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RESEARCH PAPER

Chromium Selenide Nanoparticles: Hydrothermal Synthesis in the Presence of a New Selenium Source

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ABSTRACT

Chromium selenide (Cr_2Se_3) nanoparticles were prepared by hydrothermal method from $Cr(NO_3)_3.9H_2O$ and $SeCl_4$ as precursors. These nanoparticles could be produced simply in the presence of cetyltrimethyl ammonium bromide, sodium dodecyl sulfate and polyethylenglycole 600 (PEG600) and 4ml of hydrazine hydrate ($N_2H_4.H_2O$) at 180 ˚C for different times. By varying the reducing agent to potassium borohydride (KBH_4), agglomerated structures with different morphologies were produced. The effects of surfactant, reducing agent, reaction time and temperature on the morphology of the products was investigated.

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INTRODUCTION

The metal selenides were produced first time by Kutscher in 1960s' as producing PbSe with chemical bath deposition [1]. After the Kutscher, the researchers synthesized the other metal selenides [2–6]. Chromium selenide is an inorganic compound. It exhibits semiconductor-metal transformations at elevated temperatures [7, 8]. The semiconductor-to-metal transition in CrS is accompanied by a transition to the NiA s structure. On the other hand, the resistance transition in CrSe is not associated with an identified structural transition. In order to study the possibility of pressure induced semiconductor-to-metal transitions, the high-pressure resistivities of these compounds were determined up to 70 kbar [9]. Different structural forms of chromium selenide are well-documented (CrSe, Cr_2Se_3). The Cr_2Se_3 has a rhombohedral structure (space group: R3) based on NiAs-type structure [10, 11]. The CrSe crystallizes in the monoclinic structure immediate between NiAs- and PtS-type [12].

Na_2SeO_3, NaHSe, H_2Se, $Se(C_2H_5)_2$, selenium powder, bis (trimethylsilyl) selenium $Se(TMS)_2$, selenourea ($H_2NC(Se)NH_2$) and SeO_2 have been introduced as selenium reagents for the synthesis of metal selenides [13–18]. $SeCl_4$ was selected in our experiments to provide a highly reactive selenium source in aqueous solution and has given good results. The aim of this paper was synthesis of the CrSe nanostructures by hydrothermal method. Over recent years, a great deal of research effort has been devoted to the research in metal selenide semiconductors. Hence, investigations on the synthesis and modification of nanosized Cr_2Se_3 have attracted tremendous attentions. However, properties of transition metal selenides are quite different from those of oxides since d electrons in selenides participate in covalent bonding. Such covalent bonding in selenides reduces the formal charge on transition metals and favors formation of metal-metal bonds. Metal-metal interactions indeed play a significant role in determining the properties of many of the transition metal

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selenides. The influence of such interactions on the electronic structure of these solids can be studied by means of their transport properties and these interactions become particularly important in transition elements selenides of the second and third series [19]. To the best of our knowledge, it is the first time that SeCl4 is used as Se source for the synthesis of chromium selenides. The $SeCl_4$ can be fast reduced by hydrazine and formed in to Se^{2-} ions, which has influence on the sizes and morphologies of the resulting samples and is the basis of this synthetic route. This route may be extended to the fabrication of other metal selenides with novel morphologies and properties.

MATERIALS AND METHODS

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and were used as received without further purification. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. SEM images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. TEM images and SAED pattern were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. EDS analysis with 20 kV accelerated voltage was done.

Synthesis of chromium selenide nanoparticles

The chromium selenide nanoparticles were prepared as follows: first, an aqueous solution of $Cr(NO_3)_3.9H_2O$ was prepared, then a certain amount of surfactant was added the solution under strong magnetic stirring at room temperature. Second, an aqueous solution of $SeCl_4$ was added to the above solution, then 4 ml of hydrazine was added drop-wise. The color of the colorless solution changed to black, indicating reduction of $SeCl_4$. The solution was added to a Teflon-lined stainless steel autoclave and maintained at 180°C for 12, 18 and 24h. After the autoclave was cooled to room temperature on its own, the black precipitate was separated by centrifugation. The precipitate was washed with deionized water and anhydrous ethanol several times and was dried at 60ºC under vacuum for 4 h. Fig. 1 shows the formation process of the Cr_2Se_3 nanoparticles.

RESULTS AND DISCUSSION

The morphology and particle size of the samples were investigated by SEM and TEM images. Fig. 2 shows the SEM images of samples 1 and 2 obtained in the presence of KBH_4 and different surfactants including SDBS (Fig. 2a and b) and CTAB (Fig. 2c and d). We used four surfactants in our experiment to investigate their influence

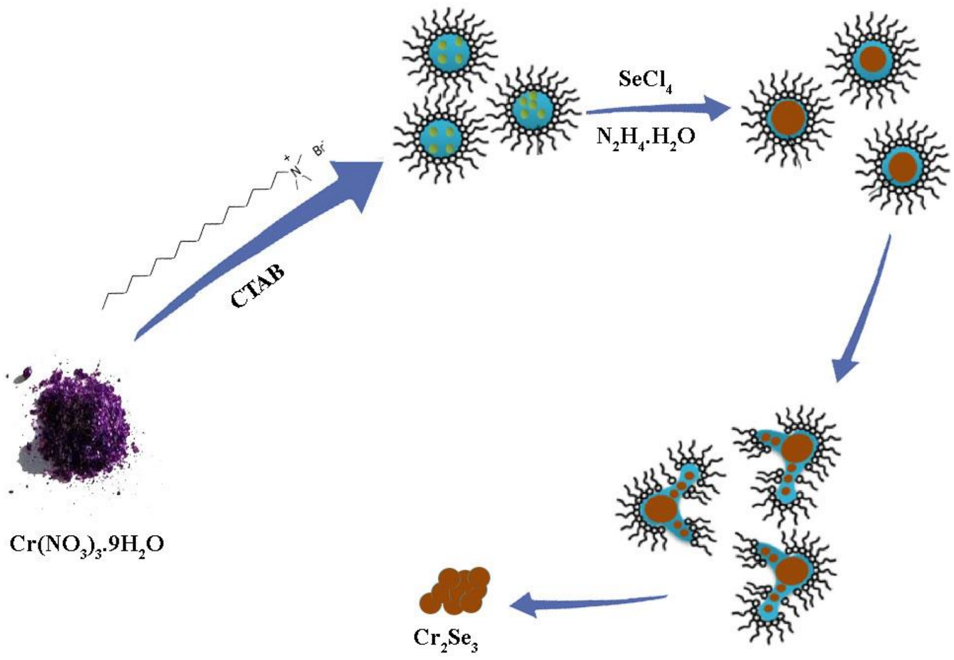

Fig. 1. Schematic diagram illustrating the formation of the chromium selenide nanoparticles.

on samples morphology. In the presence of KBH_4 when SDBS and CTAB are used, the products are in nano-size but their size and morphology are different: hexagons, prisms and spheres. As can be seen in Fig. 2, KBH_4 is not a good surfactant in the current experiment, because it is clear that by using it, the products did not separate well and are agglomerated (Fig. 2).

With exchange of reductant from KBH_4 to hydrazine (Fig. 3) at 180 ˚C for 12 h, agglomeration nanoparticles were formed, as shown in Fig. 3. Hydrazine limits the particle size, protects particles from further aggregation and plays an important role in the formation of nanoparticles. In the presence of PEG600, polymeric molecules adsorb preferentially on the nuclei surface to inhibit aggregation by steric hindrance mechanism (Fig. 3a and b). SDS monomers act as excess electrolyte, which in turn lowers the electrostatic repulsion barrier for coalescence to occur and can prevent particles from formation of big nanostructures (Fig. 3c and d).

In other side, the effect of reaction time on the morphology and particle size of the products was investigated. Fig. 4 shows that reaction time has a small influence on the morphology and particle

Table 1. The reaction conditions of the products synthesized in this work.

Sample	Se Source	Cr Source	Surfactant	Reductant	Temperature (˚C)	Time (h)	Morphology
1	$SeCl_4$	$Cr(NO_3)_3.9H_2O$	SDBS	KBH_4	180	12	Polyhedrons, prisms, spheres, particles
2	$SeCl_4$	$Cr(NO_3)_3.9H_2O$	CTAB	KBH_4	180	12	Polyhedrons, prisms, spheres, particles
3	$SeCl_4$	$Cr(NO_3)_3.9H_2O$	PEG600	Hydrazine	180	12	Nanoparticles
4	$SeCl_4$	$Cr(NO_3)_3.9H_2O$	SDS	Hydrazine	180	12	Nanoparticles
5	$SeCl_4$	$Cr(NO_3)_3.9H_2O$	CTAB	Hydrazine	180	18	Nanoparticles
6	$SeCl_4$	$Cr(NO_3)_3.9H_2O$	CTAB	Hydrazine	180	24	Nanoparticles

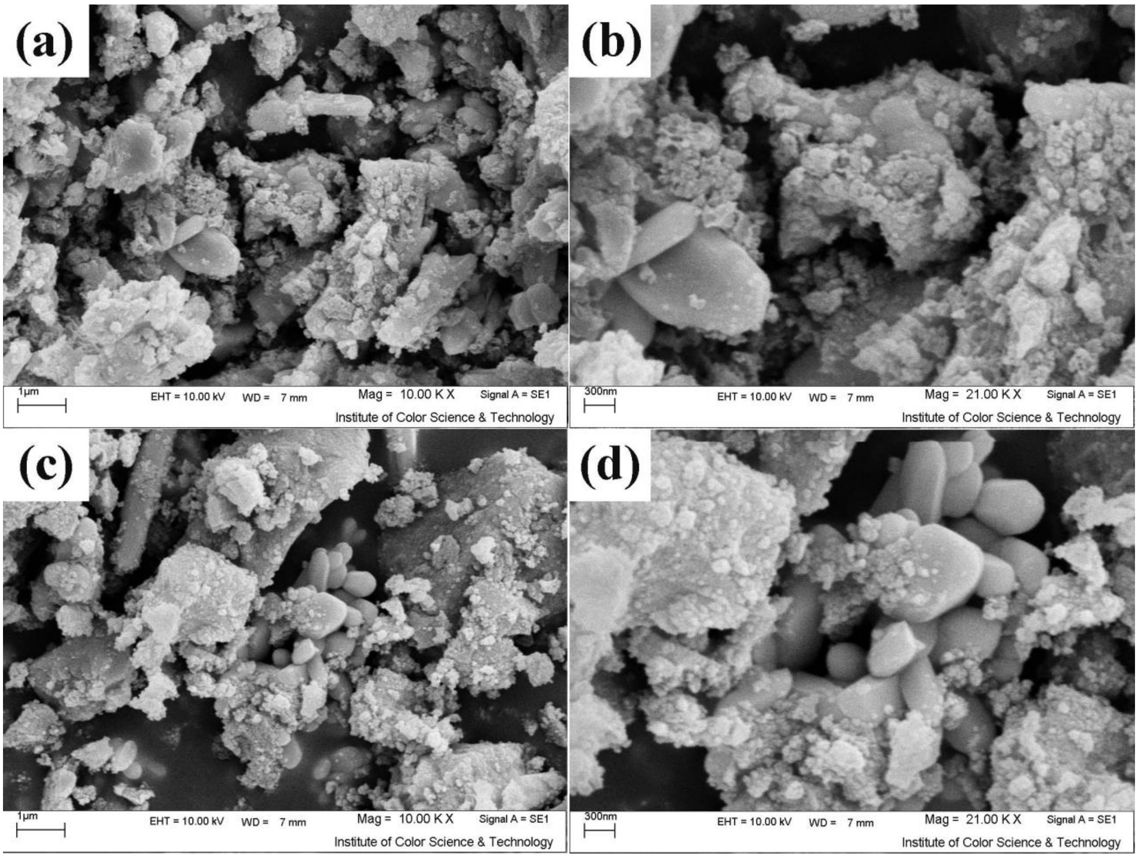

Fig. 2. SEM images of prepared samples from $SeCl_4$ and $Cr(NO_3)_3.9H_2O$ at 180 ˚C for 12h, in the presence of KBH_4 and: (a,b) SDBS (sample 1) , (c,d) CTAB (sample 2).

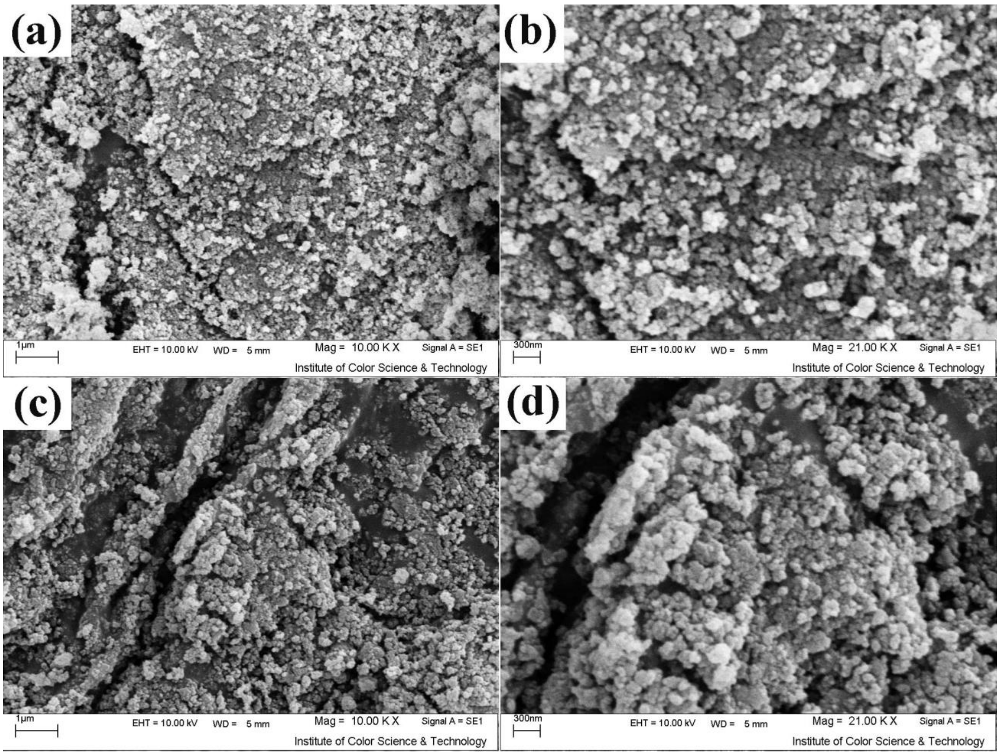

Fig. 3. SEM images of prepared samples from $SeCl_4$ and $Cr(NO_3)_3.9H_2O$ at 180 ˚C for 12h, in the presence of 4ml of hydrazine and: (a,b) PEG600 (sample 3) , (c,d) SDS (sample 4).

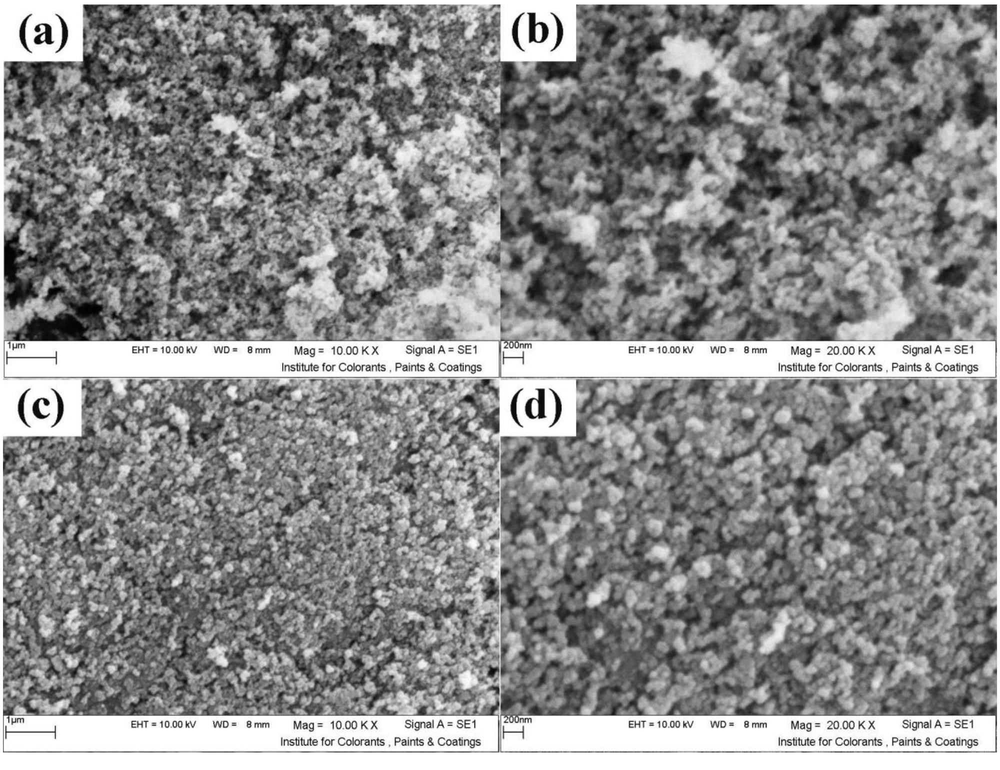

Fig. 4. SEM images of prepared samples from $SeCl_4$ and $Cr(NO_3)_3.9H_2O$ in the presence of 4ml of hydrazine and CTAB, at 180 ˚C for: (a,b) 18h (sample 5) , (c,d) 24 h (sample 6).

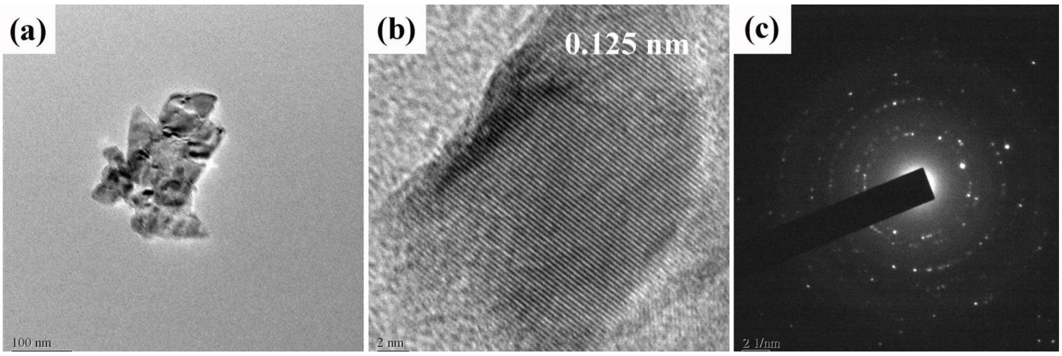

Fig. 5. (a) low-magnification, (b) high-magnification TEM images, (c) SAED pattern of sample 5.

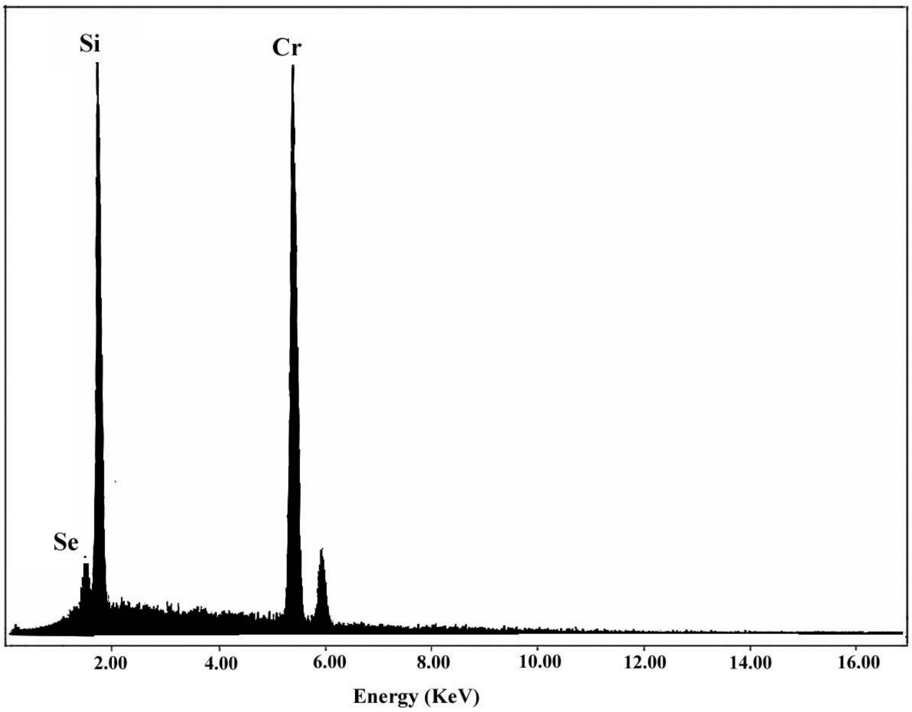

Fig. 6. EDS pattern of sample 6.

size of the Cr_2Se_3 nanostructures. For instance, when the reaction time increased from 12 to 18 (Fig. 4a and b) and then 24h (Fig. 4c and d) in samples 5 and 6, respectively, morphology of samples remained nearly constant; and particle size and agglomeration of nanoparticles were decreased and increased a little, respectively, as shown in Fig. 4. This figure shows that samples 5 and 6 with grain diameter about 50 nm have nearly even distribution.

TEM image of sample 5 obtained in the presence of CTAB and hydrazine at 180 ˚C for 18h (Fig. 5a), shows the nanoparticles are agglomerated and their particle sizes are in the range 20–50 nm. The HRTEM image of Cr_2Se_3 nanoparticles in Fig. 5b shows the nanoparticles are highly crystalline and distance between the two adjacent planes is measured to be 0.125 nm. The high-order diffraction spots and diffused halo ring in the SAED spectrum in Fig. 5c indicate that the nanoparticles prepared in the presence of CTAB and hydrazine are well crystallized.

EDS technique was used to determine the chemical composition of the products. Fig. 6 shows the EDS spectrum of the sample 6 obtained in the presence of CTAB and hydrazine. This figure shows the presence of Cr and Se elements in the products. In addition, neither N nor C signals were detected in the spectrum, which means there is no solvent or capping agent in the sample.

In our experiment, when Cr(NO$_3$)$_3$.9H$_2$O and SeCl$_4$ are added in the deionized water, a completely clear acidic solution is obtained that contain H$_2$SeO$_3$; however, H$_2$SeO$_3$ can be converted to Se, by N$_2$H$_4$.H$_2$O, quickly up on heating, which has high reactivity and is easy to be disproportionate into Se^{2-} ion under alkaline conditions (Eqs. (1)–(3)). Under the given condition, free Cr^{3+} ions can react with Se^{2-} ions (Eq. (4)) to form Cr$_2$Se$_3$. The proposed mechanism for the synthesis of Cr$_2$Se$_3$ can be expressed in the following equations:

$$SeCl_4 + 3H_2O \rightarrow H_2SeO_3 + 4HCl \qquad (1)$$

$$H_2SeO_3 + N_2H_4.\ H_2O \rightarrow Se \downarrow + N_2 \uparrow + 3H_2O \qquad (2)$$

$$3Se + 6OH^- \rightarrow 2Se^{2-} + SeO_3^{\,2-} + 3H_2O \qquad (3)$$

$$Cr^{3+} + Se^{2-} \rightarrow Cr_2Se_3 \downarrow \qquad (4)$$

CONCLUSIONS

A novel hydrothermal synthetic route to Cr$_2$Se$_3$ semiconductors was developed. For the first time, SeCl$_4$ was used as selenium source. The effect of some parameters such as, reductant, capping agent and reaction time on the particle size and morphology of the obtained products were investigated. The composition, structure and morphology of products were assigned with XRD, EDS, SEM and TEM.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Bube RH. Photoconductivity. Wiley Encyclopedia of Electrical and Electronics Engineering. 1960.
2. Salavati-Niasari M, Esmaeili-Zare M, Sobhani A. Cubic HgSe nanoparticles: sonochemical synthesis and characterisation. Micro & Nano Lett. 2012; 7(12):1300-4.
3. Salavati-Niasari M, Esmaeili-Zare M, Sobhani A. Synthesis and characterisation of cadmium selenide nanostructures by simple sonochemical method. Micro & Nano Lett. 2012; 7(8):831-4.
4. Sobhani A, Salavati-Niasari M. Synthesis and characterization of FeSe$_2$ nanoparticles and FeSe$_2$/FeO(OH) nanocomposites by hydrothermal method. J. Alloys Compd. 2015; 625:26-33.
5. Sobhani A, Salavati-Niasari M. Hydrothermal synthesis, characterization, and magnetic properties of cubic MnSe$_2$/Se nanocomposites material. J. Alloys Compd. 2014; 617:93-101.
6. Sobhani A, Salavati-Niasari M. Synthesis and characterization of a nickel selenide series via a hydrothermal process. Superlattices and Microstruct. 2014; 65:79-90.
7. Kamigaichi T, Masumoto KI, Hihara T. Electrical Properties of Chromium Sulfides. J. Phys. Soc. Japan. 1960; 15(7):1355-.
8. Masumoto KI, Hihara T, Kamigaichi T. Anomalies in Electrical Conductivity and Magnetic Susceptibility of Chromium Selenides. J. Phys. Soc. Japan. 1962; 17(7):1209-10.
9. Adler D. Mechanisms for metal-nonmental transitions in transition-metal oxides and sulfides. Revs. Mod. Phys. 1968; 40(4):714.
10. Adachi Y, Ohashi M, Kaneko T, Yuzuri M, Yamaguchi Y, Funahashi S, Morii Y. Magnetic Structure of Rhombohedral Cr2Se3. J. Phys. Soc. Japan. 1994; 63(4):1548-59.
11. Ohta S, Narui Y, Sakayori Y. Effect of Te-substitution on magnetic properties of Cr2Se$_{3-y}$Te$_y$ (0< y < 0.15). J. Magn. Magn. Mater. 1997; 170(1-2):168-78.
12. Jellinek F. The structures of the chromium sulphides. Acta Crystallogr. 1957; 10(10):620-8.
13. Peng Q, Dong Y, Deng Z, Li Y. Selective synthesis and characterization of CdSe nanorods and fractal nanocrystals. Inorg. Chem. 2002; 41(20):5249-54.
14. Peng Q, Dong Y, Deng Z, Kou H, Gao S, Li Y. Selective synthesis and magnetic properties of α-MnSe and MnSe$_2$ uniform microcrystals. J. Phys. Chem. B. 2002; 106(36):9261-5.
15. Du W, Qian X, Niu X, Gong Q. Symmetrical six-horn nickel diselenide nanostars growth from oriented attachment mechanism. Cryst. Grow. Des. 2007; 7(12):2733-7.
16. Stuczynski SM, Brennan JG, Steigerwald ML. Formation of metal-chalcogen bonds by the reac-tion of metal-alkyls with silyl chalcogenides. Inorg. Chem. 1989; 28(25):4431-2.
17. Yadav AA, Barote MA, Masumdar EU. Studies on cadmium selenide (CdSe) thin films deposited by spray pyrolysis. Mater. Chem. Phys. 2010; 121(1):53-7.
18. Fan H, Zhang M, Zhang X, Qian Y. Hydrothermal growth of NiSe$_2$ tubular microcrystals assisted by PVA. J. Cryst. Growth. 2009; 311(20):4530-4.
19. Devillanova F.A., Handbook of Chalcogen Chemistry, Department of Inorganic and Analytical Chemistry, University of Cagliari, Italy, 2007.