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Note

Agarose and gellan as morphology-directing agents for the preparation of selenium nanowires in water

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ABSTRACT

Commercially available polysaccharides, agarose and gellan, were used as morphology-directing agents for the synthesis of t-Se nanowires in water at room temperature in the presence of ascorbic acid as reducing agent. The nanostructures were characterized using XRD, SEM, and TEM. The diameter of the nanowires varied from 100 to 208 nm for nanowires obtained in the presence of agarose and from 51 to 145 nm for nanowires from gellan, as evidenced by SEM and TEM. Agarose and gellan have then a potential as environmentally acceptable morphology-directing agents to generate Se nanostructures in water.

Preparation of one-dimensional (1D) nanostructures has attracted recently much attention due to their potential application in nanodevices.[1] Several methods have been developed for the synthesis of nanomaterials, involving microwaves,[2] or shape control by surfactants.[3,4] More recently, biomacromolecules have been used to generate 1D nanomaterials.[5]

Polysaccharides are large macromolecules, involving a high diversity of molecular architectures, which might be used as templates. Among them, agarose is an excellent gel-forming polysaccharide produced by red seaweeds. Its repeating unit is →3)-β-D-Gal*p*-(1→4)-3,6-An-α-L-Gal*p*-(1→. Gellan is a gel-forming and texturing anionic microbial heteropolysaccharide consisting of →3)-β-D-Glc*p*-(1→4)-β-D-Glc*p*A-(1→4)-β-D-Glc*p*-(1→4)-α-L-Rha*p*-(1→. Several reports have recently focussed on the synthesis of Te[5c,d] or $YBa_2Cu_4O_8$ (Y124)[5b] nanowires using commercial polysaccharides.

Selenium is an important elemental semiconductor exhibiting interesting physical properties with commercial applications.[6] Several methods have been developed to obtain Se nanowires under various experimental conditions.[7] Especially, it has been recently reported that a commercially available cyclic oligosaccharide, cyclomaltoheptaose (β-cyclodextrin), could be used for the preparation of Se nanowires having a pure trigonal phase by using ascorbic acid as the reducing agent.[7b] In this study, we investigated the morphology-directing capabilities of agarose and gellan for the synthesis of Se nanowires using ascorbic acid as the reducing agent in water at room temperature following the reaction scheme in (a):

$$H_2SeO_3 + 2C_6H_8O_6 \rightarrow Se\downarrow + 2C_6H_6O_6 + 3H_2O \qquad (a)$$

A brick-red suspension was observed soon after solutions of SeO_2, and the polysaccharides were poured into the solution containing ascorbic acid, indicating the formation of amorphous Se.[7b,i] After 12 h stirring, the precipitate was collected and allowed to age in ethanol. The product crystal phase was confirmed by X-ray diffraction (XRD). In Figure 1, all the diffraction peaks could be indexed to a single phase of the trigonal-structured Se with lattice constants of $a = 4.370$ Å and $c = 4.947$ Å for the wire directed by agarose (Fig. 1a) and of $a = 4.365$ Å and $c = 4.952$ Å for the product of gellan (Fig. 1b) (JCPDS 06-0362). These patterns indicate that both polysaccharides in aqueous solution at room temperature clearly act as morphology-directing agents for the synthesis of the Se nanowires during the reduction step by ascorbic acid.

The morphology of the Se nanostructures was also investigated using SEM. Figure 2 shows representative SEM images, displaying the general morphology of the Se nanowires prepared in the presence of agarose (Fig. 2a) or gellan (Fig. 2b). Mixtures of amorphous Se and short Se rods[7b] were just observed when no polysaccharide was added.

The morphology and structure of the Se nanowires were further investigated by TEM. Figure 3 shows TEM images of the nanowires

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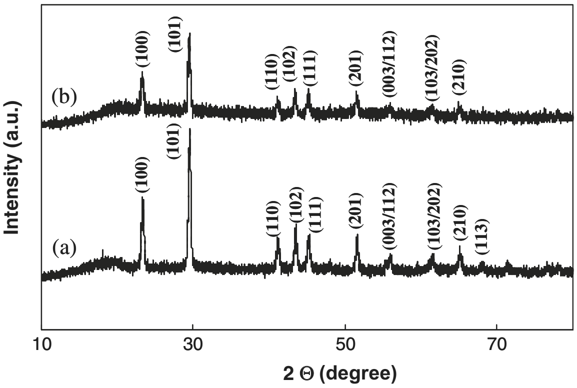

Figure 1. XRD patterns of the Se nanowires obtained using (a) agarose and (b) gellan and ascorbic acid as reducing agent in water at room temperature.

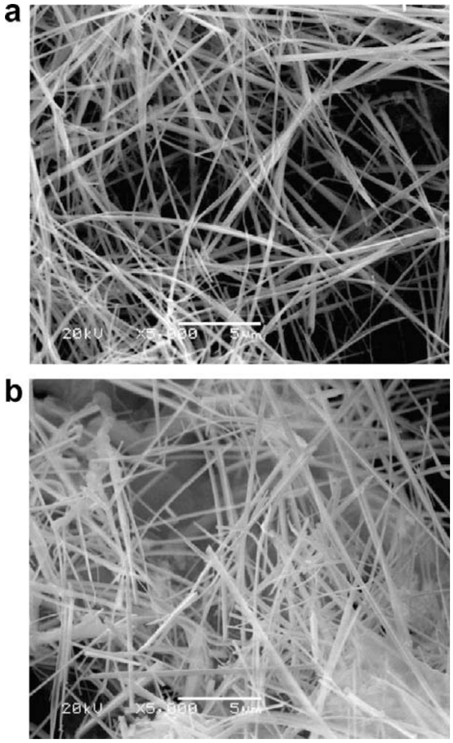

Figure 2. SEM images of the Se nanowires obtained from (a) agarose and (b) gellan gum.

prepared from agarose (Fig. 3a) or gellan (Fig. 3b). The bright and dark strips on the nanowires confirm the single crystal property of the wires.[7e] Selected area electron diffraction (SAED) patterns were taken on an individual nanowire obtained from agarose (Fig. 3c) or gellan (Fig. 3d), confirming the single-crystallinity of the Se nanowires and their preferential growth along the [001] direction. From these data, the nanowires are over several micrometers in length, consistent with the SEM results. The diameters of the nanowires varied in the range of 100–208 nm for the product in the presence of agarose and of 51–145 nm in the presence of gellan (Table 1).

We also investigated the morphology-directing ability of other commercially available polysaccharides, that is *i*-carrageenan, hyaluronate, and chondroitin sulfate, under the same experimental conditions but the three polysaccharides had no effect on the growth of the nanowires. The results suggest that molecular patterns and physicochemical properties of polysaccharides might play key roles in the successful growth of the Se nanostructures.

Though the growth mechanism of the highly anisotropic Se nanowires is not clearly elucidated, it is clear that agarose and

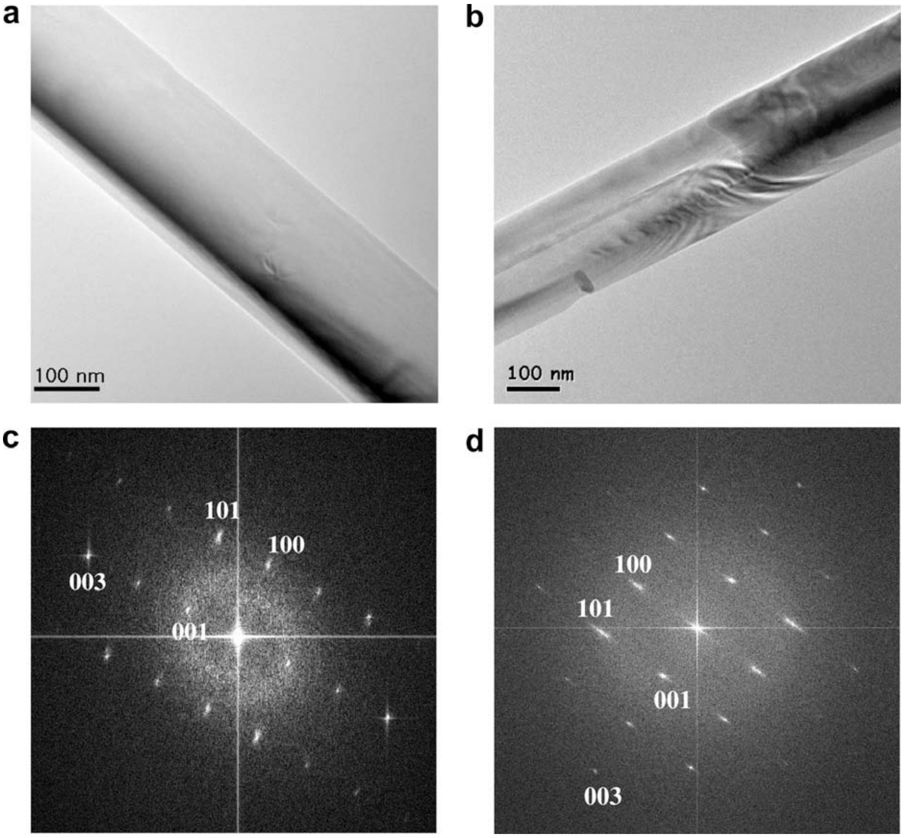

Figure 3. TEM images of an individual nanowire obtained from (a) agarose and (b) gellan and SAED patterns of an individual wire from (c) agarose and (d) gellan.

Table 1
Morphology and diameter of Se nanowires depending on polysaccharides

Carbohydrates	XRD	Diameter (nm)[a]
Agarose	Trigonal	100–208
Gellan gum	Trigonal	51–145
i-Carrageenan	–	–
Hyaluronate	–	–
Chondroitin sulfate	–	–

[a] The diameters were determined by TEM results.

gellan gum play critical roles in the process of nanowires formation. It is well known that linear polysaccharides interact with inorganic ions to form chain-shaped intermediates,[9] which might serve as a template for the synthesis of 1D nanomaterials. Also, hydroxyl groups on the surface of agarose or gellan gum could react with $SeO_3{}^{2-}$ groups to form chain-shaped intermediates, which could be decomposed to form Se crystals upon reduction by ascorbic acid. During the process, the growth of Se nanowires might occur through a phase-changing mechanism.[7b,i] In other words, amorphous Se colloids formed at the initiation step of the reaction could gradually dissolve in EtOH solution during the aging process. Considering their 3D structures, and hydrogen bonding ability in aqueous solution, we assume that the Se nanosystem could be nucleated in the template provided by agarose or gellan, then assembled into crystalline Se nanowires via metastable states[5b,7i] in EtOH during the aging step.

In conclusion, commercial polysaccharides such as agarose and gellan can function as morphology-directing agents for the synthesis of Se nanowires in aqueous solution in the presence of ascorbic acid as reducing agent. This method might be of interest in the fields of nano- or nanobiotechnologies.[8] We are planning to extend these results to the preparation of other elemental nanostructures.

1. Experimental

1.1. Chemicals

Agarose type II, chondroitin sulfate sodium salt, and hyaluronic acid potassium salt were purchased from Sigma–Aldrich Inc. (St. Louis, MO, USA), and gellan gum and *i*-carrageenan were purchased from Fluka Chemie AG (Switzerland). Selenium dioxide (SeO_2, purity >99.9%) was purchased from Sigma–Aldrich Co. Ultrapure water from a purification system and EtOH (HPLC-grade) were used in this study.

1.2. Preparation of the Se nanowires

The Se nanowires were prepared as previously described.[7b] In brief, SeO_2 (50 mg) and the polysaccharide (50 mg) were first dissolved in water (10 mL) and stirred for about 30 min at room temperature. The soln was added to aq ascorbic acid (10 mL, 0.028 M) and then stirred for 12 h at room temperature. After 12 h, the suspension was centrifuged and washed with water and EtOH several times. The samples were then suspended in EtOH and allowed to age for 6 h without stirring. After centrifugation, the samples were dried at room temperature.

1.3. Characterization of the Se nanowires

XRD was carried out on a Japan Rigaku Rotaflex diffractometer equipped with a rotating anode and using filtered Cu Kα radiation (λ = 1.54056 Å) in the $\theta/2\theta$ range of 10–80°. The SEM images were taken on a JEOL JSM 6380 scanning electron microscope. The TEM analysis was performed using a FEI TECNAI G2 transmission electron microscope with accelerating voltage of 300 kV.

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