science and technology. While carbon nanomaterials have received much attention ranging from fabrication to application,[1,2] similar work on Si nanomaterials is comparatively limited. Because of its biocompatibility and huge microelectronics market, Si nanostructures are arguably the most attractive and important semiconductor nanomaterial.[3−6] Size, shape, and order control of Si nanostructures are essential for further development of Si-based nanodevices. Consequently, fabrication of ordered Si nanostructures directly from bulk Si materials (p- or n-type) of predetermined characteristics is an attractive strategy. Particularly, size- and shape-controlled fluorescent Si quantum dots (SiQDs) in the range of 1−4 nm are important for understanding quantum phenomena and for microelectronics, optoelectronics and biomedical applications. Extensive efforts have been devoted to the synthesis and the growth mechanisms of SiQDs and silicon nanowires (SiNWs).[3−10] However, the current synthetic methods invariably suffer from the drawbacks of high-temperature processing, special equipment and conditions, and tedious procedures. Notably, size and orientation control of SiQDs remains difficult.[6−10] SiQDs, Si nanoparticles (SiNPs), and Si nanostructures are readily prepared by electrochemical etching of Si,[9,10] however the SiQDs thus prepared are composed of a mixture of sizes (1.0, 1.7, 2.15, 2.9, and 3.8 nm), which required complex separation methods (e.g., chromatography, etc) to separate them into monodisperse SiQDs.

Here, we demonstrate that the use of polyoxometalates (POMs) in an electrochemical method can produce highly monodisperse SiQDs (∼1, ∼2, ∼3, and ∼4 nm) with a narrow size distribution requiring no further separation. In addition, this method also can realize the controlled synthesis of a variety of Si nanostructures, ranging from Si nanoparticles (SiNPs), SiNWs, to ordered Si micro-/nanostructures. POMs are know to have many unique functions for catalysis, such as structural robustness and unique electronic characteristics, which have played an important role in catalytic behavior.[2b,11−14] In light of this, POMs were introduced into the present electrochemical etching system.

In a typical experiment, the process was performed in an electrochemical cell with graphite as anode and Si (n- or p-type) wafer as cathode. The electrolyte was prepared by mixing ethanol and HF solution with a suitable amount of H_2O_2 and $H_3PMo_{12}O_{40}\cdot nH_2O$ (POM) as catalyst (H_2O_2 + POM = HPOM). The applied current intensity range was 1∼50 mA/cm^2, and the etching process lasted several hours. Significantly, the current density and catalyst (HPOM, POM, and/or H_2O_2) are the factors that control the nature of Si nanostructures. Scheme 1 shows the relationship between the current density, catalyst, and the obtained Si nanostructures.

Scheme 1. Relationship between the Current Density, Catalyst, and the Products



The optimal current density for producing SiQDs was less than 20 mA/cm^2 using HPOM as catalyst. Importantly, the current density determines the size of Si nanoparticles: higher current density yields 1 nm particles, while lower density yields larger particles. A range of 15−20 mA/cm^2 produces highly monodisperse nanoparticles of about 1 nm in size. Reducing current density yields SiQDs with increasing size; for example, 8−12, 5−8, and 1−5 mA/cm^2 produces ∼2, ∼3, and ∼4 nm SiQDs, respectively. It is important to note that SiQDs with a narrow size distribution are directly synthesized with no need of separation; for example, about 90%, 85%, 75%, and 65% of the as-produced particles have, respectively, the size of 1 ± 0.1, 2 ± 0.1, 3 ± 0.2, and 4 ± 0.2 nm (see Supporting Information). The catalyst HPOM clearly is instrumental in controlling the size of SiQDs, and SiQDs in all sizes were produced with high monodispersity. Notably, using only H_2O_2 the particle size could not be well controlled, whereas with only POM, SiNPs of 30−50 nm were the major product (Scheme 1).

Figure 1a shows the transmission electron microscopy (TEM) image of SiQDs of ∼1 nm, while Figure 1 panels b, c, d, and e show the high-resolution TEM (HRTEM) images of SiQDs of 1, 2, 3, and 4 nm, respectively. The lattice fringe spacing of ∼0.34 nm agrees well with the ⟨111⟩ plane spacing of Si crystal. Figure 1f is the typical TEM images of SiNPs of about 30 nm obtained using POM as catalyst. Figure 1g displays the photoluminescence (PL) spectra of different-sized SiQDs. It shows that ∼1 nm particles emit a blue band at 450 nm and a weak structureless tail at 500−700 nm, ∼2 nm particles an intense green peak at 520 nm, ∼3 nm particles an intense red band at 640 nm, and ∼4 nm particles an infrared band at 740 nm. The red shift of the PL band with increasing SiQDs size and the larger band energy than Si indirect band gap of 1.1 eV demonstrate distinctly the quantum confinement effect in SiQDs smaller than 4 nm.[4,9] The strong and tunable emission in the visible spectral range suggests these SiQDs are promising candidates for biomarker applications.[7,8] All SiQDs are terminated with Si−H bonds, as revealed by Fourier-transform infrared spectroscopy (FTIR) measurement, which shows strong stretching monohydrides Si−H bonds at 900 cm^{-1} and coupled H−Si−Si−H stretching bonds at 2090 cm^{-1} (see Supporting Information).[7,8]

When current density was increased to 20−50 mA/cm^2 using HPOM as catalyst, complex micro-/nanostructures were obtained from etched Si wafer surface. Their SEM images are shown in Figure 2. It can be seen from these images that the complex

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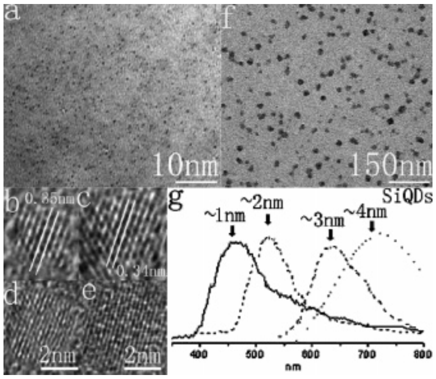

Figure 1. (a) Typical TEM and (b−e) HRTEM images of SiQDs; (f) typical TEM images of SiNPs; (g) typical PL of different-sized SiQDs.

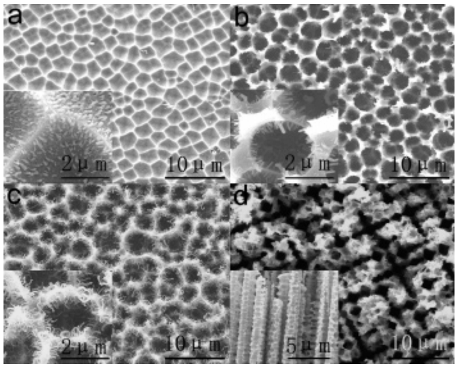

Figure 2. Typical SEM images of the complex structures: nanoparticles-in-micropores (a), nanorods-in-micropores (b), and nanowires-in-micropores (c), microholes and silicon pillars (d).

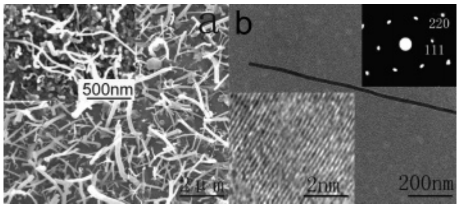

Figure 3. Typical SEM (a) and TEM (b, inset images are SAED pattern and HRTEM image) images of the SiNWs.

structures in products are composed of nanoparticles-in-micropores, nanorods-in-micropores, or nanowires-in-micropores structures. The diameter of the nanoparticles falls in the range of 30−80 nm. With increasing reaction time, the product changes from SiNPs at 1 h to silicon nanorods (SiNRs) at 3−5 h, and to SiNWs at 7 h, as shown in Figure 2a−c. The SiNRs and SiNWs are all grown perpendicular to the wall of the pores. In the initial stage of growth, the microporous structures are not completely formed, but become regular and distinct with increasing reaction time. The thick microporous walls are gradually replaced by nanorods and nanowires, and eventually transformed to the complex structure in the product. The orientation and large surface areas make these complex structures potential materials for applications in solar cells, catalysis, and sensing devices. Using the same current density, 20−50 mA/cm^2, and H_2O_2 as additive, the products changed into microholes and Si pillars as shown in Figure 2d. This kind of porous structures was attributed to the anodic oxidation of Si wafer in the HF aqueous electrolyte.[15] However, using only POM as catalyst, SiNWs (or SiNRs) were obtained instead (Scheme 1). Figure 3a shows SiNWs (or SiNRs) are about 30−90 nm in diameter and several μm (1−3 μm) in length. Figure 3b is the typical TEM image of SiNWs, while the insets show the selected-area electron diffraction (SAED) and HRTEM image. The lattice fringe spacing of 0.31−0.32 nm agrees well with the ⟨111⟩ plane of Si crystal.

Using current density over 50 mA/cm^2 and either POM, HPOM, or H_2O_2 as the catalyst, similar products with no well-defined nanostructures were obtained; that is, microsize holes, dendrite structures, and sub-microsize wirelike Si structures (see Supporting Information).

POMs clearly play a vital role in controlling the size of SiQDs and formation of Si nanostructures. It may be attributed to the unique electronic characteristics of POMs in that they can gain and donate electrons simultaneously while keeping their structure unchanged.[12−14] However, at high current densities, POM or HPOM may not affect the etching results, since similar products were obtained using POM, HPOM, or H_2O_2.

The above results demonstrate that current density and POM catalyst are the key factors determining the formation of well-defined Si nanostructures. To gain finer control of the synthesis, choosing a better candidate, for example, the right types of POM, may be important to the method. While the mechanisms of the electrochemical reactions are not fully understood, the important role of POMs is clear.[3] It may be anticipated that POMs may similarly facilitate the control synthesis of other ordered nanostructured materials (ZnO, etc.) via electrochemical reactions.

In summary, a simple POM-assisted electrochemical method was developed for the control synthesis of SiQDs, SiNPs, SiNWs, and complex Si nanostructures. It represents a convenient and rational synthesis of a variety of Si nanostructures via the simple control of current density and choice of catalyst POM. The synthetic method may be extended to other ordered nanostructures.

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Supporting Information Available: Experimental details, detailed characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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