



A green and low-cost approach for the large-scale production of uniform t-Se microspheres and their photoluminescence properties

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ABSTRACT

A green and economical hydrothermal route was developed to synthesize uniform trigonal selenium (t-Se) microspheres with an average diameter of 1 μm by using ascorbic acid (Vc) as a mild reducing agent and Se powder as the selenium source. The as-prepared products were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Experimental results reveal that the morphology of t-Se microspheres is strongly dependent on the reaction conditions such as the amount of Vc, reaction temperature and reaction time. The tentative growth mechanism of t-Se microspheres is also discussed in this letter. Photoluminescence spectrum indicates that the t-Se microspheres with an average diameter of 1 μm exhibit a strong red-emitting peak at 675 nm.

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1. Introduction

Selenium, as an important elemental semiconductor, has been widely applied to solar cells, rectifiers and xerography due to its intriguing properties [1]. In the nature, selenium exists as three phases: trigonal, monoclinic and amorphous. Over the past decade, much effort has been devoted into the formation of t-Se micro/nanostructures [2–11]. It is worthwhile noting that Se nanostructures will greatly restrict device applications because of their poor crystallinity, surfactants absorption and abundant defects [9]. In contrast, it has been found that selenium microstructures with special morphologies display unique optical and other potential properties [10,11]. Thus, it is reasonable to expect that t-Se microspheres may also exhibit unique properties. This inspired us to explore efficient approaches to the morphology-controlled synthesis of t-Se microspheres especially with unique properties. However, to the best of our knowledge, there have been few reports on t-Se microspheres. Ni et al. reported t-Se microspheres employing SeO_2 as the selenium precursor, polyvinylpyrrolidone (PVP) as the surfactant [12]. Recently, Wang et al. fabricated t-Se microspheres in the presence of L-tyrosine using H_2SeO_3 [13]. However, these methods are limited to the preparation of t-Se microspheres using toxic or expensive chemicals such as selenium precursors (e.g. H_2SeO_3 , Na_2SeO_3 and SeO_2), reducing agents (e.g. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and NaBH_4), organic solvents or additives, which might bring about great difficulties to the large-scale production and environmental protection. Therefore, developing

a facile but economical and green strategy for the large-scale synthesis of t-Se microspheres is highly desirable.

Herein, we report an environmentally friendly and low-cost route for the high-yield synthesis of t-Se microspheres. During the reaction, Se powder and ascorbic acid (Vc) act as mild agents, and no additives are used. It was found that t-Se microspheres were grown directly from the solution and no amorphous selenium ($\alpha\text{-Se}$) was formed. A possible growth mechanism is discussed. In addition, the as-obtained 1 μm -sized t-Se microspheres show a strong red-emitting peak at 675 nm.

2. Experimental

In a typical synthesis, 0.2 mmol Se powder and 2 mmol Vc were added into 30 ml deionized water. Then, an appropriate amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25–28%) was added. Finally, the system was transferred into the autoclave and maintained at 180 $^\circ\text{C}$ for 6 h. After the autoclave was cooled to room temperature naturally, the precipitate was washed with absolute ethanol and then dried at 60 $^\circ\text{C}$.

The samples were characterized by X-ray diffractometer (XRD, Bruker, D8 Advance diffractometer), scanning electron microscopy (SEM, JEOL, JSM-6480), transmission electron microscope (TEM, JEOL, JEM-2100) and Photoluminescence spectrum (PL, Photon Technology International, Quanta MasterTM 40).

3. Results and discussion

Morphology and structure of t-Se microspheres: Fig. 1a shows the XRD pattern of the as-obtained t-Se microspheres. All the diffraction peaks can be readily indexed into the trigonal phase of selenium (JCPDS no. 06-0362). Fig. 1b and c show typical SEM

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images in low and high magnifications of the t-Se microspheres, from which uniform microspheres with a diameter of about 1 μm can be clearly observed. A representative TEM image (Fig. 2d)

indicates that the obtained microsphere is well-defined and solid. Moreover, its diameter is $\sim 1 \mu\text{m}$, which is in good agreement with the SEM result.

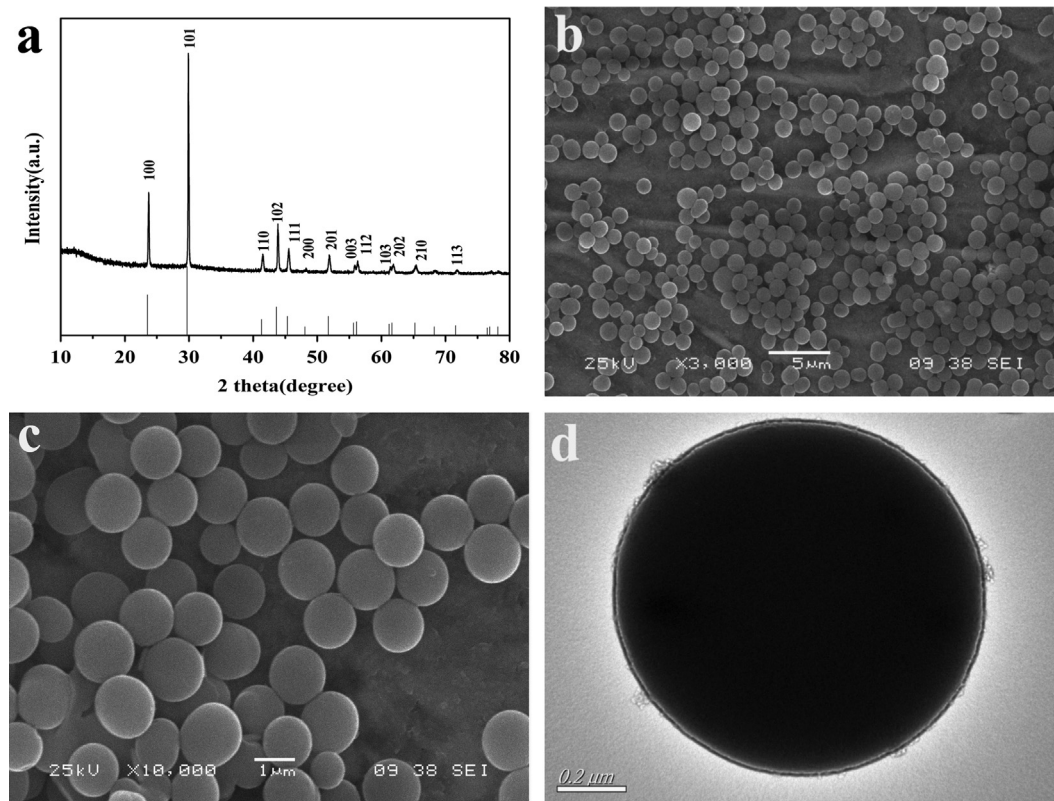


Fig. 1. (a) XRD pattern, (b) low- and (c) high-magnification SEM images, (d) TEM image of the sample.

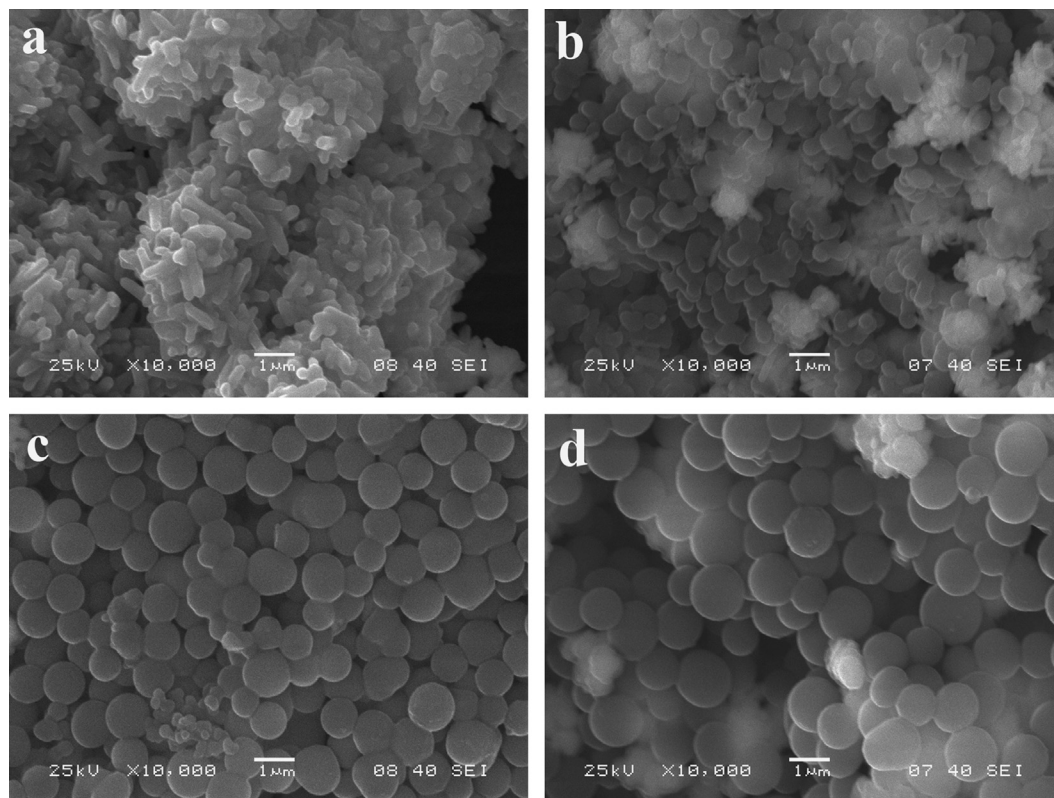


Fig. 2. SEM images of the samples synthesized by adding different amounts of Vc: (a) 0 mmol; (b) 4 mmol; (c) 6 mmol; (d) 8 mmol.

Effects of reaction conditions on the growth of t-Se microspheres:
The amount of Vc plays an important role in the formation of t-Se microspheres. In the absence of Vc (Fig. 2a), only Se aggregates

with coarse surface were obtained. When 4 mmol Vc was added, a few spherical particles appeared (Fig. 2b). When the amount of Vc was increased to 6 mmol and 8 mmol, the products

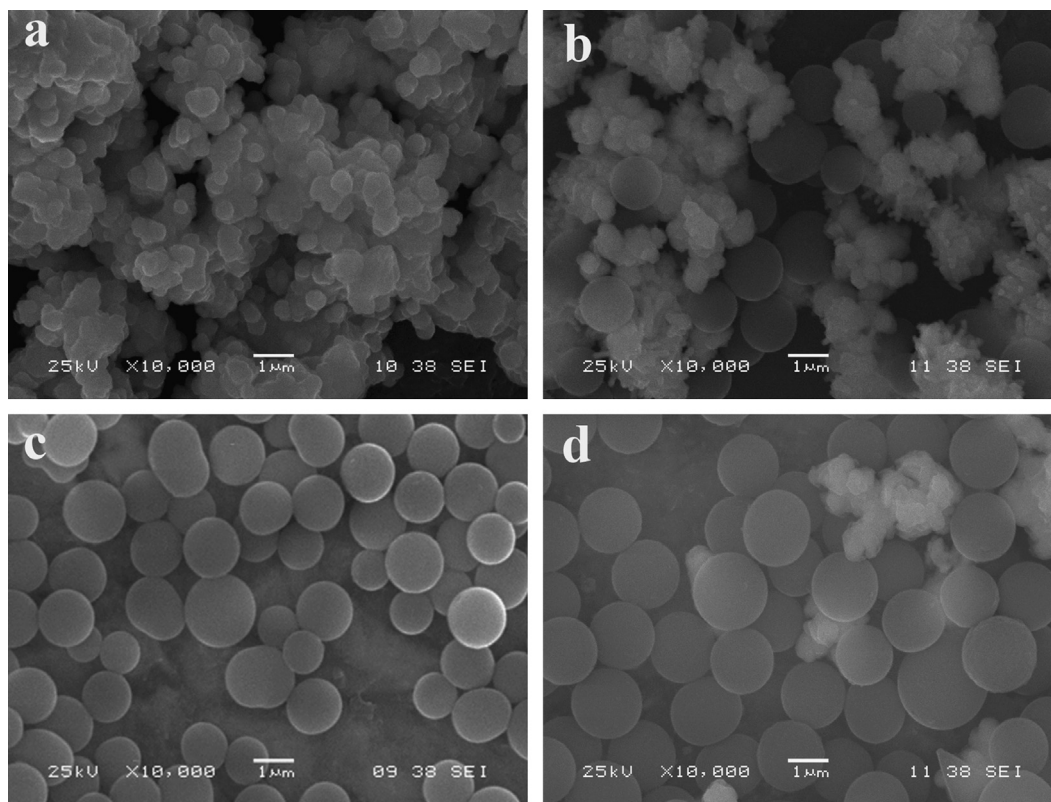


Fig. 3. SEM images of different reaction temperatures: (a) 120 °C; (b) 150 °C; (c) 180 °C; (d) 200 °C.

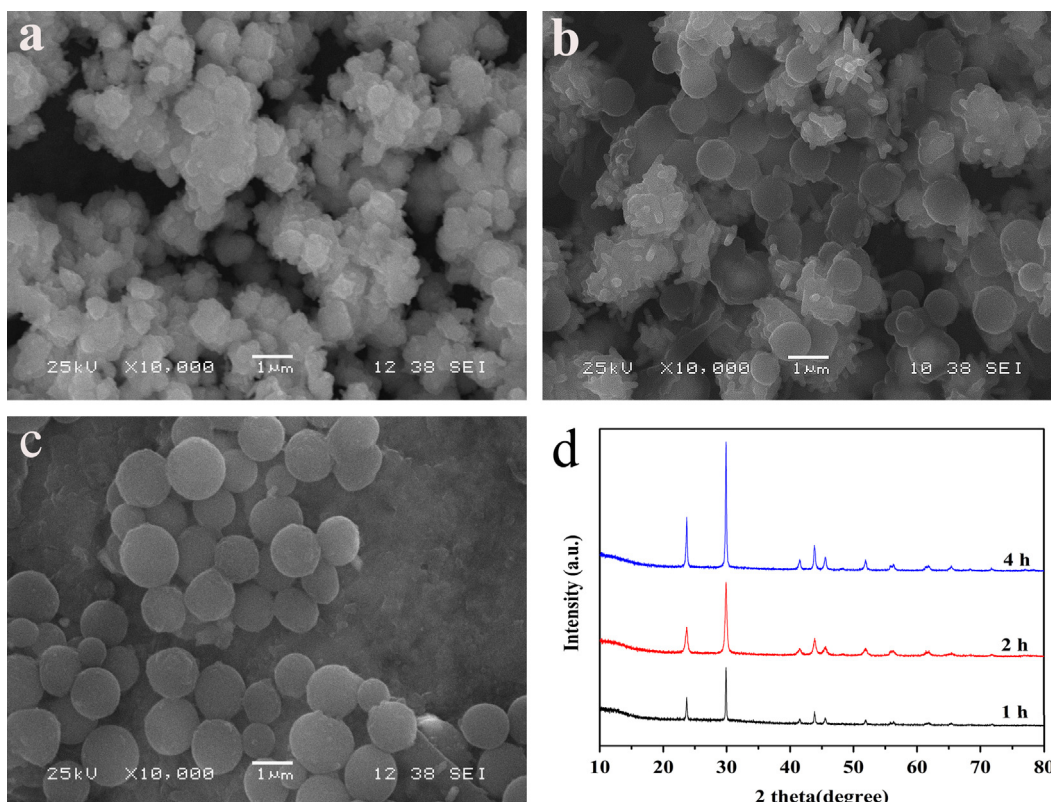


Fig. 4. SEM images of different reaction time: (a) 1 h; (b) 2 h; (c) 4 h; (d) 6 h.

were mainly composed of interconnected Se microspheres (Fig. 2c and d).

Moreover, the reaction temperature also affects the formation of t-Se microspheres. When the temperature was increased from 120 °C to 150 °C, the morphology of the as-synthesized products changed from Se aggregates assembled with nanoparticles to microspheres gradually (Fig. 3a and b). When the temperature reached 180 °C, the as-obtained sample presented nice Se microspheres (Fig. 3c). When the temperature was at 200 °C, larger Se microspheres and irregular particles coexisted (Fig. 3d).

To investigate the tentative growth mechanism of as-obtained Se microspheres, the time-dependent experiments were further conducted. At reaction time of 1 h (Fig. 4a), the ill-defined structure formed by direct aggregation of Se particles. After 2 h of reacting, a small amount of Se microspheres have grown out from large Se aggregates (Fig. 4b). After 4 h, 1 μm -sized coarse Se microspheres were obtained (Fig. 4c). After 6 h of growth, smooth and highly dispersed Se microspheres were finally obtained (Fig. 1c). Fig. 4d shows the XRD patterns of products obtained at 1 h, 2 h and 4 h, respectively. It should be noted that Se existed in the form of bulk t-Se for different hydrothermal durations, which is similar to the result of Srivastava et al. [14].

According to the above results, the possible growth mechanism is deduced: First, Se powder reacts with ammonia to form SeO_3^{2-} , and then Vc reduces SeO_3^{2-} to Se. The Se will grow into t-Se nanoparticles after the initial nucleation. However, the surfaces of the nanoparticles are not protected well without foreign additives such as surfactants, so they have the tendency of self-aggregation to release the high surface energy. Driven by the minimization of interfacial energy, irregular aggregates disappear gradually and finally well-defined Se microspheres are achieved.

Photoluminescence properties: As shown in Fig. 5, the as-prepared t-Se microspheres show an intense emission at 675 nm when the PL spectrum was excited at 450 nm. It should be noted that there is a large red shift relative to the results obtained by Zhang et al. (~ 341 nm and 428 nm) [15], which is possibly due to the unique size and morphology of our products. Emission maximum at 675 nm in the visible region indicates that the t-Se microspheres may have potential application in biolabeling and bioimaging [16].

4. Conclusions

Well-dispersed t-Se microspheres have been successfully synthesized through a green and low-cost approach. Based on the observations, we propose a possible growth mechanism for the formation of t-Se microspheres. More importantly, the 1 μm -sized t-Se microspheres, which show a strong red-emitting peak

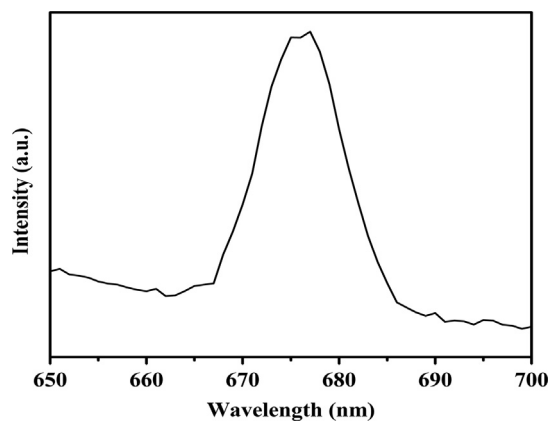


Fig. 5. PL spectrum of the typical sample at $\lambda_{\text{ex}}=450$ nm.

at 675 nm, may have potential application in biolabeling and bioimaging.

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