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ORIGINAL RESEARCH ARTICLE

Preparation and characterization of branched micro/nano Se

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ABSTRACT

Branched micro/nano Se was prepared by the redaction of L-Cys•HCl and H_2SeO_3 in hydrothermal method, as β-CD was used as soft template. The structures of products were characterized by SEM, TEM and XRD. Some important factors influencing the morphology of products were studied and discussed, including the amounts of soft template, the reaction temperature and the reaction time. The results showed that external causes had a potent effect on the morphology of micro/nano Se. The uniform branched micro/nano Se prepared under the optimal reaction condition was rhombohedral trigonal selenium t-Se^0, but its crystallinity degree was low.

Keywords: Branched Se; β-CD; Micro/Nanoparticles; Morphology; Rhombohedral Phase

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1. Introduction

Selenium is an important elemental semiconductor material with excellent photoelectronic and catalytic properties and is widely used in photosensitive elements, solar cells, ceramic coatings, functional catalytic materials and other application fields[1]. Meanwhile, as an essential trace element in human body, selenium has important physiological functions such as scavenging free radicals, antagonizing toxins, promoting reproduction, regulating metabolism and enhancing immunity[2]. In the traditional selenium supplement products, inorganic selenium and organic selenium have some disadvantages, such as higher toxicity, difficult absorption and high price. In contrast, nano-selenium has significant low toxicity and high efficiency, making it an ideal selenium source for selenium supplement preparations[3].

At present, the reported synthesis methods of nano-selenium mainly include template method, microemulsion method, ultrasonic chemistry method, temperature control method, interface chemistry method, etc.[4,5]. In this study, Se^0 was prepared by hydrothermal method with reductive L-Cys•HCl and H_2SeO_3, and β-CD was used as template agent to control the growth of Se^0 particles. The effects of surfactant dosage, reaction temperature and reaction time on the morphology, particle size and structure of micro-nano Se^0 were studied.

2. Materials and methods

2.1 Materials and instruments

Materials: SeO_2(A.R), L-Cys•HCl(A.R), food-grade β-CD, industrial alcohol, re-steam water, deionized water.

Instruments: S-4,800 scanning electron microscopy (HITACHI), FEI Tecnai G2 F20 transmission electron microscopy (JEOL), Y-4Q X-ray diffractometer (Dandong Ray), DHG-9101-3SA type air blowing drying oven (Shanghai SANFA), DS-8510DTH ultrasonic cleaning instrument (Shanghai SXSONIC), TGL-16A centrifuge (Jintan Huanyu), F1004B electronic balance (Shanghai YUEPING).

2.2 Experimental methods

L-Cys•HCl with a weight of 0.6306 g (4.0 mmol was placed in a reaction kettle. A certain amount of template β-CD solution (0.5 g/L) was dropped and shaken evenly, then 80 mL 0.05 mol/L H_2SeO_3 was added. At this time, n (L-Cys•HCl) : n (H_2SeO_3) = 1:1 in the reaction system. After shaking well, the product was placed in a drying oven with air blast and heated at constant temperature for a certain time. The product was ultrasonic cleaned with deionized water for 4 times, and then ultrasonic cleaned with industrial alcohol for 4 times. Se^0 product was obtained after centrifugation and natural drying. The effects of β-CD dosage, reaction temperature and reaction time on Se crystal morphology and crystal state were studied by single factor experiment.

3. Experiment and analysis

3.1 The influence of the ratio of reactant substance to the reaction rate

Fixed H_2SeO_3 dosage as 4.0 mmol (80 mL 0.05 mol/L); used different reactant molar ratios, namely, n (L-Cys•HCl) : n (H_2SeO_3) = 1:3, 2:3, 1:1, 4:3, 5:3, 2:1; no β-CD template was added, and the reaction was conducted at 110 °C. Three parallel experiments were conducted for each mole ratio, and the time of the solution turning into light orange was recorded and the average value was taken. The result is shown in **Figure 1**.

With the increase of the amount of L-Cys•HCl in the reactants, the discoloration time of the reaction solution is rapidly shortened within the range of 1:3 to 4:3 when the ratio of (L-Cys•HCl : H_2SeO_3) to the amount of reactants increases, indicating that the reaction speed is accelerated, but the ratio of the amount of reactants is greater than 4:3, the discoloration time basically remained unchanged, indicating that increasing the amount of L-Cys•HCl could not significantly accelerate the reaction rate.

3.2 Influence of the ratio of reactants to reactants on product yield

Fixed H_2SeO_3 dosage as 4.0 mmol (80 mL 0.05 mol/L); used different reactant molar ratio, namely n (L-Cys•HCl) : n (H_2SeO_3) = 1:3, 2:3, 1:1, 4:3, 5:3, 2:1; no β-CD template was added and the reaction was conducted at 110 °C for 2 h. Three parallel experiments were performed for each mole ratio. The product was cleaned by ultrasonic cleaning with deionized water once, and then by ultrasonic cleaning with industrial alcohol once. After natural drying, the product was weighed and the average yield was calculated. The result is shown in **Figure 2**.

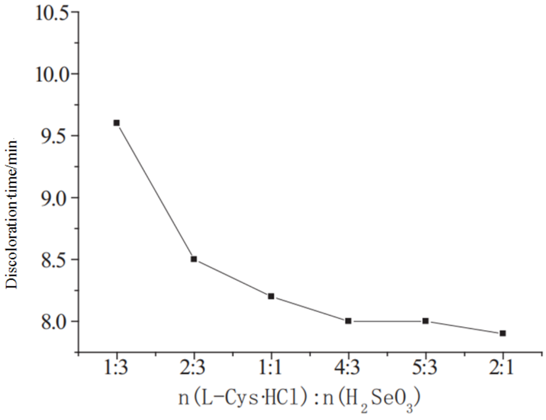

Figure 1. Effect of the ratio of reactants to substances on the reaction rate.

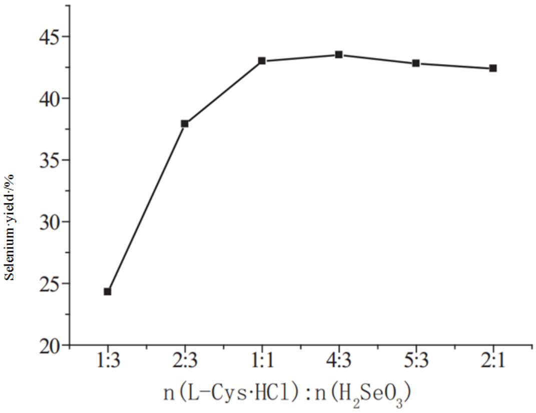

Figure 2. Effect of the ratio of reactants to substances on the yield.

With the increase of the dosage of L-Cys•HCl, the yield of reactant mass ratio *n* (L-Cys•HCl) : *n* (H_2SeO_3) was in the range of 1:3–1:1, but the increase rate gradually decreased. When the molar ratio of reactants was 1:1, the yield fluctuated slightly but did not increase significantly, indicating that the selenium in selenite could not be reduced by hydroxylamine hydrochloride under experimental conditions. Compared with the preparation of Se^0 by Vc and H_2SeO_3, the lower selenium yield in this method also confirms the weak reducibility of L-Cys•HCl. The fluctuation of yield after the molar ratio of 1:1 was related to the quality loss caused by cleaning products.

Based on the above facts, the molar ratio of the reactants *n* (L-Cys•HCl) : *n* (H_2SeO_3) = 1:1 is appropriate.

3.3 Influence of dosage of template agent on product morphology

Using the experimental method in 2.2, the reaction temperature was fixed at 110 °C and the reaction time was 2 h, and 0.5 g/L β-CD solution 0, 2.0, 4.0, 8.0, 16.0 ml (equivalent β-CD is 0, 1.0, 2.0, 4.0 and 8.0 mg) was added respectively, and the single factor comparison test is carried out. After ultrasonic cleaning, the product is detected by SEM, as shown in **Figure 3(a)** ~ **Figure 3(e)**.

The product prepared without β-CD was severely adhered selenium balls, similar to ginger cubes, as shown in **Figure 3(a)**. At this time, because there is no soft template in the reaction solution, the selenium grains cannot be stable after generation, and inevitably adsorb and combine with each other. In the deposition, the nucleation rate in solution is less than the nuclear growth rate, and the small-scale selenium nanoparticles cannot be obtained. When 2.0 mL β-CD solution was added, the aggregation and adsorption of selenium grains were prevented under the control of β-CD macromolecules, and the products were dispersed to a certain extent. At this time, dispersed selenium pellets were obtained, with cracks visible on the surface, as shown in **Figure 3(b)**. When 4.0 mL β-CD solution was added, selenium pellets increased and a large number of short selenium buds grew on some selenium pellets, as shown in **Figure 3(c)**. When 8.0 mL β-CD solution was added, the buds of selenium grew significantly and became selenium filaments. Some of the selenium filaments connected to each other and formed branched selenium, as shown in **Figure 3(d)**. When 16.0 mL β-CD solution was added, the selenium in the branches was significantly reduced and the diameter of selenium pellets was slightly increased, as shown in **Figure 3(e)**.

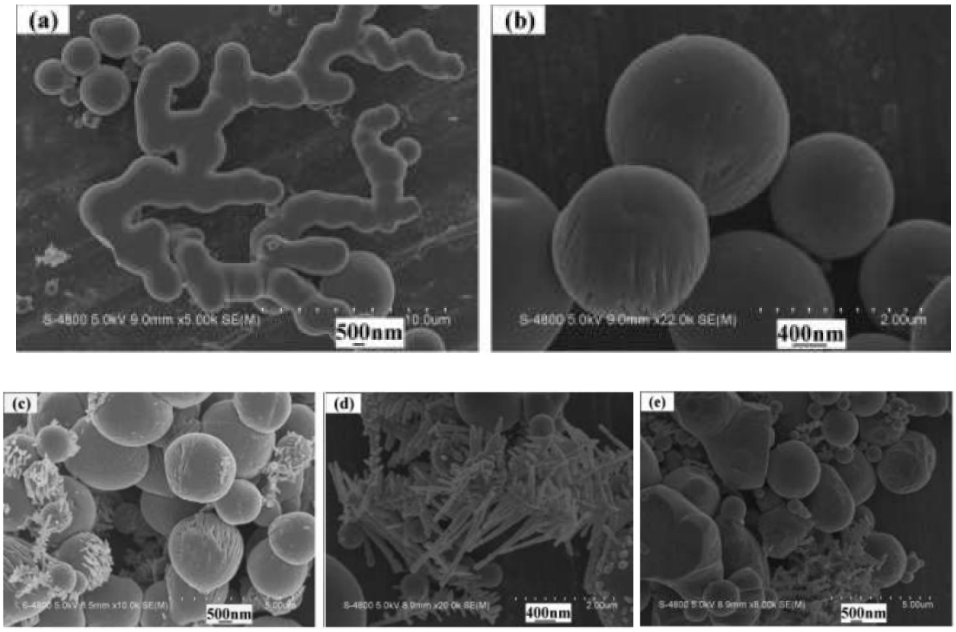

Figure 3. Effect of the amount of β-CD on the morphology of the product.

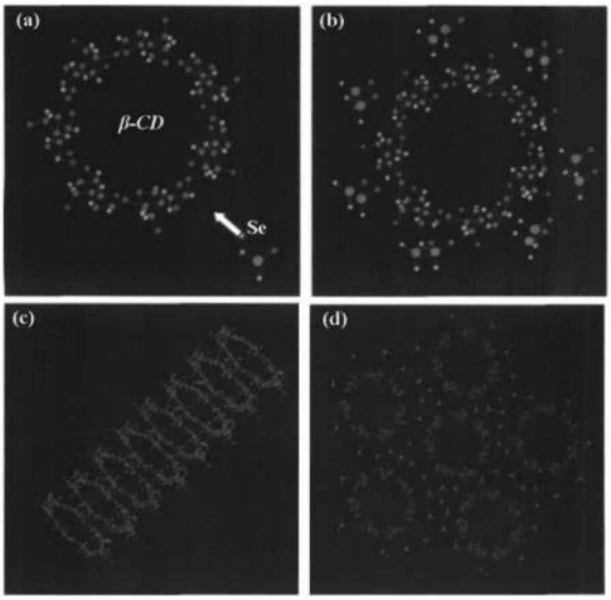

Figure 4. The self-assembly principle for β-CD adsorbing Se.

The appearance of selenium with the above morphology is related to the soft template β-CD, which has many hydroxyl groups in the structure, and its self-assembly principle is as follows[6]: the Se nuclei generated in aqueous solution preferentially adsorb on the active hydroxyl groups through hydrogen bonds (**Figure 4a**, **Figure 4b**), and complete self-assembly in two directions with the assistance of template agent β-CD. Among them, β-CD molecules interact longitudinally (**Figure 4c**), extending and assembling into a one-dimensional long chain structure as a whole. In the transverse direction (**Figure 4d**), under the guidance of its special inner hydrophobic and outer hydrophilic structure, β-CD assembles a planar two-dimensional structure. Finally, β-CD self-assembled into a three-dimensional ordered supramolecular shell, which became a reticular limiting template to guide the growth of selenium grains. Selenium nanocrystals are deposited and grown into selenium spheres. With the increase of the concentration of β-CD, the volume of the cross-linked macromolecules will increase, and the particle size of the selenium materials grown by its guiding limit will inevitably increase.

Based on the above experimental results, the optimal concentration of β-CD solution (0.5 g/L) was determined to be 8.0 mL (equivalent to 4.0 mg β-CD).

3.4 Influence of reaction temperature on product morphology

Using the experimental method described in step 2.2, the amount of soft template β-CD solution was 8.0 mL (equivalent to 4.0 mg β-CD). The reaction temperature was set at 90, 110, 130, 150, 170 °C for 2 h, and the single factor comparison test was conducted. The morphologic changes of ultrasonic cleaning products were shown in **Figure 5(a)** ~ **Figure 5(e)**.

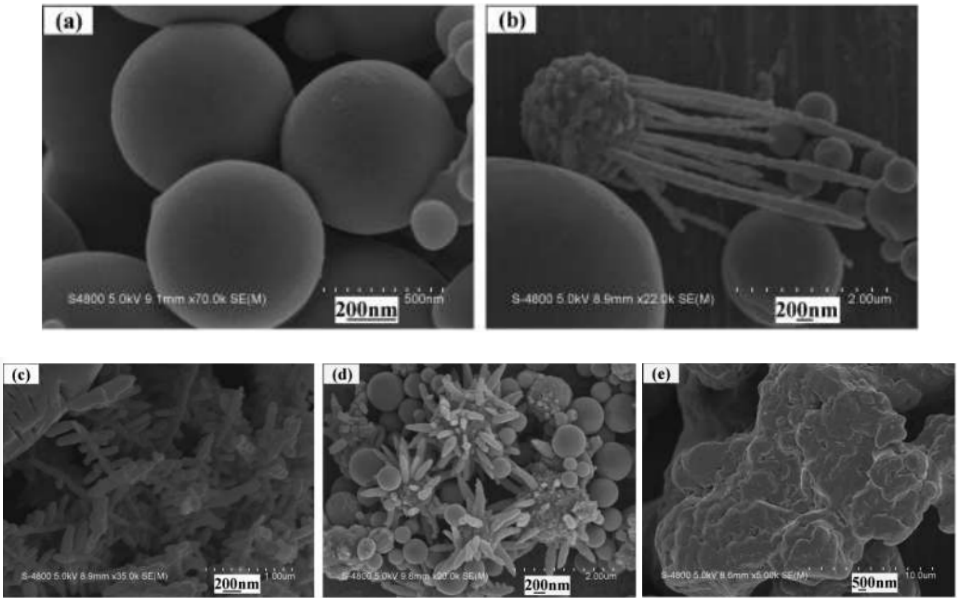

Figure 5. Effect of reaction temperature on the morphology of products.

A small number of light red products were prepared at 90 °C. The morphologies were relatively smooth selenium spheres with a diameter of about 500 nm, as shown in **Figure 5(a)**. At 110 °C, slender selenium filaments grow on the surface of some selenium pellets. The surface of these selenium pellets is uneven, and the protrusions are suspected to be selenium buds without growth and formation, as shown in **Figure 5(b)**. At 130 °C, selenium filaments increased significantly, and selenium appeared as shown in **Figure 5(c)**. The products prepared at 150 °C contained both smooth selenium balls and a selenium ball with large selenium buds, shaped like sea urchins, as shown in **Figure 5(d)**. When the reaction temperature was set at 170 °C, the selenium pellets disappeared and the products turned into large particles bonded together, as shown in **Figure 5(e)**.

Relevant studies have shown that β-CD has different inclusion ability at different temperatures[7]. At low temperature, β-CD has a strong inclusion ability for (quasi-) metallic elements, and it is easy to obtain selenium pellets with large particle size under the guidance of β-CD limit, as shown in **Figure 5(a)**. With the increase of reaction temperature, the solubility of β-CD increases, which is conducive to the formation of cysteine-cyclodextrin copolymerization hydrogel that can better disperse and stabilize selenium grains, resulting in the emergence of fine selenium buds and selenium branches, as shown in **Figure 5(b)** and **(c)**[8]. However, heating also has adverse effects: on the one hand, it will intensify the thermal movement of grains, increase the probability of collision and binding of crystal nuclei, and destroy the stability of β-CD soft template on selenium grains, resulting in the fusion of small selenium filament and selenium bud, and selenium bud becomes significantly thicker. As shown in **Figure 5(d)**, Johnson's sintering model shows that reaction temperature has a great influence on grain growth, and grain agglomeration will become more serious with increasing sintering temperature[9]. Therefore, high temperature causes selenium crystals to "sinter" together, as shown in **Figure 5(e)**.

According to the above facts, the optimum temperature for the growth of selenium was determined to be 130 °C.

3.5 Effect of reaction time on product morphology

Using the experimental method described in step 2.2, the amount of fixed template agent β-CD solution (0.5 g/L) was 8.0 mL, and the reaction temperature was set at 130 °C. The reaction time was set as 0.5, 1, 2, 3 and 4 h, respectively, and the single-factor comparison test was conducted. The products obtained were repeatedly cleaned by ultrasonic and detected by SEM, as shown in **Figure 6(a)** to **Figure 6(e)**.

The products prepared by reaction of 0.5 h are selenium balls of different sizes, as shown in **Figure**

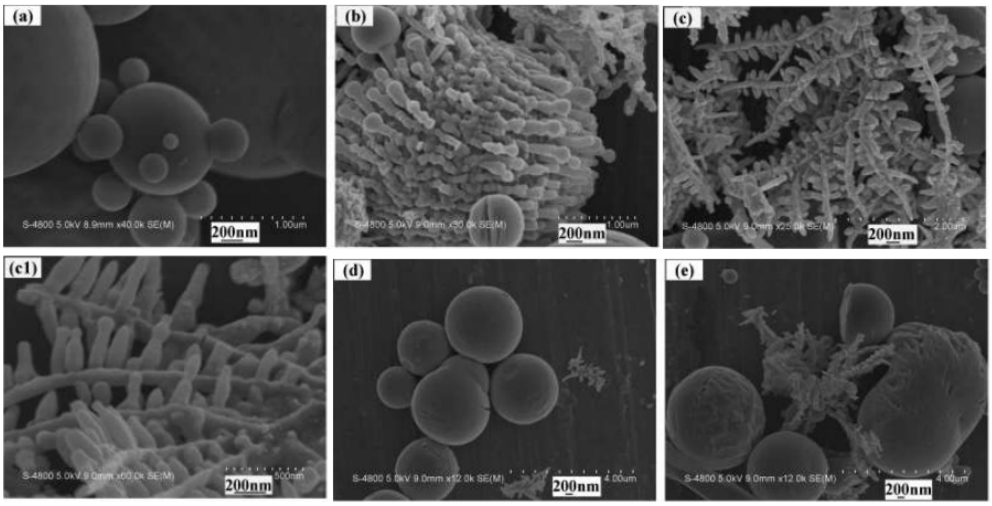

Figure 6. Effect of reaction time on the morphology of products.

6(a). After heating for 1 h, a large number of selenium buds appeared, as shown in **Figure 6(b)**. After 2 h of reaction, selenium buds grew and cross linked with each other, and a large number of selenium shoots began to emerge, as shown in **Figure 6(c)** and **Figure 6(c1)**. After reaction for 3 h, there were few selenium buds, selenium filaments and selenium branches, and cracks appeared on the surface of selenium ball, as shown in **Figure 6(d)**. After heating for 4 h, the selenium pellets continued to increase, and the diameter was 2–4 μm. The selenium sticks were obviously stuck together, as shown in **Figure 6(e)**. The morphology was not significantly different from that of the product after heating for 3 h.

The reason for the above changes may be that β-CD can self-assemble into supramolecular shells through adsorption and hydrogen bonding, but this process requires time, and prolonged reaction time is conducive to β-CD self-assemble into supramolecular shells[10]. Under the guidance of β-CD supramolecular shells, selenium crystals grow in a limited position in this three-dimensional template, and finally the dendritic selenium with neat appearance is obtained. However, at higher temperatures, the long-term reaction will lead to aggregation and fusion of small-scale products. Gao Shanmin *et al.* pointed out that there is a competitive process of grain dissolution and crystallization in the reaction system[11]. If the reaction time is prolonged at a higher reaction temperature, the crystallization speed will gradually exceed the dissolution speed, resulting in the gradual reduction of small grains, the continuous settlement of large grains, the smaller and smaller suspended grains in the solution, and the product has an obvious tendency of floccumulation.

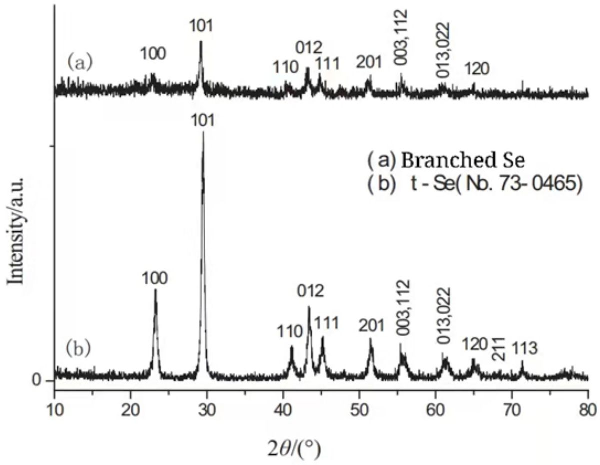

Figure 7. XRD pattern of branched micro nano selenium.

Based on the above facts, the optimum reaction time for selenium growth was determined to be 2 h.

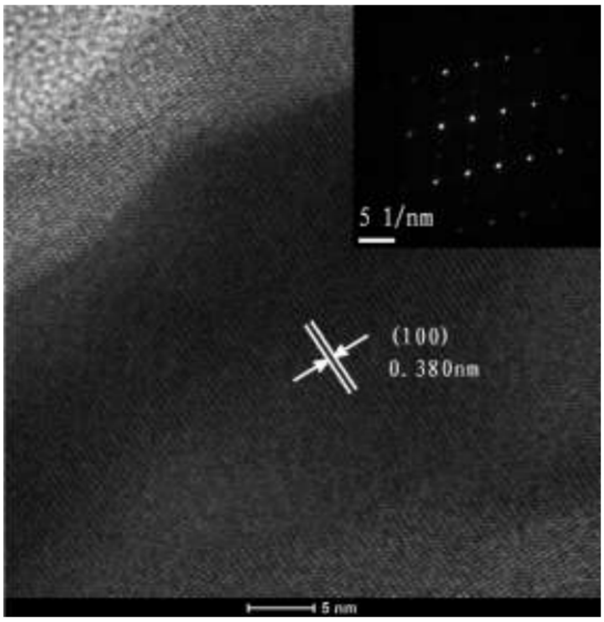

Figure 8. HRTEM spectra of branched micro nano selenium.

3.6 XRD and TEM characterization

The branched selenium prepared under the corresponding experimental conditions in **Figure 6(c)** was naturally dried and made into powder. Dandong Y-4Q X-ray diffrotometer was used for detection. The XRD pattern (**Figure 7**) showed that the absorption peak intensity was weak, but the background intensity was large. The whole peak shape was basically consistent with the tripartite selenium absorption peak data in JCPDS card (No.73-0465), and only a few weak absorption peaks could not be displayed. **Figure 8** shows the HRTEM (high resolution transmission electron microscopy) pattern of the dendritic selenium. The illustration shows the SAED (selective electron diffraction) pattern of the corresponding region. The aperture diameter is 0.1 μm, and the diffraction pattern shows that the product has a single crystal structure. The crystal lattice fringes in **Figure 8** are clear, indicating that the product has good crystallinity. The distance between adjacent crystal planes is about 0.380 nm, which is very close to that of t-Se (100) crystal plane at 0.3781 nm. The above detection indicated that the prepared selenium was tripartite t-Se under experimental conditions, and the micro-nano Se^0 of such a dendritic structure had not been reported in the literature before.

4. Conclusions

The results showed that the reducibility of L-Cys•HCl was weak, and the yield of selenium was not high. β-CD soft template has a great influence on the morphology of selenium nanoparticles. β-CD has hydrophilic outer surface and hydrophobic inner surface, under the combined action of hole effect, coordination effect and steric hindrance effect, it can effectively inhibit the growth and agglomeration of selenium nuclei, slow down the growth rate of selenium nuclei, promote the rapid nucleation and slow growth of selenium crystals, and finally obtain dendritic selenium with unique morphology. Selenium spheres with large particle size also appeared in the test. According to the hydrogen bond theory explaining powder agglomeration, the hydrogen bond initiated by hydroxyl group is the root of hard agglomeration[12]. β-CD, as a macromolecular, contains a lot of hydrogen bonds, and its ability as a soft template to stabilize nanoparticles is weaker than that of anionic surfactant. Hence, the particle size of selenium crystal prepared with β-CD as template is large. In this study, the amount, reaction temperature and reaction time of β-CD have different effects on the morphology of the product. After comparison, the most suitable reaction conditions for the growth of branch selenium are as follows: adding in 0.6306 g L-Cys•HCl in turn 8.0 mL of β-CD solution (0.5 g/L), 80 mL of H_2SeO_3 solution (0.05 mol/L), and n (L-Cys•HCl): n (H_2SeO_3) = 1:1 in the reaction system. After the reaction kettle is shaken evenly, it is placed in a blast drying oven and heated at 130 ℃ for 2 h to prepare gray products. The gray products are cleaned for many times with deionized water and industrial alcohol, centrifuged and naturally dried to obtain dendritic micro nano selenium.

Conflict of interest

No conflict of interest was reported by the author.

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