Chemical Physics Letters 455 (2008) 252–255

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Nanomaterials separation by an ultrasonic-assisted phase transfer method

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ARTICLE INFO

Article history:
Received 11 December 2007
In final form 26 February 2008
Available online 2 March 2008

ABSTRACT

Nanomaterials in different sizes can be separated by an ultrasonic-assisted phase transfer method. A two-phase polar–non-polar liquid system composed of alcohol (polar, C_1–C_3 or their mixture), alkane (non-polar, C_5–C_{10} or their mixture) and DI water is used in this method. The separation is achieved via the surface tension of the interface and the dynamic equilibrium established between nanomaterials of different weights. Different nanostructures can be separated to exist in layers of different polarity or in the interface throughout the sonication process, with the small-sized nanostructures staying in the upper layer and the large-sized one in the lower layer and interface.

1. Introduction

Nanoscale materials in the nanometer scale attracts intense interest, because they exhibit different properties from the corresponding macromaterials [1–3]. Nanomaterials have a larger surface-to-volume ratio, which leads to greater reactivity, different mechanical strength and electrical properties. As the dimension further reduces, quantum-size effect emerges and dominates the behaviour of materials at nanoscale, and drastically changes the optical, electrical and magnetic behaviours, etc [4–12]. Nanotechnology deals with design, characterisation, production, and application of nanostructures, devices and systems by controlling shape and size at the nanometer scale. For nanotechnology, obtaining the size- and shape-controllable nanoscaled building blocks is an essential task for its further development. There are two approaches in this issue: The first one is to achieve direct controlled synthesis of monodisperse distribution nanomaterials, while the other is to develop a general method for separation of nanomaterials according to sizes and morphologies. In comparison, the first one is more difficult to achieve, while the second one is more practical.

Silicon (Si) is of great interest to many areas of science and technology. Recently bulk silicon nanowires (SiNWs) have been synthesized successfully by thermal evaporation of silicon monoxide (SiO) without catalysis [4], and their properties extensively investigated. Particularly, it has been demonstrated from scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements [4] that small-diameter SiNWs (1–7 nm) have a band gap energy increasing with decreasing wire diameter, and also higher oxidation resistance towards air [5]. These findings suggest promising potential of silicon-based nano-optoelectronic devices. The oxide-assisted growth (OAG) method is an effective method for bulk-quantity production of SiNWs which has been described in our previous work [4–6,13–16]. However, bulk SiNWs samples are composed of wires of a distribution of diameters, and sometimes different morphologies. Therefore, one of the challenging issues in the field of nanomaterials is the sorting of high-quality, high-purity quantum-sized SiNWs into different dimensions and morphologies. In this study we demonstrate the separation of nanomaterials by an ultrasonic-assisted phase transfer process: the quantum-sized SiNWs (diameter $\leqslant$ 5 nm) can be separated from the bulk SiNWs product, and additionally SiQDs, Si nanoparticles (SiNPs), Si nanoribbon (SiNRs) and Si nanocones (SiNCs) also can be separated from their raw products. Similarly, silica NWs or silicon nanocores also can be separated from the silica NWs/silicon nanocore hierarchical structures.

2. Experimental

In our experiments, all the chemicals were purchased from Sigma-Aldrich. SiNWs were prepared by the OAG method via direct thermal vaporization of pure SiO powder at 1350 °C and a heating rate of 50 °C/min [14]. The oxide layers of the as-grown SiNWs were removed by 5% hydrogen fluoride (HF) solution to generate

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doi:10.1016/j.cplett.2008.02.090

H–SiNW surfaces. SiQDs and SiNPs were prepared by electrochemical etching of Si wafer [15]. The mixture of SiNRs and SiNCs/SiNWs, and silica nanowires (NWs)/silicon nanocore hierarchical structures were both prepared by thermal evaporation method [16]. The ZnO sample of nanorods and nanoparticles (ZnO NPs) with different diameter was prepared by plasma-enhanced chemical vapour deposition (PECVD) method. The CdS sample with different diameter nanowires (CdS NWs) and nanoribbons (CdS NRs) was prepared by thermal evaporation method. Typically, 50 cm^3 centrifuge tube with a diameter of 3 cm was used as the separation chamber, which could deal with ~0.1 g SiNWs or ~0.5 g ZnO sample. Counting the nanoparticles on randomly selected grids in the transmission electron microscope (TEM), the present separation is effective and complete with over 95% target sample separated from the raw materials.

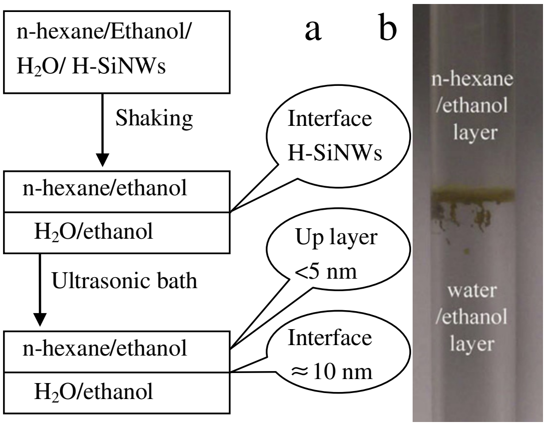

Fig. 1. (a) Flowchart of SiNWs separation, (b) optical photograph showing the interface in the two-phase system after separation.

TEM images of SiQDs and SiNWs were obtained by a FEI/Philips Techal 12 BioTWIN TEM, while the high-resolution (HR)-TEM images were obtained by a CM200 FEG TEM.

3. Results and discussion

The separation was carried out in a two-phase liquid system under ultrasonic condition, in which phase transfer took place from the alcohol/H_2O to alcohol/alkane phase. The typical two-phase liquid system was composed of two organic solvents of alcohol and alkane together with deionized (DI) water. The alkane used was any alkane from C_5 to C_{10} or their mixture. Alcohol was limited to those having less than C_3 or their mixture. In practice, the raw H–SiNWs were put into ethanol for ultrasonic dispersion, followed by adding a suitable amount of *n*-hexane and DI water to disperse the liquid for nanomaterial separation with shaking until interface appeared. After ultrasonic treatment, a small-sized SiNWs, found in the *n*-hexane/ethanol (upper) layer, was partially transparent in color. Fig. 1a shows the working flowchart of the separation process. Fig. 1b shows the photograph of H–SiNWs segregated at the two-phase interface. The bulk sample was a mixture of H–SiNWs of different diameters (average diameter is about 15 nm), which is shown in Fig. 2a. The diameter of the separated H–SiNWs at

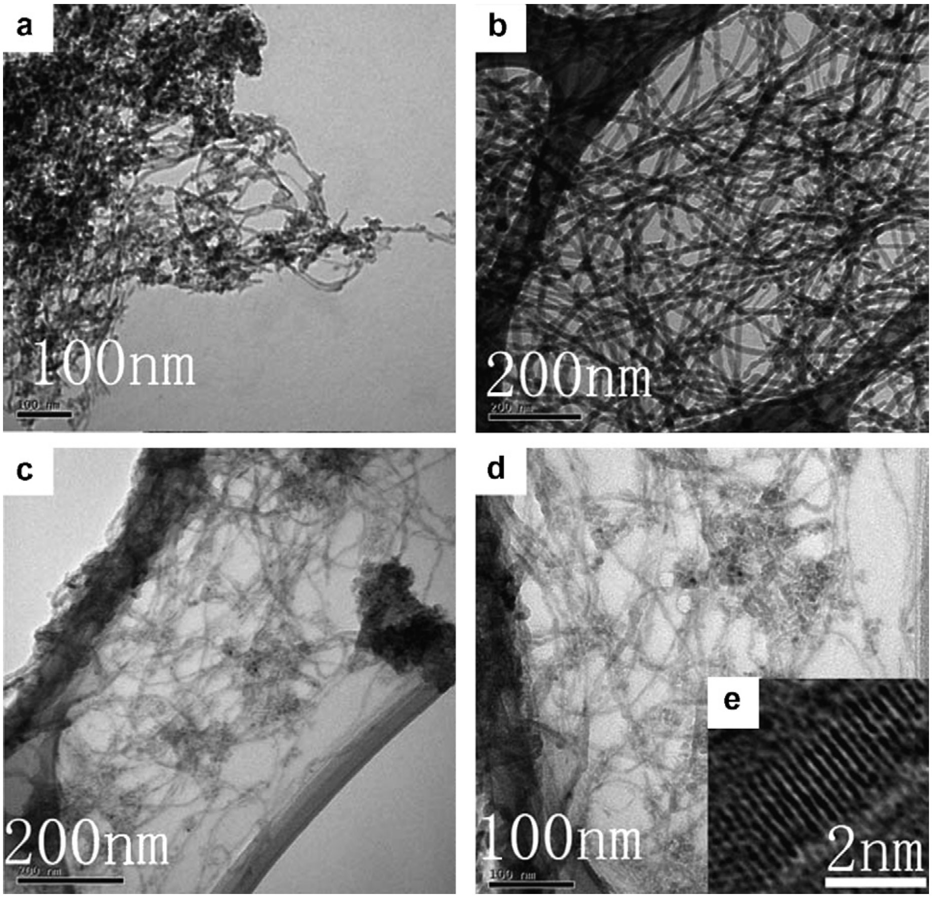

Fig. 2. TEM image of (a) bulk H–SiNWs, and (b) H–SiNWs in the interface after separation. TEM images of (c) and (d) small-diameter H–SiNWs in *n*-hexane/ethanol layer (upper layer) after separation, and (e) HR-TEM of a small-diameter H–SiNW in *n*-hexane/ethanol layer after separation.

the interface was about 10 nm (Fig. 2b), whereas that of the separated H–SiNWs in the upper layer was about 2–3 nm (Figs. 2c and d). Fig. 2e shows the HR-TEM image of the separated H–SiNWs with a diameter of 2 nm, where the lattice fringe spacing of 0.31–0.32 nm agrees well with the ⟨1 1 1⟩ plane spacing of Si single crystal.

Besides SiNWs, the same method was also applied to separate SiQDs and SiNPs. SiQDs (1–10 nm) were produced by the electrochemical method, but small fragments of silicon wafer were also present in the product as shown in Fig. 3a. After separation, pure SiQDs were segregated and dispersed in the upper layer as shown in Fig. 3b, where the TEM image reveals no other small silicon fragments after separation. Separation of SiNPs was also achieved by the same method from the silicon wafer fragments in the product as shown in Fig. 3c. Pure SiNPs with a diameter of 30–50 nm were obtained at the interface after separation as shown in Fig. 3d. Similar process also can be used for the separation of other large-sized and complex Si nanostructures. Fig. 4a shows the TEM image of a bulk sample consisting of SiNRs, SiNWs and SiNCs. After separation the TEM image in Fig. 4b shows only SiNWs and SiNCs (30–50 nm in diameter) in the upper layer. Fig. 4c shows the TEM image of SiNRs (about 50–100 nm in width and several microns in length) after separation. Moreover, the method also can be used for the separation of silica and Si complex structure. Fig. 4d shows the TEM images of bulk silica NWs and Si hierarchical nanostructure consisting of high-density amorphous silica nanowires radial standing on a single-crystal silicon core. After separation, the silica nanowires can be separated from the silicon core. Fig. 4e shows the TEM image of silica NWs in the upper layer and interface after separation, while Fig. 4f shows the Si nanocores in the lower ethanol/H_2O layer.

In the present ultrasonic-assisted phase transfer method, the two-phase liquid system plays an important role in nanomaterials separation. Liquid alkanes (C5–C10) are preferably used as one phase, while alcohols with 1–3 carbons, especially ethanol, are preferably used as the second phase. The separation was achieved by the surface tension of the interface and the dynamic equilibrium established by the weight of nanomaterials under ultrasonic condition. For a sample mixture of H–SiNWs of different diameters, the migration of smaller diameter H–SiNWs (lower mass) towards the non-polar upper layer is faster. On the contrary, the larger diameter species are trapped in the interface or migrate towards the lower layer instead. This differential tendency of segregation can be understood as follows. Since H–SiNWs used are all hydrogen terminated and the SiH bonds are hydrophobic in nature, the non-polar *n*-hexane would favor the migration of smaller-sized species due to their higher non-polar surface character and lower mass, whereas the larger-sized nanomaterials would preferentially remain at the interface. As a result, these factors would favor the migration of the smaller-sized H–SiNWs to the upper layer, while the larger-sized ones would be trapped at the interface, or migrate to the lower layer during separation. Similar phenomena would also exist for other silicon-based nanostructures, such as SiQDs, SiNPs, SiNRs, and SiNCs, when the present separation method was applied to them. Further separation of nanomaterials can be achieved by regulating the power of ultrasonic bath. In addition, the same method can also be applied for the separation of other inorganic semi-conductor nanomaterials (see supporting information for separation of ZnO, CdS, etc). Using the same volume of solvent, the separation ability increases with increasing diameter of the separation apparatus. About 0.1 g SiNWs can be separated out using a 50 cm^3 centrifuge tube with a diameter of 3 cm, while

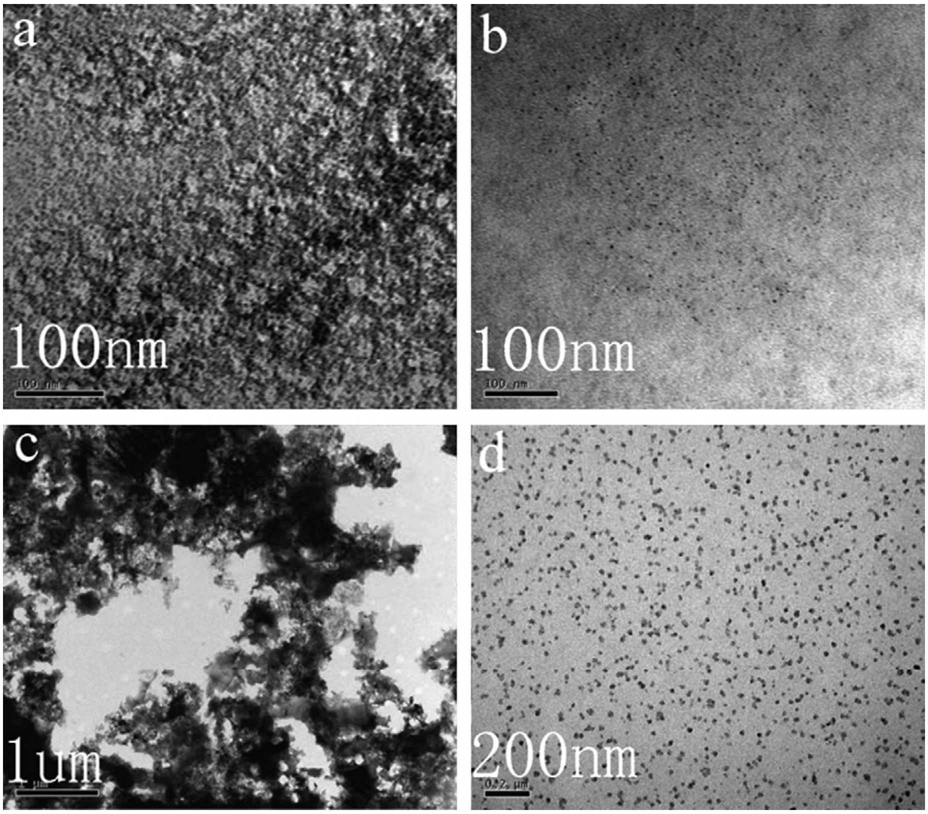

Fig. 3. TEM images of (a) bulk SiQDs sample and (b) small-diameter SiQDs in the upper layer of *n*-hexane/ethanol after separation. TEM images of (c) bulk SiNPs sample and (d) small-diameter SiNPs in the upper layer of *n*-hexane/ethanol after separation.

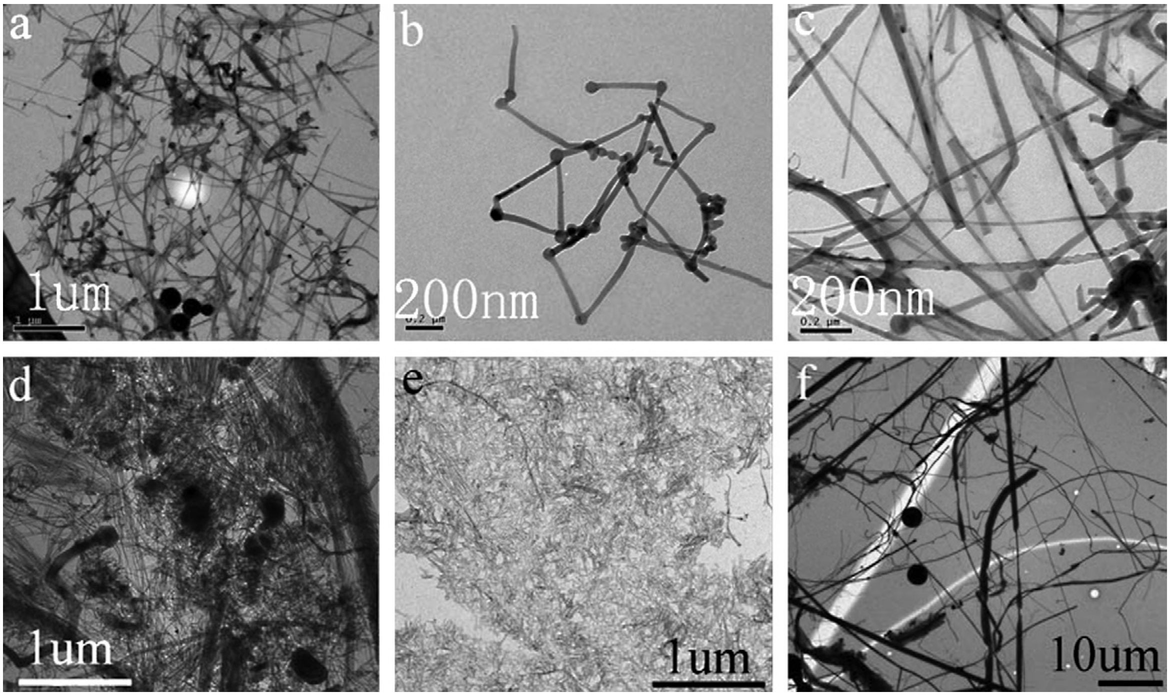

Fig. 4. TEM image of (a) bulk SiNRs, SiNWs and SiNCs sample, (b) SiNWs and SiNCs in *n*-hexane/ethanol layer after separation, and (c) SiNRs after separation. TEM image of (d) bulk silica NWs and Si nanocore samples, (e) pure silica NWs in the upper layer or interface of *n*-hexane/ethanol after separation, and (f) pure Si nanocores in the lower layer.

~0.15 g can be separated out using a centrifuge tube with a diameter of 5 cm. On the other hand, 0.3–0.5 g SiNWs can be separated out by using a 100 cm^3 centrifuge tube with a diameter of ~5 cm. Significantly, this method can guarantee large-scale separation of small-sized nanomaterials from the bulk sample mixture.

4. Conclusion

In summary, silicon and related semi-conductor nanomaterials can be separated by a two-phase liquid system composed of *n*-hexane, ethanol, and water. Different nanostructures can be separated and exist in different layers or at the interface throughout the sonication process. The separation was achieved by the surface tension of the interface and the dynamic equilibrium established between nanomaterials of different weights. The present method may provide a promising and practical approach for the large-scale separation of differently sized nanomaterials.

Acknowledgements

The work described in this Letter was supported by the Research Grants Council of Hong Kong SAR (Nos. CityU 102206 and CityU 3/04C), the National Basic Research Program of China (973 Program) (Grant Nos. 2006CB933000 and 2007CB936000), and the National High-tech R&D Program of China (863 Program) (Grant 2006AA03Z302).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2008.02.090.

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