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Selenium Nanoparticles Prepared from Reverse Microemulsion Process

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Abstract: Selenium nanoparticles were prepared by a reverse microemulsion system. Sodium selenosulfate was used as selenium source. The results showed that hydrochloric acid concentration and reaction temperature had great influence on the morphology of products. The crystalline selenium nanowires and amorphous selenium nanorods were obtained in given condition.

Keywords: Reverse microemulsion, selenium nanoparticles, preparation.

Selenium possesses excellent photoelectrical and semiconductor properties which make it extensively used in duplicate, photography, cells and rectifiers[1]. Selenium is also one of essential trace elements in the human body and has great importance in nourishment and medicine[2]. Like other nanoparticls, selenium nanoparticles would have some unique mechanical, optical, electrical, biologic and chemical properties as compared with other bulk materials. For example, it has been reported that the redness selenium nanoparticles has high biological activities and low toxicity [3], and nanowires of trigonal selenium have novel photoconductivity [4]. Thus selenium nanoparticles have caused the great interest of researchers and a variety of synthesis methods have been exploited [5~8]. This article describes the reverse microemulsion synthesis of selenium nanoparticles.

Reverse microemulsion was first developed by Boutonnet[9] and has recently been used to prepare various nanoparticles[10~12]. In reverse microemulsion system, water droplets, which dispersed in a continuous oil phase, not only work as nanoreactors for the formation of nanoparticles but also inhibit the aggregation of nanoparticles. As reported, the nanoparticles prepared with this method were mostly spherical or quadrate, since the synthesizing was confined in the water droplets. In this paper, selenium nanorods and selenium nanowires were fabricated with this method by two processes: the microemulsion reaction and the interface growth.

Experimental

Microemulsion A, consisting of 10 mL cyclohexane, 0.25 mL 0.1 mol/L Na_2SeSO_3 prepared as literature[13], 0.3 g sodium dodecane (SDS) and 0.3 mL *n*-butanol, was ultrosized until it formed clear transparent solution. Microemulsion B, consisting the same materials except the Na_2SeSO_3, which was replaced by hydrochloric acid (HCl) with

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certain concentration, was obtained by the same performance. The subsequent synthetic process involved two steps.

First, microemulsion A and microemulsion B were mixed under ultrasonic treatment and then this solution was placed in stillness for 20 minutes at 20°C or 40°C. Second, an appropriate amount of the mixture of acetone and water (volume ratio 1:1) was added to the reaction solution under stirring. After keeping for a while, the reaction solution divided into two transparent layers and was then kept stillness for 40 minutes at room temperature. The out products, suspended in the interface between two solution layers, were separated by centrifugation, washed with ethanol and water, dried in a desiccator and characterized by X-ray diffraction meter (XRD) and transmission electron microscopy (TEM).

Results and Discussion

During the first step, the following reaction occurred through the collision of water droplets and the exchange of reactants between water droplets: $Na_2SeSO_3 + 2HCl \rightarrow Se\downarrow + SO_2\uparrow + 2NaCl + H_2O$. When the reaction solution turned into orange colloid from colorless, it indicated that the amorphous spherical selenium nanoparticles were formed[4]. The TEM images showed that the products formed at first step were uniform sphericity. In second step, the spheric nanoparticles could grow up into various shapes with the collision, dissolution and reaggregation of the nanoparticles in the interface between two solution layers.

The HCl concentration affected the morphologies of products: the selenium nanorods were obtained from 2.0 mol/L HCl solution (**Figure 1a**) and the chain-like selenium nanoparticles were obtained from 3.0 mol/L HCl solution (**Figure 1b**). The results could be explained as follows. With 3.0 mol/L HCl solution, the reaction occurred so fast that as-produced elemental selenium had no time to make nanorods, which lead elemental selenium to grow in various directions and form the selenium spheres. In second step, the selenium spheres as-formed would aggregate to chain-like nanoparticles due to stacking the nanocrystals in the same direction and provided energetically favorable link between them[14]. With 2.0 mol/L HCl solution, strand-rods assembled with little spherical particles. These feeble nanorods could further grow by combining little particles and be transited to solid nanorods.

Reaction temperature also affected the morphologies of products. The products obtained at 20°C were nanorods (**Figure 1a**), which were further confirmed to be mostly amorphous selenium by XRD. But at 40°C (with 2.0 mol/L HCl solution), nanowires consisting of the fibers bundling in parallel were obtained (**Figure 2**). **Figure 3** shows the XRD pattern obtained from the as-prepared nanowires. All the diffraction peaks in the XRD pattern could be indexed as the trigonal phase of selenium nanowires. This result suggested that the selenium nanowires were highly pure in chemical composition with all selenium atoms crystallized in the trigonal lattice. The abnormal intensity of the (100) peak indicated that these nanowires had preferentially grown along the 001 direction. From this XRD pattern, the lattice constants were calculated as a=0.437 nm, c=0.495 nm, which corresponded well to those of the trigonal phase (a=0.434 nm, c=0.495 nm) reported in literature[15].

Figure 1 The TEM images of selinium nanoparticles prepared at 20°C with different HCl concentration solution: (a) 2.0 mol/L; (b) 3.0 mol /L.

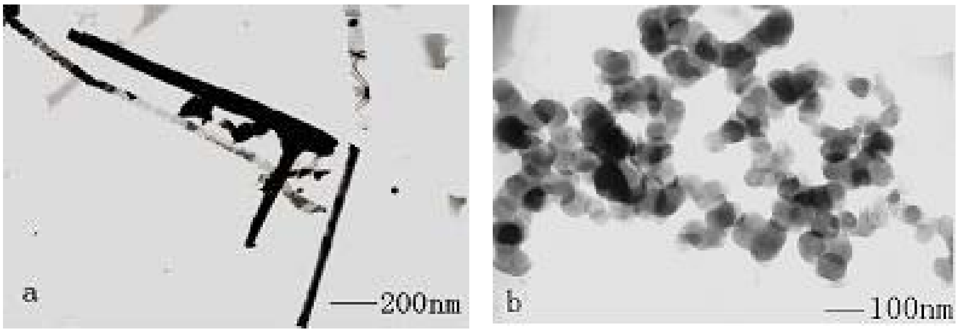


Figure 2 The TEM image of selenium nanowires. The inset was the SARD pattern of selenium nanowires.

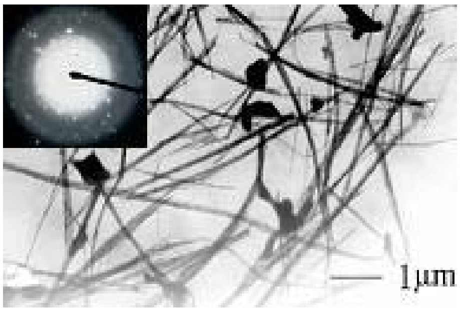
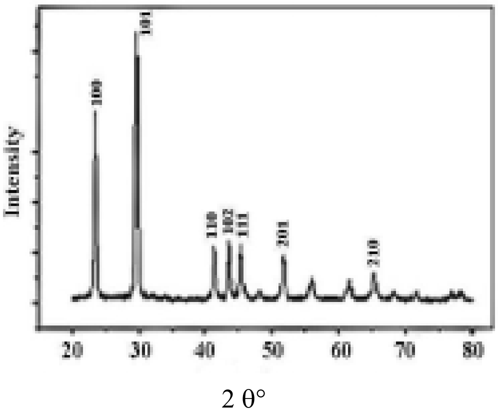


Figure 3 The XRD image of selenium nanowires.



Here the influence of reaction temperature on morphologies of products was discussed. The transformation of amorphous selenium into crystalline selenium requires higher temperature[16]. At 40°C, more amorphous selenium nanoparticles would be dissolved into the solution due to their higher free energy, which would favor the formation of crystal selenium nanoparticles. On the other hand, the hoist of the temperature could weaken the adsorption of surfactants to nanoparticles in certain direction and facilitate the escape of the SO_2 gas produced in the reaction. These two functions of temperature could provide anisotropy microenvironment that played an important roll in the formation of crystal selenium nanoparticles[15]. Thus more crystal selenium seeds were produced in first step. In second step, a various of nanoparticles were released from the water droplets and suspended in the interface between two solution layers. The elemental selenium, which was continuously provided through the dissolution of amorphous selenium, deposited on the surfaces of crystal seeds. With the induction of surfactants and the thrust of temperature, the crystal seeds assembled along the same direction and translated into trigonal selenium and the nanowires were obtained.

It usually took a long time to form selenium nanowires[4,7,8], but here the selenium nanowires were synthesized in one hour, if the local concentration of selenium in the interface between two solution layers is higher and the temperature also can accelerate the growth speed of the nanowires.

The mechanism of the formation of the wide nanowires is not clear yet. Abdelouas and his co-workers had obtained the wide selenium strand-wires contained several nanoparticles in parallel due to attachment of nanoparticles to single strand wires[13]. In our system, it may be speculated that fibers formed had the high free energy and aggregated in parallel to form wide nanowires in the interface of solutions.

Conclusions

In summery, we have provided a convenient and fast approach for the preparation of selenium nanoparticles. The synthesis included two processes: the microemulsion reaction and the interface growth. The condition of the microemulsion reaction process influenced on the morphology of final products. Crystalline selenium nanowires and amorphous selenium nanorods were obtained by controlling HCl concentration and reaction temperature. Further study may extend this method for the preparation of other nanoparticles.

Acknowledgments

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