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# Solvothermal syntheses of $\beta$ -Ag<sub>2</sub>Se crystals with novel morphologies

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## Abstract

Crystalline  $\beta$ -Ag<sub>2</sub>Se with treelike, plumelike, pebblelike, rodlike, tubular, polyhedral, and spherical morphologies have been prepared by the solvothermal reaction of silver carbonate and selenium at low temperature (190°C) and characterized by elemental analysis, X-ray diffraction pattern, and scanning electron microscopy. The morphologies and sizes of the products are affected not only by the kind of solvents but also by the reactant concentrations and reaction time and can be conveniently obtained under controlled conditions. The influences of the solvents, the reactant concentrations and reaction time on the shapes and sizes of crystalline Ag<sub>2</sub>Se are discussed.

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*Keywords:* Solvothermal synthesis; Silver selenide; Crystalline; Morphology

## 1. Introduction

Metal selenides have attracted much attention during the past few years due to their special electronic and optical properties and potential applications [1]. Silver selenide exists as a low-temperature phase ( $\beta$ -Ag<sub>2</sub>Se), and a high-temperature phase ( $\alpha$ -Ag<sub>2</sub>Se) with the phase transition point at 133°C [2].  $\alpha$ -Ag<sub>2</sub>Se is a well-known superionic conductor that is useful as the solid electrolyte in photochargeable secondary batteries.  $\beta$ -Ag<sub>2</sub>Se is a narrow-band-gap semiconductor and has been widely used for a photosensitizer in photographic films or thermalchromic materials. The  $\beta$ -phase is also a promising candidate for thermoelectronic applications because of its relatively high Seebeck coefficient ( $-150 \mu\text{V/K}$  at 300 K), low lattice thermal conductivity, and high electrical conductivity [3]. Many techniques have been developed to synthesize crystalline Ag<sub>2</sub>Se, including mechanical alloying method using a high-energy ball mill [4], microemulsion [5], electrolysis [6], and chemical route at room or elevated temperature [7–10]. With few exceptions [9,10], most of the resulting crystalline Ag<sub>2</sub>Se usually exhibited spherical morphology and no special morphologies.

Crystalline solids with different morphologies are of great interest and importance, because they may exhibit different physical and chemical properties even if their chemical compositions are same [11,12]. The synthesis of inorganic crystals with respect to the control of their morphology and size, however, is underdeveloped and still complicated [12,13]. The development of synthetic methods and understanding the mechanisms by which the morphology and size of the crystals can be effectively varied remain an ultimate challenge of modern material research. We have recently prepared some metal chalcogenides with different morphologies through solvothermal process in various solvents at low temperature [13]. In this work, we extend this route to prepare Ag<sub>2</sub>Se and study the effects of media, reactant concentration and reaction time on the crystal growth in order to optimize the experimental conditions. As a result, a series of treelike, plumelike, pebblelike, rodlike, tubular, polyhedral, and spherical crystalline  $\beta$ -Ag<sub>2</sub>Se was fabricated, which were characterized by elemental analyses, X-ray powder diffraction (XRPD), and scanning electron microscopy (SEM). Silver selenides with dendritic and tubular morphologies are rare and, to our knowledge, only two papers studied on the growths of dendritic and tubular crystalline Ag<sub>2</sub>Se are available in the literature [9,10b]. It is reasonable to expect that the these Ag<sub>2</sub>Se crystals with different and novel morphologies and high stability could bring in new properties and applications.

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Table 1  
Crystalline  $\beta$ -Ag<sub>2</sub>Se prepared from Ag<sub>2</sub>CO<sub>3</sub> and Se under controlled conditions<sup>a</sup>

No.	Solvents (25 mL)	Ag <sub>2</sub> CO <sub>3</sub> /Se (molar ratio)	Time (h)	Atomic ratios (Ag:Se) <sup>b</sup>	Morphologies	Yields <sup>c</sup> (%)	Figs.
1a	en	1:2.5	12	1.97:1	Spherical	95	2a
1b	en	1:2.5	36	1.97:1	Pebblelike	95	2b
1c	en	1:2.5	72	1.99:1	Rodlike	96	2c
1d	en	1:1.25	36	1.97:1	Plumelike	94	2d–e
2a	dien	1:2.5	36	1.97:1	Rodlike	89	3a
2b	dien	1:1	36	1.98:1	Treelike	91	3b
3a	py	1:2.5	36	1.95:1	Long-rodlike	90	4a
3b	py	1:1	36	1.96:1	Short-rodlike	90	4b
4a	H <sub>2</sub> O	1:2.5	36	1.95:1	Rodlike + spherical	87	5a
4b	H <sub>2</sub> O	1:2	36	1.95:1	Tubular + spherical	87	5b
4c	H <sub>2</sub> O	1:1	36	1.96:1	Polyhedral + spherical	85	5c + 5d

<sup>a</sup>All the reactions were carried out at 190°C.

<sup>b</sup>ICP results.

<sup>c</sup>Based on Ag<sub>2</sub>CO<sub>3</sub>.

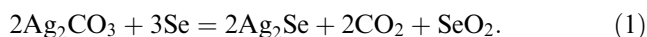
## 2. Experimental

In a typical procedure, appropriate amount of analytically pure Ag<sub>2</sub>CO<sub>3</sub> and Se was put into a Teflon-lined stainless autoclave of 35 mL capacity, which was filled with 25 mL ethylenediamine (en), diethylenetriamine (dien), pyridine (py) or water. The autoclave was kept constantly at 190°C for 12–72 h and then cooled to room temperature naturally. The excess Se powder in the samples, obtained from dien, py, and water, was removed by dissolving them in en. The products were washed with distilled water and absolute ethanol respectively to remove residual impurities and dried in a vacuum at 70°C for 2 h.

XRPD were conducted on a Japan Rigaku Damax  $\gamma$ A X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The scanning rate of 0.05°/s was applied to record the patterns in the  $2\theta$  range of 10–70°. The atomic ratios of the products were measured on a Seiko electronics SPD 1200A inductively coupled plasma (ICP) emission analyzer with a pump flow of 1.85 mL/min and auxiliary gas (Ar 99.99%) flow rate of 0.5 L/min. SEM images were taken with a Hitachi X-650 SEM using a Ni–Co alloy plate.

## 3. Results and discussion

The detail conditions and results of the experiments are summarized in Table 1. The synthetic reactions were carried out in an autoclave and were based on the disproportionation of elemental selenium [1]



In this work, en, dien, py, and water were used as the reaction media. According to the XRPD studies, to initiate the reactions, the reaction temperatures should

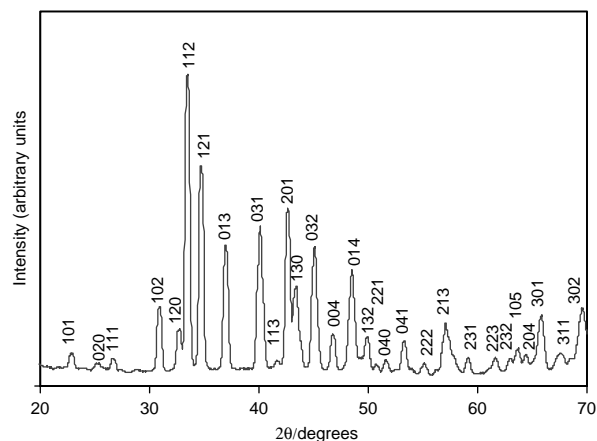


Fig. 1. XRPD pattern of the as-grown crystalline Ag<sub>2</sub>Se that were ground from the bulk crystals of sample 1a.

be no less than 100°C for en, 130°C for trien, 160°C for py, and 170°C for water. To make the reaction proceed completely, the reaction time should be no less than 9 h for en, 12 h for dien, and 16 h for both py and water. For comparison, 190°C and 12–72 h were finally employed as the reaction temperature and time to grow Ag<sub>2</sub>Se for the four solvents. On the basis of Eq. (1), the molar ratios of Ag<sub>2</sub>CO<sub>3</sub> to Se were set to be 1:1, 1:1.25 or 1:2.5 for studying the effects of reactant concentrations on the products. Repeated experiments showed that the reactions listed in Table 1 could be readily reproduced.

All as-grown crystals are metallic light-gray with a high reflective luster. The XRPD patterns of the crystalline powder ground from the bulk crystals have little difference in relative intensity and can be represented by Fig. 1 of sample 1a. All the reflections can be indexed to the orthorhombic, low-temperature phase  $\beta$ -Ag<sub>2</sub>Se with lattice constants  $a = 4.332$ ,  $b = 7.055$  and  $c = 7.756 \text{ \AA}$ , which are in good agreement with the

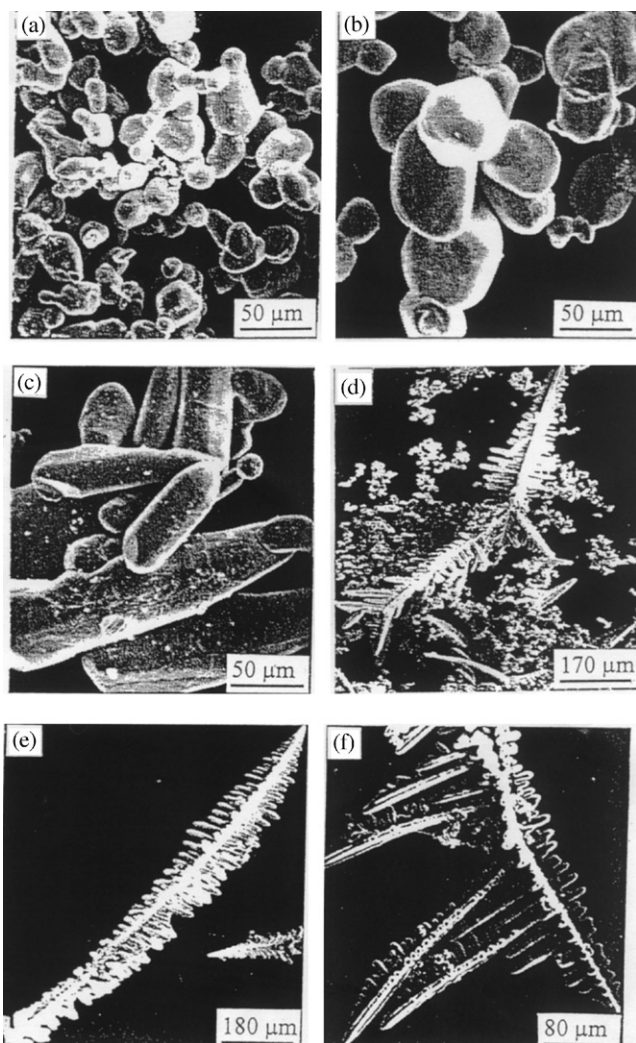


Fig. 2. SEM images of  $\text{Ag}_2\text{Se}$  synthesized with  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:2.5$  (a), 12 h (b), 36 h (c), 72 h, and 1:1 (d)–(f) 36 h in en at  $190^\circ\text{C}$ .

literature data for  $\beta\text{-Ag}_2\text{Se}$  (JCPDS Card File, 24-1041). No characteristic peaks such as  $\text{Ag}_2\text{O}$ ,  $\text{SeO}_2$ , or Se were detected. Further evidence for the formation of  $\text{Ag}_2\text{Se}$  can be derived from elemental analyses of the products, as shown in Table 1.

The SEM photographs of the as-prepared  $\text{Ag}_2\text{Se}$  crystals under various conditions are provided in Figs. 1–4. It clearly reveals that the morphologies of the products are affected not only by the kind of solvents but also by the reactant concentrations and reaction time. When the reaction was conducted with  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:2.5$  in en at  $190^\circ\text{C}$  for 12, 36, and 72 h, the products display spherical, pebblelike, and rodlike morphologies, respectively. As expected, the size of the crystals increase greatly with the reaction time varying from 12 to 72 h, as shown in Fig. 2a–c. Interestingly, varying the molar ratio of  $\text{Ag}_2\text{CO}_3/\text{Se}$  from 1:2.5 to 1:1.25 leads to the formation of an interesting and unique plumelike  $\text{Ag}_2\text{Se}$  in en at  $190^\circ\text{C}$  for 36 h, as

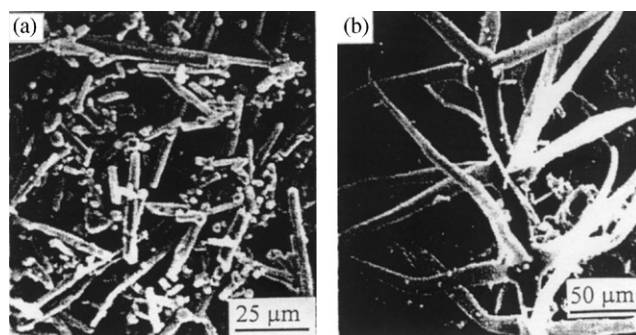


Fig. 3. SEM images of  $\text{Ag}_2\text{Se}$  synthesized with  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:2.5$  (a) and 1:1 (b) in dien at  $190^\circ\text{C}$  for 36 h.

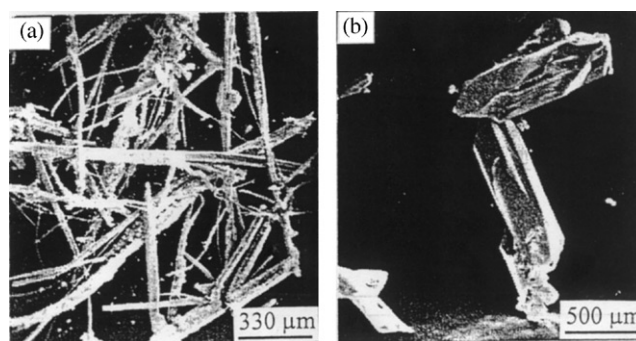


Fig. 4. SEM images of  $\text{Ag}_2\text{Se}$  synthesized with  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:2.5$  (a) and 1:1 (b) in py at  $190^\circ\text{C}$  for 36 h.

depicted in Fig. 2d–f. While short rodlike and delicate treelike crystals shown in Fig. 3 were generated for  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:2.5$  and 1:1, respectively, if the reaction was carried out in dien at  $190^\circ\text{C}$  for 36 h. It is noted that both the microtrees and microplumes were very stable and did not break during sonication. As depicted in Fig. 4, the  $\text{Ag}_2\text{Se}$  particles, prepared from py at  $190^\circ\text{C}$  for 36 h, adopt the similar rodlike morphology for  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:2.5$  and 1:1, but the lengths of the rods become shorter and the diameters become larger obviously, as the reactant concentration was lowered. As shown in Fig. 5, the  $\text{Ag}_2\text{Se}$  particles, produced from water at  $190^\circ\text{C}$  for 36 h, are composed of both rodlike and spherical crystals for  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:2.5$ , while those formed with  $\text{Ag}_2\text{CO}_3/\text{Se} = 1:1$  consist of irregular polyhedral crystallines with a trace of spherical crystallines. Rather interesting is that tubular  $\text{Ag}_2\text{Se}$  crystals co-exist with some spherical crystals when the  $\text{Ag}_2\text{CO}_3/\text{Se}$  molar ratio is adjusted to 1:2. Tubular  $\text{Ag}_2\text{Se}$  crystals has been reported previously [9].

The reaction media, time and reactant concentrations should be responsible for the distinctive morphologies and sizes of the as-prepared  $\text{Ag}_2\text{Se}$ . By comparison of the different routes listed in Table 1 to grow  $\text{Ag}_2\text{Se}$  crystals, the reactant concentration is very important to the morphology of the product. In the solvothermal



Fig. 5. SEM images of  $\text{Ag}_2\text{Se}$  synthesized with  $\text{Ag}_2\text{CO}_3/\text{Se} = 1.2.5$  (a), 1:2 (b) and 1:1 (c) in  $\text{H}_2\text{O}$  at  $190^\circ\text{C}$  for 36 h.

process, mass diffusion probably exerts an impact on the crystal nucleation and growth [1,13c]. Previous studies indicate that the growth of crystals has a low orientation, when the concentration of the reactants is low, and has a high orientation at high concentration, when the concentration is high [13]. This result is also confirmed by the present experiment. So, at  $190^\circ\text{C}$  for 36 h, the products prepared from the lower and higher concentrations of reactants exhibit pebble-like and plum-like shapes for en, rod-like and tree-like shapes for dien, long- and short-rod-like shapes for py, and tubular and polyhedral shapes (both co-exist with spherical crystallites) for water, respectively, as shown in Table 1.

The influences of reaction time on the morphologies and sizes of samples 1a–c may be explained by reaction control and growth control. When the reaction was completed in a short time, the as-prepared samples were in the reaction process for most of the time. The influence of the reaction on the process was dominant, thus affording smaller spherical particles by route 1a (12 h). With increasing time, a process dominated by growth control was observed. Controlled by the crystal habit, the spherical particles gradually grew to be bigger pebble-like and rod-like shapes by routes 1b (36 h) and 1c (72 h), respectively. Further extending the reaction period to 7 and 14 days, however, does not give rise to any significant changes in both morphologies and sizes of the products.

Although the selected four solvents provide a synthetic path to  $\text{Ag}_2\text{Se}$ , they have different influences,

even under otherwise identical reaction conditions. Elemental selenium and silver carbonate are readily soluble in en [13c], which benefits the crystal growth mostly and so affords crystals with larger sizes. In contrast, selenium and silver carbonate are almost insoluble in water, which favors the growth least and hence affords smaller particles. However, the mechanistic influence of the solvent on the morphology of crystals still remains obscure, irrespective of great efforts having been made to investigate it [14].

In conclusion, crystalline  $\beta\text{-Ag}_2\text{Se}$  with tree-like, plum-like, pebble-like, rod-like, tubular, polyhedral, and spherical morphologies have been prepared by solvothermal reaction of silver carbonate and selenium under controlled conditions and characterized by elemental analyses, XRPD, and SEM. The shapes and sizes of  $\text{Ag}_2\text{Se}$  crystals were determined by the reaction solvents, time, and reactant concentrations, and can be easily controlled by appropriate adjustment of the three factors. Further studies are in progress, which are directed toward deeper understanding of the reaction parameters influencing the crystal nucleation and growth and monitoring of the crystallization process to reveal correlations between crystal structure, morphology and reaction system by solvothermal route to inorganic materials.

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