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Fabrication of Selenium/Carbon Core–Shell Submicrowires and Carbon Submicrotubes by a Facile Solution Process

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Abstract: We show a facile one-step surfactant-assisted solution process to fabricate selenium/carbon (Se/C) coaxial core–shell submicrowires and their transformation into carbon submicrotubes by dissolution of the Se cores at ambient temperature. The formation process of the Se/C core–shell submicrowires was investigated. The results of the investigation and further experiments confirm that the thickness of the carbon shell could be tailored by controlling the experimental conditions. The as-synthesized Se/C core–shell submicrowires and the carbon submicrotubes are potentially useful in applications such as in nanodevices or biomedicine.

Keywords: carbon · core–shell structures · hydrothermal synthesis · microtubes · selenium

Introduction

Recently, one-dimensional (1D) nanomaterials such as nanowires, nanorods, nanobelts, and nanotubes have become the focus of intensive research owing to their scientific importance and potential applications.[1–3] A significant challenge in the research and synthesis of 1D nanomaterials is how to control rationally their size, geometrical arrangement, and composition to modify their properties towards desired functions in nanodevices.[4] For instance, nanowires often display high chemical reactivity and are very sensitive to air and moisture owing to their low dimensionality and high surface-to-volume ratio, which degrades the performance of nanodevices.[5] Thus, nanowires should be protected to maintain good performance for a long time. Coaxial core–shell nanowires, a new type of 1D nanocomposite made of nanowires (core) wrapped with one or more outer layers (shell), have emerged recently to meet such demands. Because nanowires are protected from contamination by the outer shell as well as the core–shell heterostructures that are formed, core–shell nanowires could exhibit superior multifunctional properties relative to naked nanowires.[6] More importantly, it is believed that such 1D nanocomposites might realize various tailor-made functions, as their intrinsic properties could be easily tuned by changing the chemical composition of both core and shell.[7]

Among the various compositions of core–shell nanowires available, semiconductor/shell 1D nanocomposites have stimulated particular interest owing to their potential applications in nanodevices such as cell separation, coaxial-gated transistors, and laser diodes.[6a,8] In recent years, much effort has been made to synthesize 1D core–shell structures with a semiconductor as core. For example, Si/SiO_2 core–shell nanowires and the coaxial three-layer structures of $SiC/SiO_2/BNC$ and $Si/SiO_2/C$ have been synthesized by laser ablation,[7a,9,10] and the three-layer sandwichlike structure of C/BN/C has been prepared by means of arc discharging.[11] Furthermore, carbothermal reduction and chemical vapor deposition have also been employed to fabricate SiC/SiO_2, GaP/SiO_x, GaP/C, and $GaP/SiO_x/C$ 1D core–shell structures.[12,13] Recently, several solution-based methods have been developed to generate semiconductor/polymer, metal/polymer, and polymer/polymer core–shell nanowires.[14] Despite these advances, few single-crystal semiconductor/carbon 1D core–shell structures have been synthesized through a mild solution route so far.[15] Therefore, the design of simple and efficient solution-based methods to fabricate single-crystal semiconductor/carbon 1D core–shell structures

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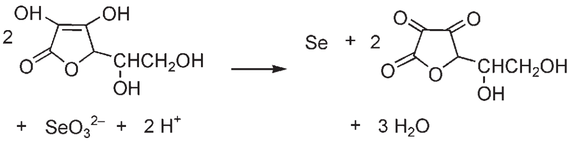
in a single step still remains a key research challenge. Recently, we successfully synthesized flexible Ag/C core–shell nanowires by a novel polymer-assisted one-step reduction and carbonization process under mild hydrothermal conditions,[16] which inspired us to attempt to produce semiconductor/carbon 1D core–shell structures by a similar one-step solution route. In this paper, we report a simple one-step solution route to fabricate selenium/carbon (Se/C) core–shell submicrowires.

We chose Se as the core because the fabrication of Se/C 1D core–shell structures by a one-step solution route is both practically important and theoretically feasible. First, Se has many excellent physical and chemical properties. As an important indirect gap semiconductor, Se has high photoconductivity ($8\times10^4\,\mathrm{S\,cm^{-1}}$), a relatively low melting point ($\approx$490 K), and excellent photoelectrical properties.[17] These promising physical properties result in its extensive application in the field of semiconductor rectifiers, solar cells, photographic exposure meters, and xerography.[18] Because of their high reactivity toward a wealth of chemicals, Se nanostructures with certain morphologies can be used as efficient templates to produce a series of other functional materials, for example, Ag_2Se, CdSe, ZnSe, and Bi_2Se_3.[19] It is reasonable to expect that the availability of Se in the form of core–shell structures would bring in new types of applications or enhance the performance of currently existing ones. Second, Se has a unique crystal structure and is thus an ideal candidate for generating 1D nanostructures.[20] Trigonal selenium (t-Se) consists of helically arranged chains of Se atoms, that is, infinite linear trigonal spirals along the c axis, which makes t-Se suitable for growing into 1D nanostructures even without the assistance of physical templates.[21] Therefore, it is feasible to fabricate Se cores with 1D structures by a simple solution-phase oxidation–reduction reaction. We treated ascorbic acid with sodium selenite (Na_2SeO_3) to obtain Se. Ascorbic acid, an excellent reducing agent,[22] can reduce SeO_3^{2-} to Se metal in solution [Eq. (1)]. As opposed to reducing agents that are difficult to handle and poisonous, such as $N_2H_4{\cdot}H_2O$, the use of ascorbic acid is safer, greener, and more environmentally friendly. More importantly, heating of a solution of ascorbic acid in autoclaves to 160–180 °C, much higher than the normal glycosidation temperature, leads to aromatization and carbonization.[23] Thus, ascorbic acid can act as both reducing agent and carbon source to form a carbon shell.

Abstract in Chinese:

通过简单的一步表面活性剂辅助液相法合成了硒/碳同轴核壳亚微米线，室温下将产物中的硒核溶解后可以进一步得到碳亚微米管。硒/碳核壳亚微米线的形成过程被研究。研究结果和进一步实验都证明能够通过控制反应条件来调节产物的碳层厚度。所合成地硒/碳核壳亚微米线和碳亚微米管在纳米器件、生物医学等领域具有应用前景。



(1)

On the basis of the above motive and idea, we designed a one-step surfactant-assisted solution route to fabricate Se/C core–shell submicrowires by a mild hydrothermal process with Na_2SeO_3, ascorbic acid, and the surfactant cetyltrimethylammonium bromide (CTAB) as the starting materials. The experimental result is in good agreement with our expectations. Furthermore, in view of the high solubility of Se in various solvents, the as-prepared Se/C submicrowires were also used as templates to fabricate carbon submicrotubes by easily dissolving the Se core at room temperature. As the approach is facile and low-cost, we believe that this is a helpful paradigm for the preparation of other semiconductor/carbon 1D core–shell structures and carbon tubes.

Results and Discussion

Characterization of Se/C Core–Shell Submicrowires

The crystallinity and phase of the products were examined by powder X-ray diffraction (XRD). All the reflection peaks of the XRD pattern can be readily indexed as a pure trigonal selenium phase (t-Se) of high crystallinity (see Supporting Information, Figure S1). The lattice constants calculated from the pattern are $a=4.368$ and $c=4.954$ Å, which is in good agreement with the literature values of 4.366 and 4.953 Å, respectively (JCPDS card file no. 73-0465).

The panoramic morphology and dimension of the as-prepared products were examined by field-emission scanning electron microscopy (FESEM). The general overview FESEM image (Figure 1 a) of the products shows exclusively 1D structures with lengths ranging from several tens to about 100 μm. Figure 1 b is a high-magnification FESEM image that shows that the diameters of the product have a wide size distribution. The size-distribution histogram of the products reveals that their average diameter is 0.3–0.6 μm (see Supporting Information, Figure S2). The inset of Figure 1 b is a higher-magnification FESEM image of the area enclosed by the square in the main figure, which shows the structural character of the core–shell structures with a bare core head.

The microstructural features of the products were demonstrated more clearly with transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (Figure 2). Figure 2 a–c reveals the distinct dark/light contrast along the radial direction, which suggests a different phase composition and character of the core–shell structures. The inner dark part corresponds to Se nanowires core, which is about 0.2–0.3 μm in diameter. The light part, outside of the core region, indicates a carbon shell about 0.1 μm in thickness. Figure 2 d shows an HRTEM image obtained at the edge of an individual core–shell sub-

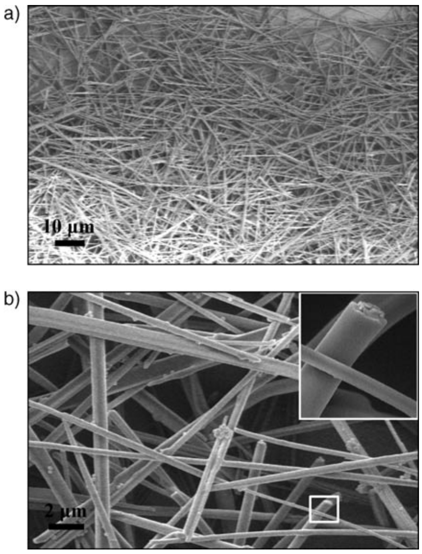


Figure 1. FESEM images of the products. a) General view of the products. b) Magnified FESEM image of the products. Inset of b): higher-magnification FESEM image of the region in the white box, clearly showing the core–shell structure of the products.

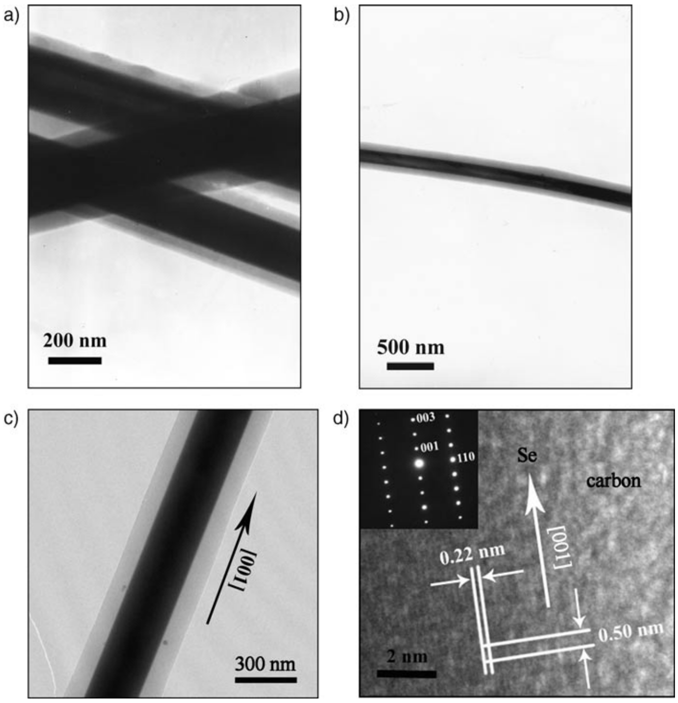


Figure 2. a)–c) Typical TEM images of the Se/C core–shell submicrowires. d) HRTEM image recorded on the edge of an individual Se/C core–shell submicrowire. Inset of d): SAED pattern of this submicrowire.

microwire, which gives more details of the crystal structure of the Se core. The two sets of fringe spacings of the lattice planes observed in this image are 0.50 and 0.22 nm, which corresponds well to the (001) and (110) lattice planes of t-Se, respectively. The selected area electron diffraction (SAED) image taken from this core–shell submicrowire is shown in the inset of Figure 2d. The HRTEM and SAED pattern analyses demonstrate that the Se core of the as-obtained composites is single-crystalline in structure and has a preferential growth direction along the [001] direction (Figure 2c and d). The growth direction is consistent with the inherent helical chain of t-Se (*c* axis).

Further evidence for the surface composition of the core–shell submicrowire was obtained by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The results are shown in Figure 3. The XPS spectrum of the products obtained (Figure 3a) shows two very strong peaks at 284.84 and 531.15 eV, which corresponds to the binding energies of the C 1s and O 1s orbitals, respectively. However, the binding energy at 54.45 eV for the Se 3d orbital is barely detectable. Figure 3b shows the Raman spectrum of the products, in which the observation of a broad peak at 1372 cm^{-1} and a strong peak at 1599 cm^{-1} can be attributed to the vibrations of the carbon atoms of disordered amorphous carbon and crystalline graphite, respectively.[24] Similarly, the characteristic resonance peak of t-Se at 235 cm^{-1} is also quite weak. It can be concluded from these results that the products have core–shell structures with an inner Se core and an outer carbon shell.

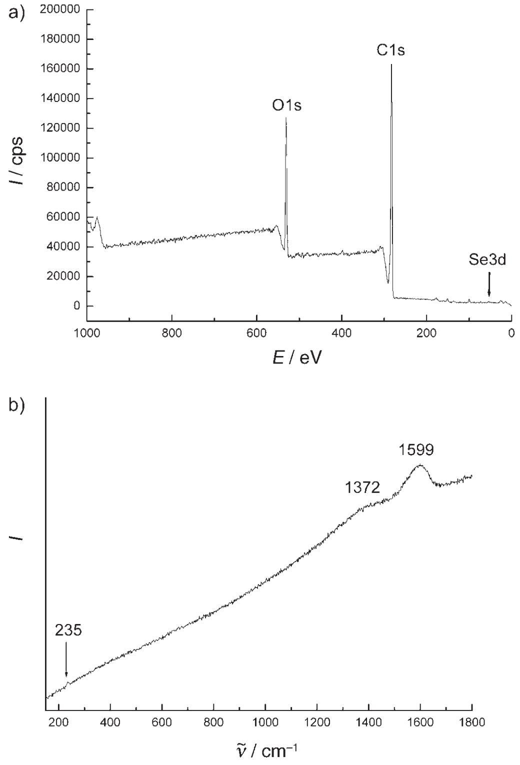


Figure 3. a) XPS and b) Raman spectra of the Se/C core–shell submicrowires obtained at 170 °C over 24 h.

UV/Vis spectroscopy was also used to characterize the Se/C core–shell submicrowires obtained. The absorption spectrum shows a very broad absorption band with a maximum at 502 nm and the absorption edge at around 670 nm (see Supporting Information, Figure S3), which is consistent with previous reports for Se 1D nanostructures.[21b,25] The result indicates that the outer carbon shell of the as-prepared core–shell submicrowires have little effect on the optical properties of the inner Se nanowire core.

According to all the above analyses, it is confirmed that Se/C 1D core–shell structures were successfully synthesized by the mild one-step hydrothermal process. As the carbon shell can protect the Se nanowire core from contamination and has little effect on its optical properties, the Se/C core–shell submicrowires might perform better in potential optoelectronic nanodevices relative to naked Se nanowires.

Formation Process of Se/C Core–Shell Submicrowires

To understand the formation process of the Se/C core–shell submicrowires, the products obtained at different stages were examined by TEM. Figure 4a–d shows the TEM images of the products obtained after different reaction times (3, 6, 12, and 20 h). Figure 4a reveals that the sample is composed of wirelike products, which indicates that a large quantity of Se nanowires were formed in a short reaction time (3 h). The inset of Figure 4a is a high-magnification TEM image of the edge of a Se nanowire. From the figure, no obvious shell can be observed on the outside of the nanowires. When the time of the hydrothermal process was prolonged to 6 h, carbon particles and a thin shell with a thickness of several nanometers appeared on the outside of the Se nanowires (Figure 4b), which indicates that the carbonization of ascorbic acid had taken place. With a further increase in reaction time (12 and 20 h), the shell of the products gradually became thicker (Figure 4c and d). In general, these TEM images demonstrate that the products were only Se nanowires at the early stages of the reaction. Later, the Se nanowires were enclosed by a carbon layer whose thickness gradually increased through continuous carbonization of ascorbic acid.

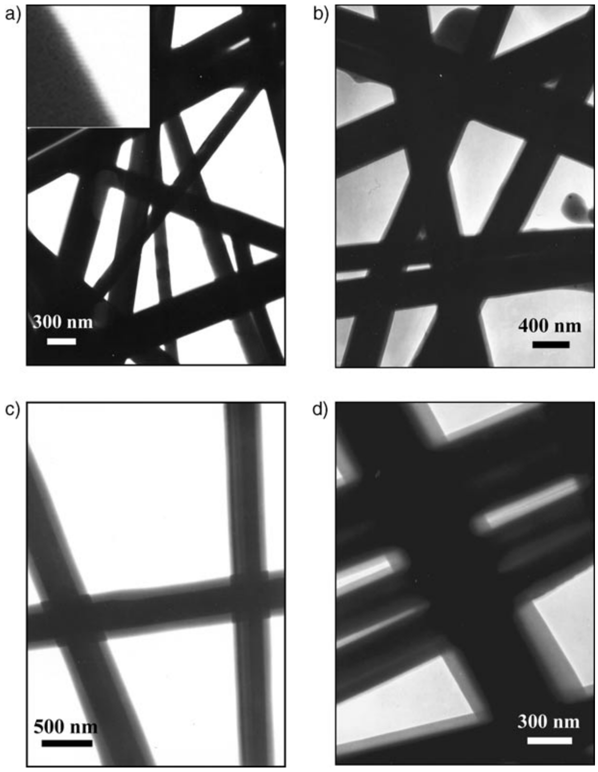


Figure 4. TEM images of the products obtained at 170 °C after reaction times of a) 3, b) 6, c) 12, and d) 20 h. Inset of a): high-magnification TEM image of the edge of an Se nanowire.

Futhermore, it was proved that the presence of CTAB in our reaction system is an important factor in the formation of the Se/C core–shell submicrowires through a contrasting experiment without CTAB. When ascorbic acid was added to the solution of Na_2SeO_3 with vigorous stirring, the liquid changed rapidly from colorless to red, which indicates that amorphous selenium (a-Se) was generated in the solution by Equation 1. Interestingly, we obtained a clear red solution and a turbid liquid (Figure 5a and b), which corresponds to the presence and absence of CTAB in the liquid, respectively. The two liquids were further stirred for 10 min. The solution with CTAB remained clear and transparent (Figure 5c). However, the liquid without CTAB changed markedly from red and turbid to colorless and clear, while a mass of brick-red particles precipitated at the bottom of the beaker (Fig-

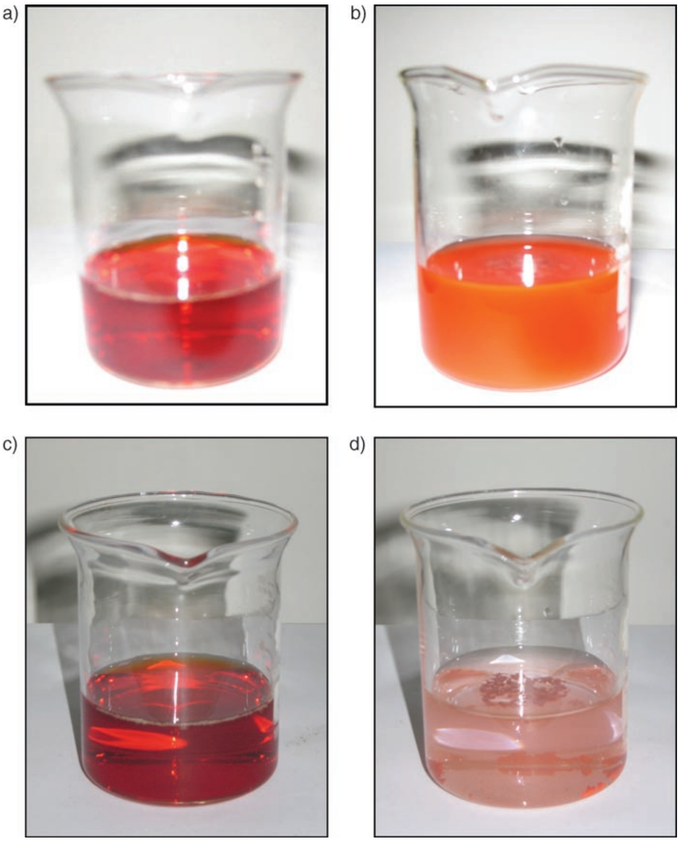


Figure 5. The state of the reaction mixture when ascorbic acid was added to a solution of Na_2SeO_3 under vigorous stirring in the a) presence and b) absence of CTAB. c) and d) The respective mixtures after being stirred for 10 min.

ure 5d). This means that a-Se congregated into large particles and separated out from the liquid phase. The mixture (liquid and precipitates) was further treated under the same experimental conditions (170 °C for 24 h). After the hydrothermal process, the resultant products were large particles, not the wirelike floccules of the typical experiment. The result reveals that the core–shell submicrowires could not be obtained without CTAB in the reaction system. As a cationic surfactant, CTAB was demonstrated to be easily adsorbed onto the surfaces of nanoparticles.[26] From previous reports and our experimental observations, we believe that CTAB adsorbed onto the surfaces of the initially formed a-Se nanoparticles and made them well-dispersed in solution. Thus, the presence of CTAB prevented the aggregation of a-Se nanoparticles into larger particles and assisted the formation of a homogeneous and stable reaction system in the initial stage. This homogeneous reaction system offered the right circumstances for the transformation of a-Se nanoparticles into t-Se nanowires. The transformation process has been investigated intensively in similar colloidal and emulsion systems.[10a,21a,27]

On the basis of the above experimental results, it can be rationally concluded that the formation of the Se/C core–shell submicrowires includes three processes: 1) Initially, ascorbic acid reacts rapidly with SeO_3^{2-} to generate red a-Se nanoparticles at room temperature. The a-Se nanoparticles are homogeneously and stably dispersed in water to form a clear solution with the assistance of CTAB, which has been demonstrated in our work to be an important factor in the formation of the core–shell submicrowires. 2) The a-Se particles are completely transformed into t-Se nanowires under hydrothermal conditions. Because the transformation is a less time-consuming process, ascorbic acid is not fully carbonized to form the carbon shell. Only Se nanowires are obtained in this stage. 3) With extension of the hydrothermal time, carbonization of ascorbic acid takes place and leads to deposition of carbonaceous products on the surfaces of the Se nanowires to form a carbon shell, thus resulting in the formation of the Se/C 1D core–shell structures.

As the Se nanowires form first and the ascorbic acid molecules dispersed in solution then adsorb onto the surfaces of the nanowires, the Se nanowires serve as templates for the carbonization of ascorbic acid on their surfaces. Under hydrothermal conditions at 170 °C, the ascorbic acid molecules adsorbed onto the Se nanowires carbonized to form a carbon shell, and then the ascorbic acid molecules dispersed in solution gradually diffused to the neighborhood of the Se nanowires and carbonized to increase the thickness of the carbon shell. The presence of the Se nanowires in the carbonization process of ascorbic acid can effectively promote the deposition of carbon that conforms to the surfaces of the Se nanowires instead of the formation of random carbon clusters. This process is similar to that in the literature, in which Te nanowires were used as templates to fabricate uniform Te/C core–shell nanowires.[15] As the formation of the carbon shell occurs through continuous carbonization of ascorbic acid and deposition of carbon on the surfaces of the Se nanowires, we believe that the thickness of the carbon shell can be easily adjusted by controlling the deposition time or deposition quantity of carbon. Figure 4b–d confirms that Se/C core–shell submicrowires with different shell thicknesses can be obtained by changing the deposition time of carbon. The deposition quantity of carbon on the surfaces of the Se core can be adjusted by changing the concentration of ascorbic acid. Further experiments also confirmed our hypothesis that the shell size of the Se/C core–shell submicrowires becomes more diverse when the concentration of ascorbic acid is altered. Figure 6 shows the TEM images of the products obtained under the same conditions except with different quantities of ascorbic acid. When 0.06 g of ascorbic acid was used, we obtained only Se nanowires (Figure 6a), because not enough ascorbic acid was carbonized to form the carbon shell. By increasing the amount of ascorbic acid to 0.8 g, the shell thickness became close to that of the products in the typical experiment (with 0.6 g ascorbic acid) (Figure 6b). As expected, the shell was clearly thicker when the amount of ascorbic acid was further increased to 1.2 g (Figure 6c). Because ascorbic acid was in excess, a large amount of carbon was gained and deposited on the surfaces of the Se nanowires. With the thickness of the carbon shell continuously increasing, several Se nanowires nearby became connected by the carbon shells to form Se/C core–shell bundles in a parallel manner (Figure 6c).

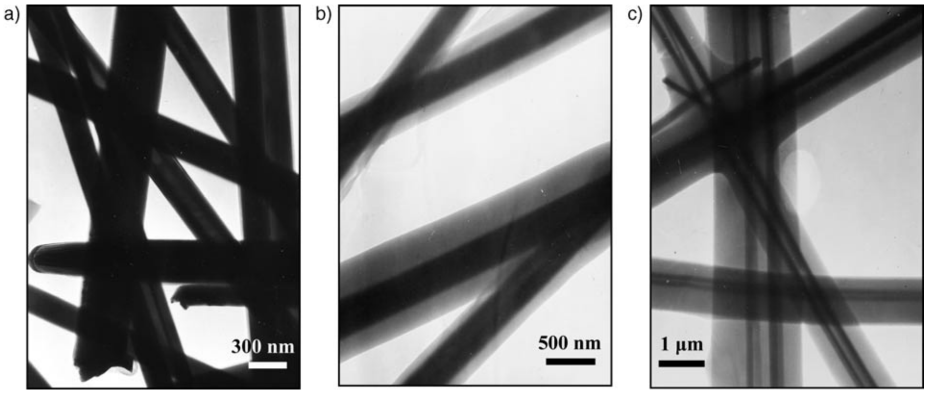


Figure 6. TEM images of the products prepared from 0.3 mmol Na_2SeO_3 with a) 0.06, b) 0.8, and c) 1.2 g of ascorbic acid.

Synthesis and Characterization of Carbon Submicrotubes

Carbon submicrotubes were obtained by soaking the as-synthesized Se/C core–shell submicrowires in pure liquid hydra-

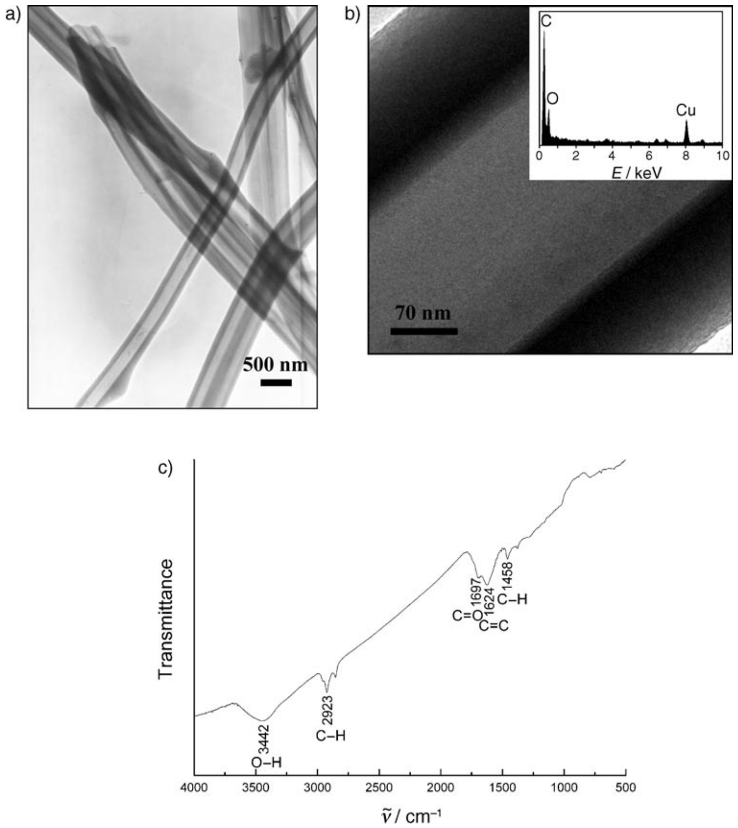


Figure 7. a) TEM images and b) HRTEM images of the carbon submicrotubes after removal of the Se nanowire core by soaking the Se/C core–shell submicrowires in pure $N_2H_4\cdot H_2O$ for 3 h. Inset of b): EDX spectrum taken from the submicrotube. c) FTIR spectrum of the carbon submicrotubes.

zine monohydrate ($N_2H_4\cdot H_2O$, 85%) for 3 h to eliminate the Se core, because Se has high solubility in $N_2H_4\cdot H_2O$. The typical TEM image in Figure 7a clearly displays the tubular structure of the sample. In Figure 7b, the HRTEM image further shows that there is nothing in the interior of the submicrotube, and that the thickness of the tube wall is about 0.1 μm. The energy-dispersive X-ray (EDX) spectrum taken from this submicrotube is also shown in the inset of Figure 7b. Because there are no characteristic peaks of Se ($L_\alpha = 1.38$, $L_{\beta 1} = 1.42$ keV) in the EDX spectrum, it confirms that the submicrotubes are composed of only carbon (the Cu peaks came from the copper grid). Fourier transform infrared (FTIR) spectroscopy was used to detect the functional groups present in the carbon submicrotubes (Figure 7c). The broad bands at about 3442, 2923, and 1458 cm^{-1} could be attributed to O–H bond vibrations and C–H bonding.[28,29] The absorption bands at 1710 and 1620 cm^{-1} are ascribed to the C=O and C=C vibrations,[30] respectively, which also supports the concept of carbonization of ascorbic acid during hydrothermal treatment.

The above analyses show that the carbon submicrotubes retain the same morphology and shell size as the Se/C core–shell submicrowires; this is because the carbon submicrotubes were acquired only by soaking the Se/C core–shell submicrowires in $N_2H_4\cdot H_2O$ at room temperature. We have demonstrated that the shell thickness of the Se/C core–shell submicrowires can be tuned by changing the experimental conditions, such as reactant concentration and reaction time. Therefore, the size of the carbon submicrotubes could also be easily tailored by adjusting the initial size of the Se/C composites. Furthermore, the presence of large numbers of functional groups may widen the application of the carbon submicrotubes in biochemistry and biomedicine.

Conclusions

In summary, a simple and environmentally friendly one-step solution process has been designed for the synthesis of Se/C core–shell submicrowires. Carbon submicrotubes can also be produced by dissolution of the Se core of the as-prepared core–shell submicrowires at ambient temperature. Investigation of the formation process of the Se/C core–shell submicrowires demonstrated that a-Se was first formed and homogeneously dispersed in solution through the assistance of CTAB, after which it was transformed into t-Se nanowires in a short time with hydrothermal treatment. Finally, ascorbic acid carbonized on the surfaces of the Se nanowires to form the Se/C core–shell structures. The results of the investigation and the practical experiments confirmed that the shell thickness of the Se/C core–shell submicrowires, as well as that of the carbon submicrotubes, could be tuned by controlling the reaction conditions. The properties of the Se/C core–shell submicrowires and the carbon submicrotubes are expected to find potential application in nanodevices and biomedicine, among other fields. Moreover, because the synthetic approach is effective, we expect that it could be extended to the fabrication of other semiconductor/carbon or metal/carbon core–shell structures. Further work in this area is under way.

Experimental Section

Synthesis of Se/C Core–Shell Submicrowires

All reagents were of analytical grade (Shanghai Chemical Reagents, Co.) and were used without further purification. A typical procedure is as follows: Na_2SeO_3 (0.3 mmol) was dissolved in a solution of CTAB (5 mM, 40 mL) to form a clear solution. Ascorbic acid (0.6 g) was then added to the solution under vigorous stirring. The mixture changed rapidly from colorless to clear red, thus indicating the formation of a-Se. After the solution was stirred for a further 10 min, it was transferred into a teflon-lined autoclave (55-mL capacity), which was maintained at 170 °C for 24 h. After the mixture was cooled to room temperature, a large quantity of black floccules was collected by centrifugation and cleaned by several cycles of centrifugation/washing/redispersion in distilled water and absolute ethanol. Finally, the products were dried in vacuum at 50 °C for 6 h.

Synthesis of Carbon Submicrotubes

The as-synthesized Se/C core–shell submicrowires were dispersed in $N_2H_4{\cdot}H_2O$ (30 mL, purity: 85 %). The mixture was left at room temperature for 3 h, after which it was centrifuged to isolate the products. The products were washed by distilled water and absolute ethanol three times, and were then dried in vacuum at 50 °C for further characterization.

Characterization

The products were characterized by powder XRD with a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.541781$ Å). FESEM images were taken on a JEOL JSM-6700F scanning electron microscope. TEM images were taken with a Hitachi H-800 transmission electron microscope at an accelerating voltage of 200 kV. HRTEM images and the corresponding SAED patterns were recorded by using a high-resolution transmission electron microscope operating at 200 kV (JEOL-2010). EDX spectra were recorded with a JEOL-2010 high-resolution electron microscope equipped with an EX24095JGT energy-dispersion X-ray fluorescence analyzer. Raman spectroscopy was performed at room temperature with a LABRAM-HR Confocal Laser MicroRaman spectrometer with an argon ion laser at an excitation wavelength of 514.5 nm. XPS spectra were collected on an ESCALAB 250 VG Lited X-ray photoelectron spectrometer with nonmonochromated $Al_{K\alpha}$ ($h\nu = 1486.6$ eV) X-rays as the excitation source. FTIR spectra were recorded on a Bruker EQUINOX55 FTIR spectrometer over wavenumbers of 500–4000 cm^{-1} at room temperature. The samples were pressed into disks with KBr. Absorption spectra were collected on a UV/Vis spectrophotometer (Shimadzu UV-240) at room temperature.

Acknowledgements

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