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## Simultaneous inducing synthesis of semiconductor selenium nanorods and nanochains by garlic roots for live template

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In this article, multi-armed nanorods and nanochains of semiconductor selenium were simultaneously synthesised through living bio-membrane bi-templates of garlic at room temperature. The multi-armed nanorods are 60–80 nm in diameter and 1.0–1.5  $\mu\text{m}$  in length; the nanochains are made of a series of nanospheres and each nanosphere is 100–150 nm in its diameter. The X-ray diffraction pattern indicates that these nanocrystals were crystallised in the hexagonal structure and were of high purity. The possible formation mechanism is investigated in the article. It is expected the method reported here can be easily adapted to any future preparation of low-dimension nanomaterials.

**Keywords:** selenium; inducing synthesis, garlic roots; nanorods; nanochains

### 1. Introduction

As a compulsory trace element for humans, selenium plays important roles in biology and pharmacology. Supplements of selenium at proper levels can enhance immunity, prevent disease, delay aging and reduce the damage produced by heavy metals [1]. It has been reported that red selenium nanostructures exhibit unique properties [2], such as a relatively low melting point, high photoconductivity and reactivity and higher bio-reactivity than normal selenium. Selenium nanostructure plays such an important role in balancing metabolism and preventing cancers that it could become an ideal antioxidant and immunity regulator. As a result, there has been extensive interest in studying the red selenium nanomaterials [3–5].

So far, there have been many reports on how to prepare selenium nanomaterials, among which the templates approach has been canonised [6–10]. The structure and morphology of selenium nomaterial can be easily controlled through templates. However, the traditional templates method employs surfactants or catalysers, which make the synthesis process complicated and only a single product is produced. It is well known that teeth, bones and shells are the products of biological mineralisation by cells and these nano-dimensional materials are synthesised by the organism itself [11–13]. A living bio-membrane of animal and plant with orderly arrangement could control the effective

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transfer of inorganic ions and induce biological mineralisation, thus becoming an ideal bio-template to induce synthesis of nanomaterials. There are scarcely any reports on how to utilise living garlic systems to manipulate synthesis of one-dimensional nanomaterials, although living substances have been used before [14]. But with regard to the multi-armed nanorods and nanochains of semiconductor selenium, there has rarely been any report on their synthesis, let alone their simultaneous synthesis.

In this article, wonderfully, they were simultaneously synthesised by the bio-membrane bi-templates of the garlic. The nanorods are 60–80 nm in diameter and 1–1.5  $\mu\text{m}$  in length. The nanospheres are 100–150 nm in diameter and linked in series to form the nanochains. The possible formation mechanism was investigated in the article. It is expected the method reported here can be easily adapted to any future preparation of low-dimension nanomaterials.

## 2. Experimental

### 2.1. Reagents and instruments

Chemicals employed:  $\text{KBH}_4$  (94%), Selenium (99.95%), NaAc, HAc and absolute ethanol (A.R.) (purchased from the Shanghai Chemical Reagent Factory, China); garlic (purchased from the market).

Instruments employed: (1) TEM images and electron diffraction spectrum were carried out on Hitachi Model-800 transmission electron microscope. (2) Powder X-ray diffraction (XRD) pattern of sample was measured on 1710 XRD with Cu  $\text{K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) (Philips). (3) ESEM images were carried out on Quanta 200 FEG scanning electron microscope (FEL).

### 2.2. Experimental

- (1) 0.48 g  $\text{KBH}_4$  and 0.72 g Se were dissolved in 200 mL water to make the solution of  $0.2 \text{ mol L}^{-1}$   $\text{KHSe}$  [15]; mixing 100 mL of  $0.1 \text{ mol L}^{-1}$  NaAc solution with 100 mL of  $0.1 \text{ mol L}^{-1}$  HAc solution to make the HAc–NaAc buffer at  $\text{pH} = 4.74$ .
- (2) A garlic root was washed and immersed in de-ionised water for 2 h, and then was immersed in  $0.2 \text{ mol L}^{-1}$   $\text{KHSe}$  solution at under nitrogen for 3 h (Figure 1).
- (3) The garlic was taken out and washed with de-ionised water, then immersed in 200 mL  $0.1 \text{ mol L}^{-1}$  NaAc–HAc buffer, exposing it in the air for 12 h.
- (4) When the brown-red floccules bestrewed the root of the garlic, the garlic was taken out and washed with de-ionised water and absolute ethanol, respectively. Then, the products, from inside and outside of the root, were transferred into two beakers containing absolute ethanol.
- (5) The products were separated and repeatedly washed with distilled water and then with absolute ethanol.
- (6) The structure and the morphology of the products were characterised by TEM and XRD. In addition, SEM was used to examine the difference of the root bio-morphology between pre-reaction and post-reaction.



Figure 1. Garlic immersed in the solution of  $0.2 \text{ mol L}^{-1}$   $\text{KHSe}$ .

### 3. Results and discussion

#### 3.1. Measurements of structure and morphology

The products were dispersed in absolute ethanol and observed by TEM. Figure 2(a) shows the TEM micrograph of the products obtained from the inner side of the garlic root. Nanorods were obtained: the diameters of the nanorods ranged from about 60–80 nm and the lengths ranged from about 1–1.5  $\mu\text{m}$ . These nanorods were aligned in the shape of ‘T’. The selected area electron diffraction (SAED) pattern (inset Figure 2(a)) shows that these nanorods synthesised in the experiment are multi-crystalline in structure.

Figure 2(b) shows the TEM micrograph of the products from the outer side of the garlic root. The evenly distributed nanosphere is synthesised. The diameter of the nanosphere is about 100–150 nm. The nanospheres, one by one in a line, form a nanochain. Usually, it is very difficult to synthesise [16]. The nanochain is a novel structure and it has potential applications in the assembly of nanodevices. The nanosphere is an ideal lubricant material and can improve lubricant ability without environmental pollution. The SAED pattern (inset Figure 2(b)) shows that the nanospheres synthesised in the experiment are multi-crystalline in structure.

The XRD pattern (Figure 3) indicates that these nanocrystals of inner and outer products were of high purities and were crystallised in the hexagonal structure, which is consistent with JCPDS No. 6-0362.

#### 3.2. Choice of experimental conditions

The experiment shows that conditions have certain effect on the nanomaterial growth and morphology. (1) Generally, the higher the concentration is, the faster the reaction goes. However, the unevenly distributed nanospheres were formed outside the root with an average diameter of 500 nm when the concentration was higher than  $0.4 \text{ mol L}^{-1}$  (Figure 4(a)). On the other hand, the reaction went too slow when the concentration of the reaction was lower than  $0.1 \text{ mol L}^{-1}$ . Therefore, the concentration of the reaction was optimised from 0.1 to  $0.4 \text{ mol L}^{-1}$  and a concentration of  $0.2 \text{ mol L}^{-1}$  was chosen in this article. (2) A buffer with a pH value ranging from 4.5 to 6.5 is suitable for mineral

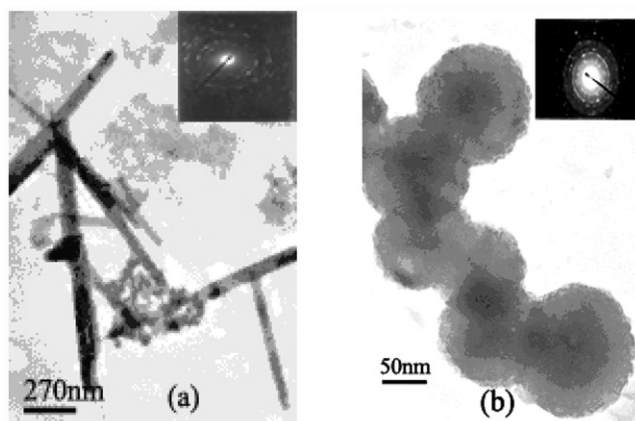


Figure 2. The TEM micrograph and SAED of Se nanomaterials. (a) Inner side of the garlic root; (b) Outer side of the garlic root.

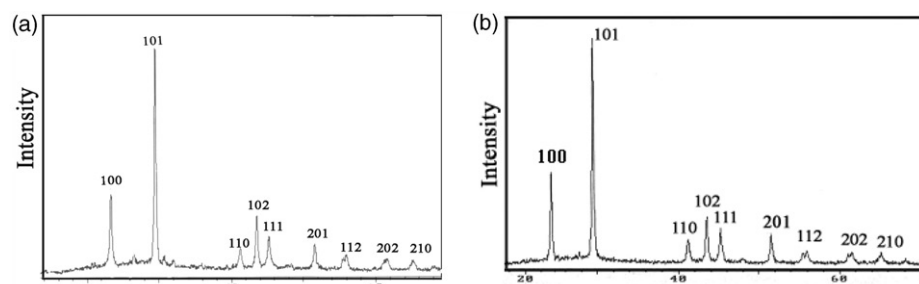


Figure 3. X-ray diffraction pattern of Se nanomaterials. (a) Inner products; (b) Outer products.

absorption and the formation of nanocrystals. In this article,  $0.1 \text{ mol L}^{-1}$  NaAc–HAc buffer (pH 5.0) was selected. According to our experiment, the Se crystallisation was affected when pH was too low; on the other hand, the nanomaterials with desired morphology could not be obtained when pH was too high. As shown in Figure 4(b), only some unevenly distributed nanoparticles were formed when the  $\text{NH}_3\text{--NH}_4\text{Cl}$  buffer with pH = 9.26 was selected. (3) Optimal temperature was found to be 20–30°C in order to keep the bio-template living and improve synthesis efficiency. (4) The length of time of immersing garlic in the  $0.2 \text{ mol L}^{-1}$  KHS solution was found to be optimal from 3 to 5 h, and  $0.1 \text{ mol L}^{-1}$  NaAc–HAc buffer was from 10 to 16 h.

#### 4. Synthetic mechanism

The synthetic mechanism of living bio-membrane templates is still unclear. According to the above experiment and relevant theories, the possible formation mechanism of selenium is proposed as follows:

The hydrophilic and hydrophobic groups in the active molecule on the bio-membrane play a key role in biological mineralisation. Figure 5 shows the ESEM of the internal and

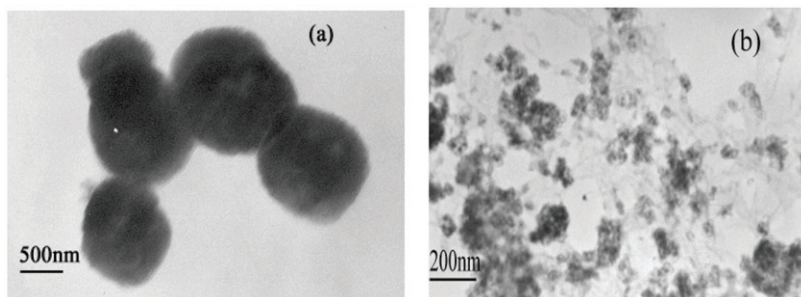


Figure 4. TEM micrograph of the outer products. (a) The concentration was  $0.4 \text{ mol L}^{-1}$ ; (b) The buffer was  $\text{NH}_3\text{-NH}_4\text{Cl}$ .

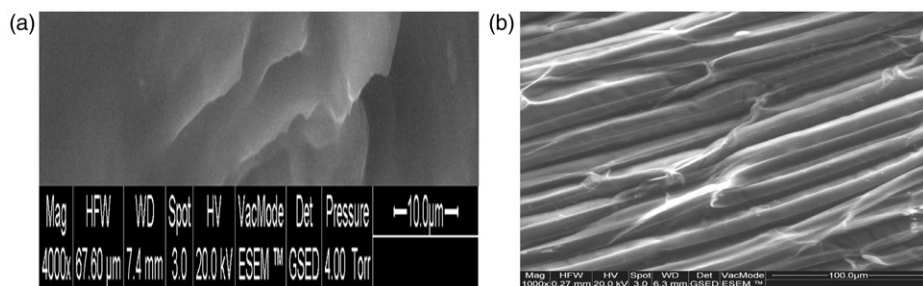


Figure 5. ESEM pattern of the root. (a) The interior; (b) The surface of the outer.

external surface of the root. The samples for SEM observation were sputter coated with gold. Figure 5 shows that the root surface is smooth and there are many vascular bundles in the stem. As a result, ions of reaction can transfer, penetrate into the membrane and be absorbed. The different surface structure of cell membrane thus provides different bio-membrane bi-templates for the synthesis of nanomaterials.

- (1) Due to the concentration gradient produced when garlic was immersed in the solution of  $\text{Se}^{2-}$  and aerated with nitrogen gas, some of  $\text{Se}^{2-}$  ions on the outside bio-membrane penetrated into the inside of the bio-membrane cells.
- (2) When the garlic, which absorbed  $\text{Se}^{2-}$  excessively, was immersed in the buffer without  $\text{Se}^{2-}$ , some  $\text{Se}^{2-}$  ions in it were released through the cell membrane. The  $\text{Se}^{2-}$  ions on the outer bio-membrane were oxidised into  $\text{Se}^0$  by the oxygen in the air immediately, while there was other  $\text{Se}^0$  simultaneously formed around its inner surface by oxygen, which had penetrated into the root.
- (3) Crystal nucleuses of  $(\text{Se})_n$  were formed with the increase of  $\text{Se}^0$  in the outer and inner surface of the root, the bio-membrane bi-templates continued to grow and the nucleuses were induced to grow into colloid nanoparticles as time increased. There was more oxygen on the external surface than on the internal surface. As a result, the nanoproducts with a different crystal nucleus number and particle radius were formed, corresponding to the structures of nanorods and nanospheres to form at 6 h (Figure 6).



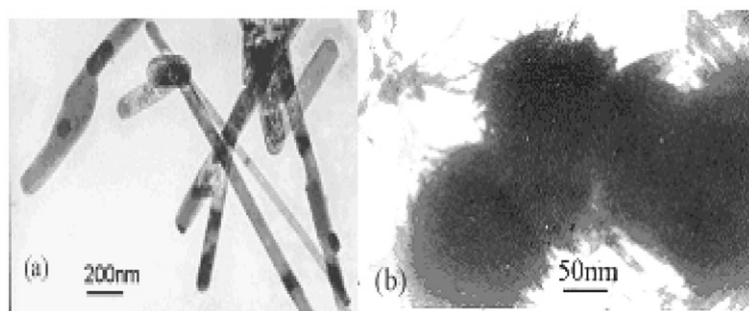


Figure 6. The TEM images of intermediate products. (a) Inner; (b) Outer.

- (4) Because the templates operating on the outer and inner membrane of garlic are different, nanorods and nanospheres were induced and self-assembled to grow into multi-armed nanorods in the shape of ‘T’ and nanochains, respectively.

## 5. Conclusions

Garlic is an ordinary vegetable. By taking advantage of its different structures between the outer and inner membrane and imitating its biological mineralisation process, the nucleation and growth of molecules are induced through a living bio-system. The garlic was kept alive throughout the experimental process. The method reported in this article is mild and convenient. Without using any surfactant or organic solvent though in a ‘balanced solution’, two morphologies and structures of selenium nanomaterials were simultaneously synthesised. It is expected that this method will play an important role in the future preparation of other new low-dimensional nanomaterials. The synthesis mechanism may be very complicated and further research is needed.

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