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Chitosan as Morphology-directing Agent for the Preparation of Multiarmed Selenium/Carbon Coaxial Nanorods

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A facile approach for the synthesis of multiarmed selenium/carbon (Se/C) coaxial nanorods by using chitosan as morphology-directing agents and selenious acid as the Se source has been demonstrated in the present study. Multiarmed Se/C nanorods, consisting of I-, Y-, T-, and cross-shaped configurations, were prepared by controlling the temperature and the ratio of amount of chitosan and Se in the reaction systems.

Nanomaterials have stimulated intensive research interest owing to their unique applications in mesoscopic physics and the fabrication of nanoscale devices.[1] The basic rationale is that nanoscaled materials have optical, magnetic, or structural properties that are not available from molecules or bulk solids.[2] Apart from colloidal nanocrystals, the synthesis of branched and multiconnection nanocrystals, like multiarmed nanoscale materials, has also been considered an attractive focus by many researchers in the fields of chemistry, electronics, and life sciences.[3] Selenium (Se) is a trace element with wide commercial applications, due to its novel physical properties, such as photoconductivity and thermoelectricity.[4] Much effort has been devoted to fabrication of Se nanomaterials by using physical vapor deposition, vapor phase diffusion, and wet chemical methods.[5] However, the synthesis of branched and other morphology nanocrystals is still a significant and challenging research subject.[6] Therefore, the search for simple and environment friendly routes to fabricate branched Se nanomaterials still constitutes an urgent priority. Recently, biomacromolecules have been used in precise shape-controlled synthesis of Se nanomaterials.[7] Polysaccharides are large macromolecules with a high diversity of molecule structure and could be used as a soft template for synthesis of nanomaterials. Chitosan, a cationic polysaccharide, has been found able to fabricate Au, Ag, ZnS, and CdS nanomaterials.[8–10] Our previous work showed that microalgal polysaccharides demonstrate abilities to control the morphology of Se nanoparticles (Nano-Se).[11] Herein, we report the synthesis of multiarmed Se/C nanorods by using a facile solution-phase approach.

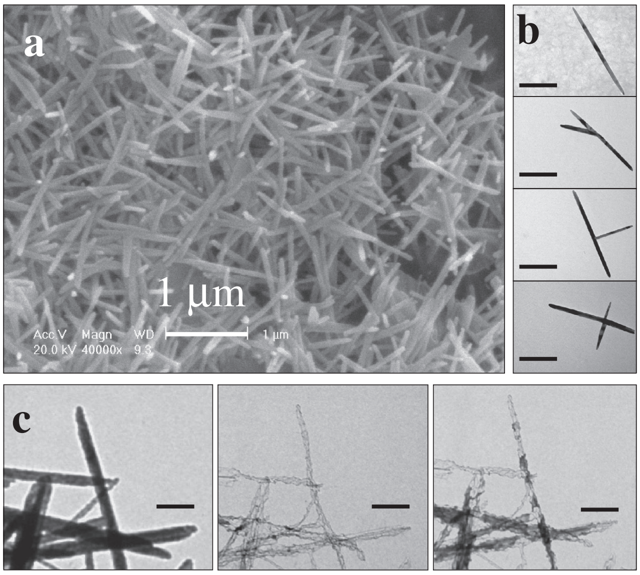

Figure 1. (a) SEM image of multiarmed Se/C nanorods. (b) TEM images of the same MNRs. (c) TEM images of the same MNRs exposed to electron beam irradiation for 30, 60, and 90 s (from left to right). (b and c) Scale bar is 200 nm.

Figure 1 shows the morphological characterization of multiarmed Se/C nanorods (MNRs) prepared by aging a solution containing 5 mM H_2SeO_3, 20 mM ascorbic acid, and 0.04% chitosan with molecular weight of 60000 and deacetylation degree of 90%, at 65 °C for 72 h. As can be seen from SEM (Figure 1a), the multiarmed morphology of MNRs has been achieved in large quantities and have a width of about 100 nm as well as length up to several micrometers. TEM images (Figure 1b) also confirmed that MNRs in I-, Y-, T-, and cross-shaped configurations were produced. Moreover, it is very interesting to find that under the TEM electron beam, the morphology of MNRs finally changed from a black and plump structure to white and empty rods in a time-dependent manner (Figure 1c) by exposing to electron beam irradiation for 30, 60, and 90 s, which suggests that Se atoms in the nanorods evaporated gradually.

The products were also characterized by XRD, Raman spectroscopy, and SEM-EDX. Figure 2a shows a typical XRD pattern of trigonal Se (t-Se). All the sharp and strong diffraction peaks can be readily indexed to reported data (JCPDS card No. 06-0362, $a = 4.3662$ Å and $c = 4.956$ Å). A thermodynamically stable t-Se is expected to favor growth along the ⟨100⟩ direction and eventually lead to the formation of one-dimensional nanostructures. As demonstrated in Figure 2a, the ⟨100⟩ diffraction peaks were stronger than others, which indicate that the MNRs preferentially grew along this direction. Figure 2b presents the Raman spectrum of the as-prepared MNRs. An intensive resonance peak at 237 cm^{-1} was assigned to the stretching vibration mode (A1 mode) of a helical chain-like structure that only exists in the t-Se phase.[12] The peak at 146 cm^{-1} corresponds to the transverse optical phonon mode (E mode). The peaks at 439 and 458 cm^{-1} were the second-order spectra of t-Se.[12,13] An elemental composition analysis employing SEM-EDX (Figure 2c) showed the presence of a strong signal from the Se atoms (87.01%), together with C atom signal (12.99%) that may be from chitosan. No obvious peaks for other elements or impurities were observed. Taken together, the results of SEM-EDX (Figure 2c) and TEM (Figure 1c) suggest that the

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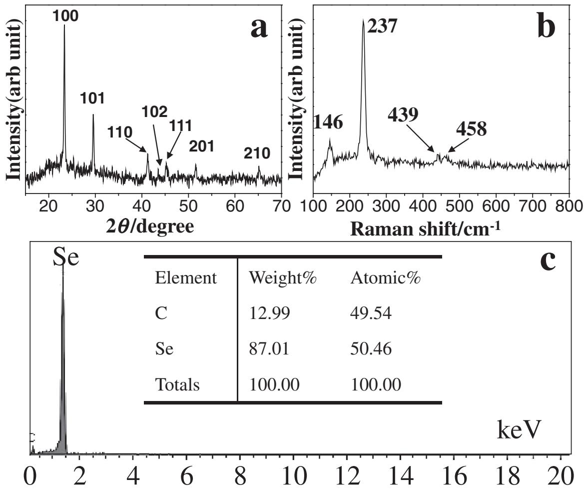

Element	Weight%	Atomic%
C	12.99	49.54
Se	87.01	50.46
Totals	100.00	100.00

Figure 2. (a) XRD pattern, (b) Raman spectra, and (c) SEM-EDX analysis of MNRs.

Se/C nanorods are coaxial structure and that their surface is covered by chitosan. The inner Se cores could be also released from the carbonaceous layers in the gas phase under the strong-energy electron beam.

During a series of experiments, we found that when the same reaction system was aged at 80 °C for 18 h, many big solids were deposited at the bottom and could not be dispersed again. In addition, the amount of chitosan also plays a vital role in the formation of final morphology. When 0 mL of chitosan is used instead of 1 mL of chitosan (1%) and other conditions remained the same (aging duration 10 h), we only got aggregated clusters (Figure 3a). On further study, the amount of chitosan was changed to 0.2 mL. A large number of rough nanorods were formed (Figure 3b). When the amount of chitosan in the reaction system was increased to 5 mL and other conditions were the same, we got a mixture of nanoparticles and nanorods (Figure 3c). In order to confirm the role of chitosan, 1 mL of PVP (1%, molecular weight: 30000) instead of chitosan was added to the reaction system and other conditions were not changed. However, only some irregular products were observed (Figure 3d). These results suggest that the chemical structure and the physicochemical properties of chitosan might play key roles in the growth of the Se nanostructures. Hydroxy groups on the surface of chitosan could react with SeO_3^{2-} groups to form special chain-shaped intermediates, which could decompose to form Se crystals upon reduction with ascorbic acid. Furthermore, the initial colloid system could be nucleated in the template provided by chitosan, then assembled into MNRs via metastable states in the system during the aging step.

In conclusion, a facile solution-phase approach for the synthesis of multiarmed Se/C coaxial nanorods (consist of I-, Y-, T-, and cross-shaped configurations) by using chitosan as morphology-directing agents has been demonstrated in the present study. The materials could be prepared by controlling the temperature and the ratio of Se and chitosan in the reaction systems. This study is significant in that it provides a greener and more environment-friendly synthesis method with lower cost to prepare multiarmed Se/C nanorods, and no organic solvents are needed. The prepared coaxial nanomaterials are constructed of the core (Se) and the shell (C), which could combine the advantages and distinctive properties of Se and C, and manipulate the surface functions of the nanomaterials to meet diverse application requirements, for instance, in drug delivery and nanodevices as electronic parts or sensors.

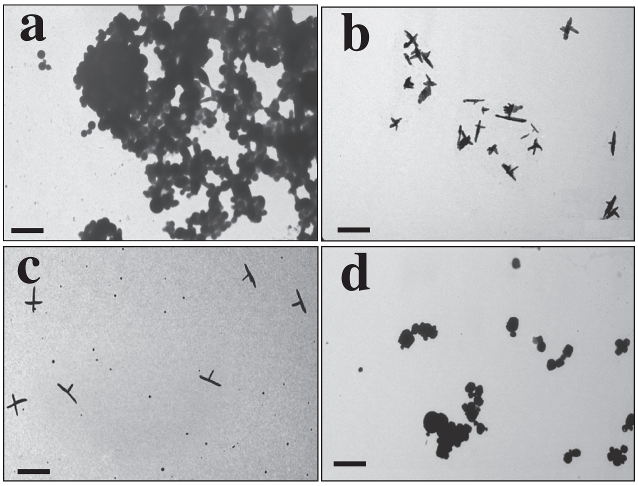

Figure 3. (a, b, c) TEM images of Se products at different amount of chitosan, (a) 0 mL chitosan (1%), (b) 0.2 mL chitosan, (c) 5 mL reacting amount of chitosan and and other conditions were not changed. (d) TEM image of Se products using 1 mL PVP (1%) instead of chitosan and other things being equal. Scale bar: 500 nm.

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