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優勝作品專輯

編 號：030008-08

作品名稱

鐵基奈米顆粒製程及物性分析

得獎獎項

化學科大會獎一等獎

美國正選代表:美國第61屆國際科技展覽會

學校名稱：臺北市立第一女子高級中學

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關鍵詞：超導體、 奈米製程、熱熔法

作者簡介

洪瑀（左）、林季潔（右）北一數資同學，一起找尋有關超導體的論文資料，與中研院教授討論後開始進行研究。近兩年來除了假日的時間，星期三、四下整個午專研時間也會到中研院做實驗。喜歡異想天開找很多題目來試試，不管是從期刊中實驗找靈感或是天外飛來一筆的想法，都曾是我們實驗的候補題目。

摘要

超導體具有兩大特性 - 抗磁性及零電阻，若善加利用便能大量減少能量損失。不過目前發現的超導體有的結構太複雜，其他則是臨界溫度太低。一年前科學家發現不同於以往銅氧組成的鐵基超導體（FeSe），結構簡單但其臨界溫度仍然太低。故我們利用原料濃度比例不同的 Fe 及 Se 以 TOPO 熱熔法析出奈米顆粒，分析其超導性質。結果顯示 Fe 比 Se 難析出，故 Fe 濃度應比 Se 多，且在油性水域中較好混合。

壹、研究動機

在報紙上讀到中研院物理團隊有關構造簡單鐵基超導體的資料，我們對此感到極大興趣，在讀過相關論文後，根據量子效應導致超導體在奈米顆粒尺寸下可能提高臨界溫度，所以我們打算製造出鐵基超導奈米，測其超導性質。

貳、研究目的

一、 找出能溶解 Se 的較佳溶劑。

二、 找出能較佳結合 Se 的含 Fe 化合物。

三、找出較佳的方法合成 FeSe 奈米顆粒。

四、 探討不同莫耳數比的 Fe 及 Se 對製造出的奈米顆粒之影響。

五、分析製造出的 FeSe 奈米顆粒的超導性質。

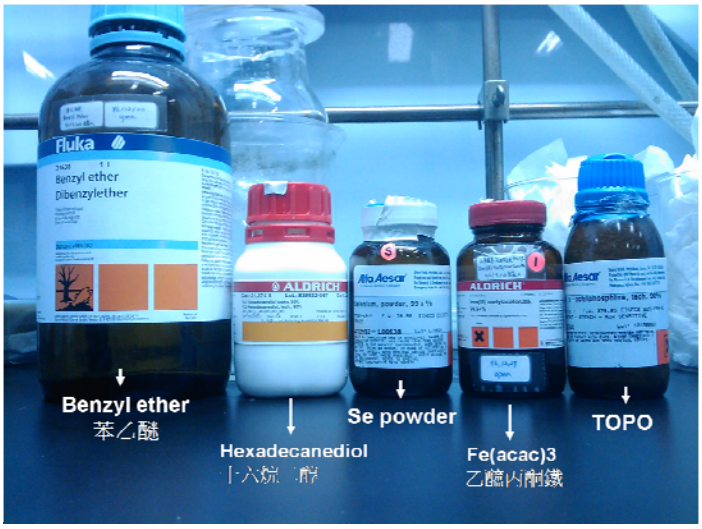
參、研究設備及器材

一、 藥品：$Fe(acac)_3$ 乙醯丙酮鐵(III)、Benzyl ether 苯乙醚、Se powder 硒、TOPO、Hexadecanediol 十六烷二醇、鹽酸、氫氧化鈉、草酸鐵、醋酸鐵

二、器材：三口燒瓶、加熱器、電子秤、離心機、TEM、SEM、XRD

1. TEM (Transmission Electron Microscope)、SEM (scanning electron microscope)：藉由穿透式電子顯微鏡及掃描式電子顯微鏡觀察所製作之 FeSe 奈米顆粒於不同條件中微觀的形貌。

2.XRD(X-ray diffraction)：利用 XRD 繞射分析所得之圖譜，與標準圖譜相比對，藉以得知所製作之奈米顆粒中含有的化合物種類與結構。



肆、研究過程或方法

一、以酸鹼中和方法合成 FeSe 奈米顆粒。

步驟一： 調製Se溶液	步驟二： 選取含Fe的化合物	步驟三： 將溶液混合	結果
將Se溶於鹽酸溶液中	將草酸鐵溶於水中	將兩者加熱	Se鹽酸溶液和氫氧化鈉溶液中，Se的溶解率只有約20%。製作出的顆粒大都是氧化鐵，極少硒化鐵。
將Se溶於鹽酸溶液中	將醋酸鐵溶於水中	將兩者加熱	
將Se溶於NaOH溶液中	將草酸鐵溶於水中	直接混合	
將Se溶於NaOH溶液中	將醋酸鐵溶於水中	直接混合	

由上述實驗中，我們發現以強酸或強鹼作為溶劑，無法作出較佳的 FeSe 奈米顆粒，故改採用介面活性劑 TOPO，將 FeSe 置於油性環境中加熱，以熱熔法製造 FeSe。

二、以 TOPO-TOP 熱熔法製造 FeSe

步驟：

1.調配溶液 A：將 $Fe(acac)_3$ 1 莫耳加入苯乙醚 5ml 中

2.調配溶液 B：將 Se powder 2 莫耳加入 TOP 2 ml，再加入 TOPO 溶液中。

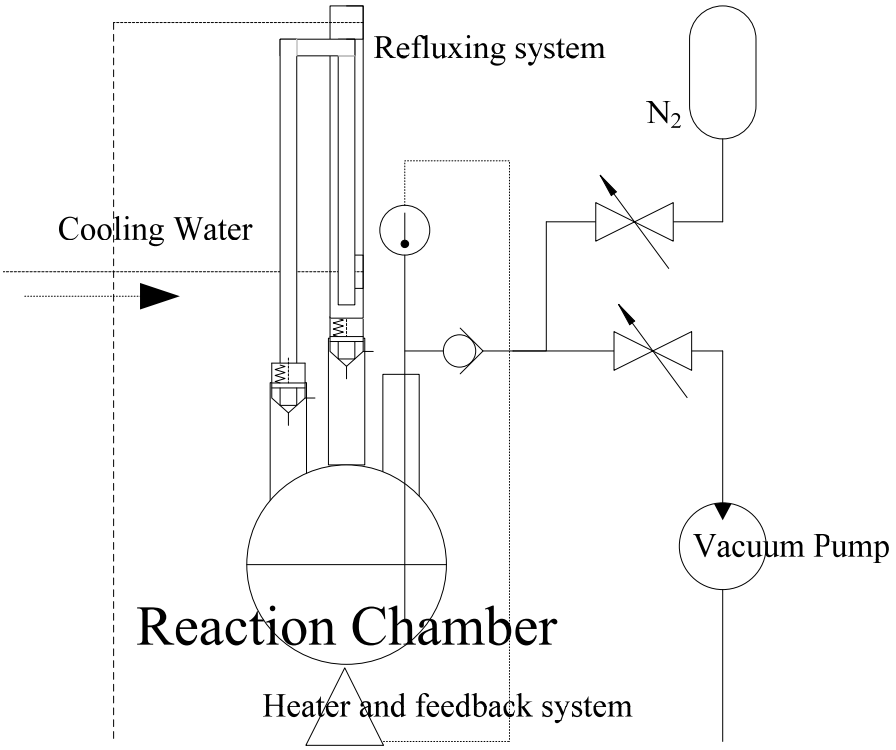
3.將 Hexadecanediol 及苯乙醚及 Sol B 加入三口燒瓶，並在充塞 N2 的密閉系統中緩慢加熱至 311℃。

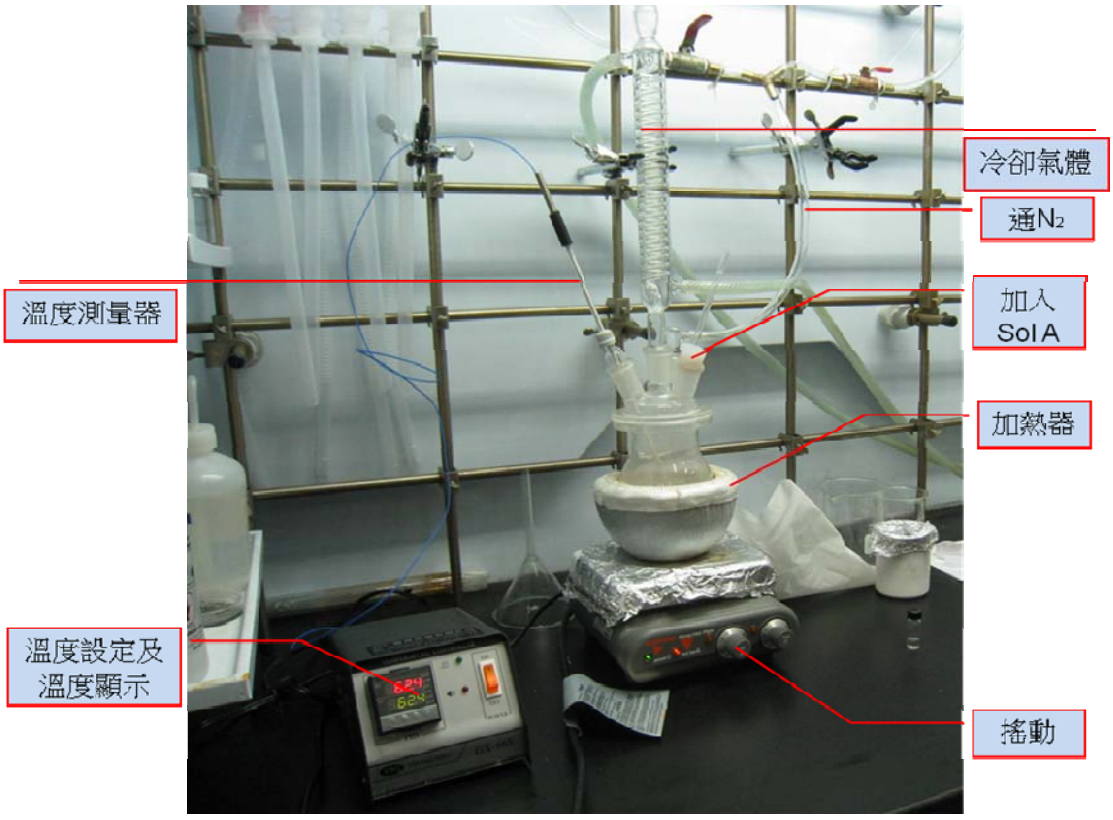
4.步驟三之溶液達到 311℃後，加入溶液 A，接著維持溫度(311℃─305℃)5 分鐘。

5.降溫後離心。

6.將上述製作出的奈米顆粒以 TEM 及 XRD 分析其物理性質。

7.重複上述步驟，惟有改變一變因：反應物 Fe:Se 的莫耳數比逐漸增加。





三、改乙醯丙酮鐵為醋酸鐵(II)

步驟：

1.調配溶液 A：將 $Fe(CH_3CO_2)_2$ 2 莫耳加入苯乙醚 5ml 中

2.調配溶液 B：將 Se powder 1 莫耳及 TOP 1 莫耳，再加入 TOPO 溶液中。

3.將 Hexadecanediol 及苯乙醚及 Sol A 加入三口燒瓶，並在充塞 N2 的密閉系統中緩慢加熱至 300℃。

4.步驟三之溶液達到 300℃後，加入溶液 A，接著維持溫度(300℃—305℃)5 分鐘。

5.降溫後離心。

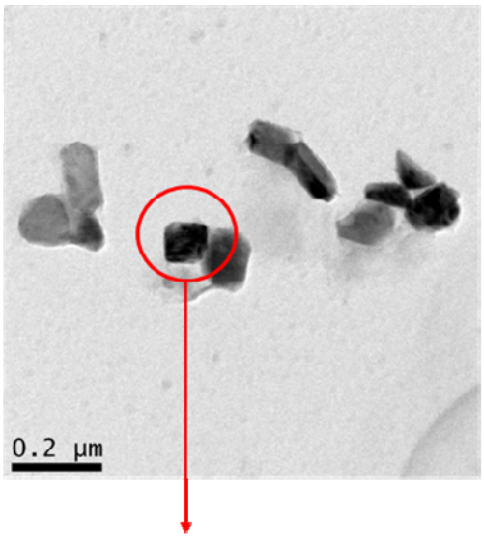
6.將上述製作出的奈米顆粒以 TEM 及 XRD 分析其物理性質。

7.重複上述步驟，惟有改變一變因：反應物 Fe:Se 的莫耳數比逐漸增加。

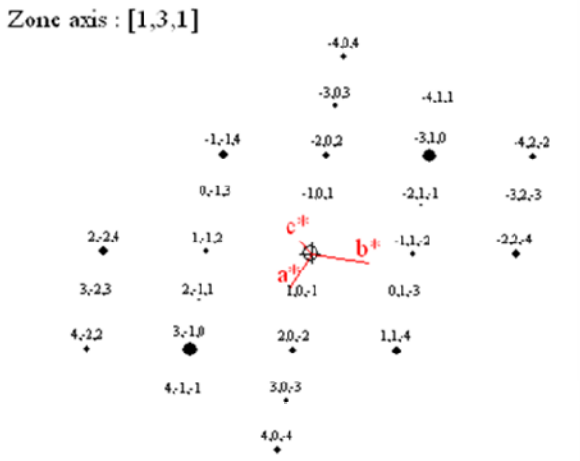
伍、研究結果

一、實驗①：

反應物 Fe:Se 的比例為 1:2→製出的奈米顆粒含 Fe_3Se_4 & Fe_1Se_2

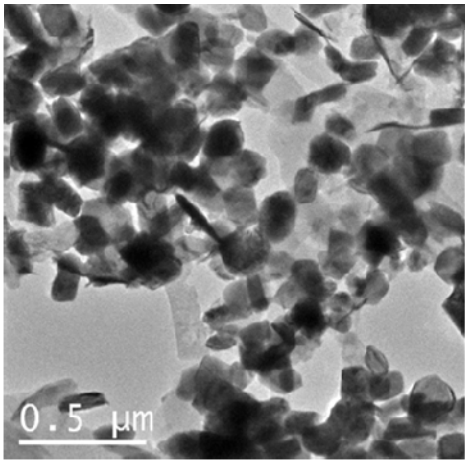


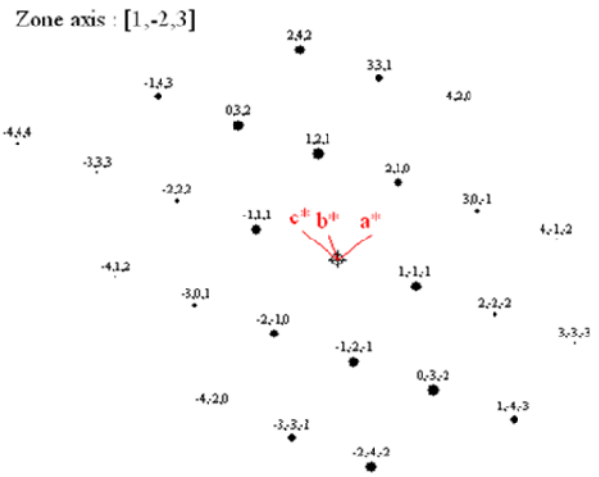
monoclinic–Fe_3Se_4



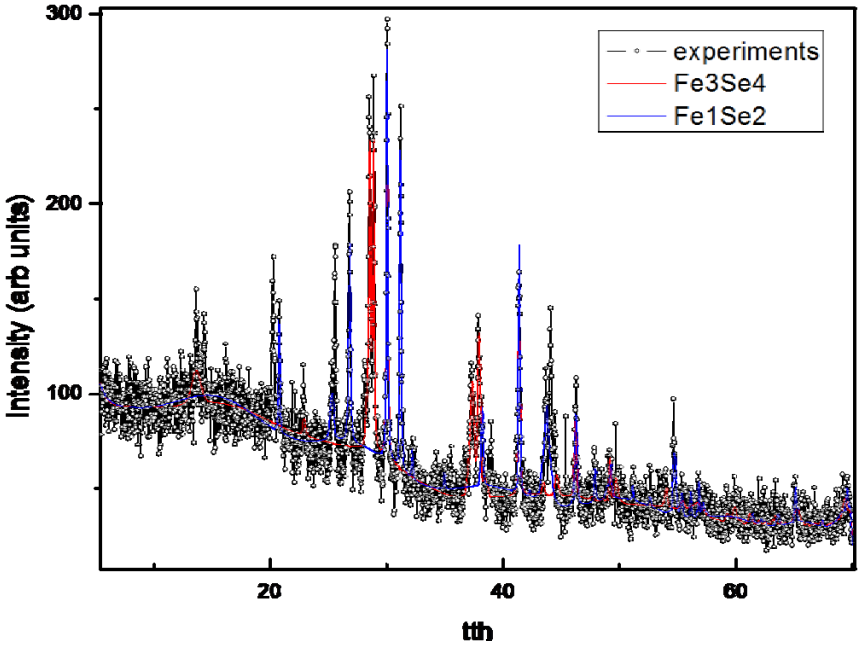
element	O	Fe	Se	Se/Fe
atomic%	40.64	24.72	34.64	1.40

orthorhombic–Fe_1Se_2

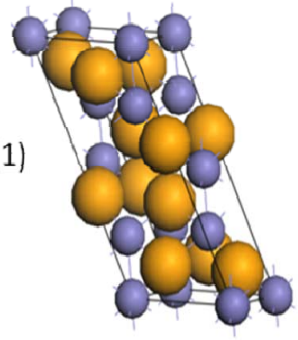




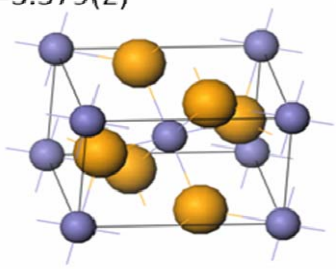
element	Fe	Se	Se/Fe
atomic%	37.82	62.18	1.64

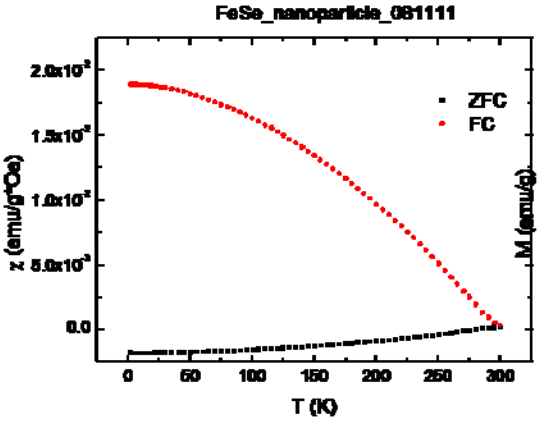


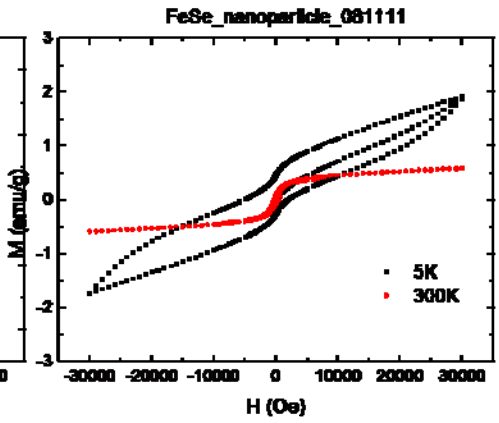
Fe_3Sc_4 Monoclinic
a=12.718(1)
b=3.513(2)
c=6.310(3)
beta=117.136(1)



Fe_1Se_2 Orthorhombic
a=4.807(4)
b=5.784(7)
c=3.579(2)







抗磁性測量： Fe_3Se_4 不具抗磁性

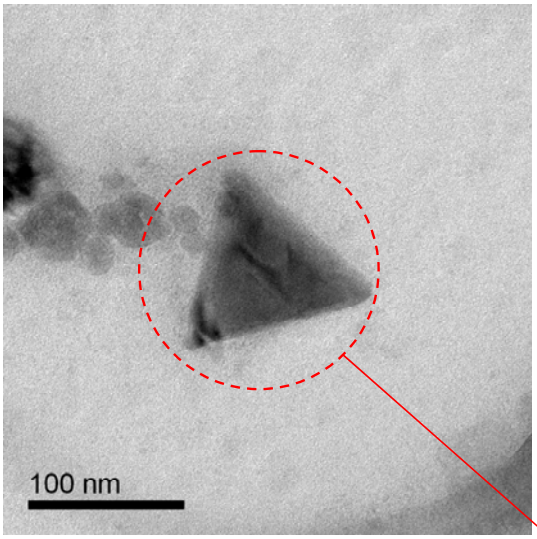
我們推測奈米顆粒可能也需要如塊材 Fe_1Se_1 相同的結構才具超導性質。

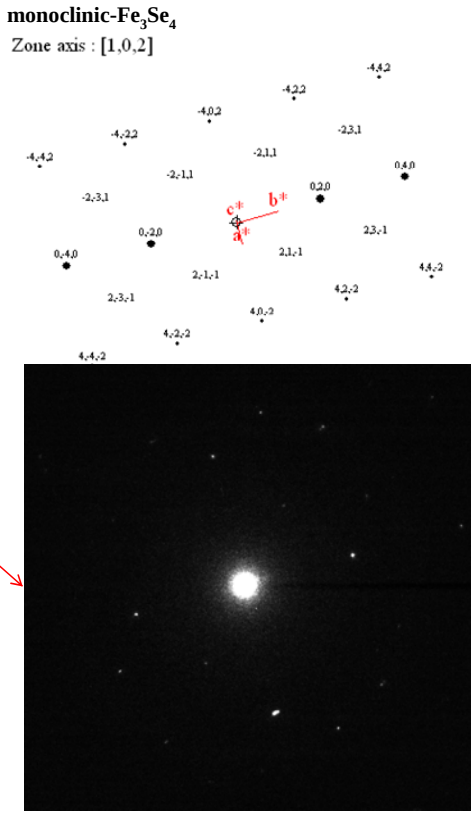
之後的實驗，我們嘗試改變反映物希望要析出 Fe_1Se_1 的奈米顆粒

二、實驗②：

反應物 Fe:Se 的比例為 1:1→製出的奈米顆粒大多為 Fe_3Se_4

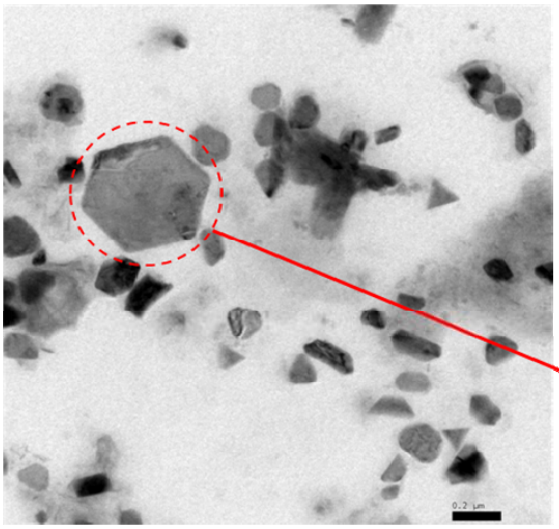
其組成與實驗一所製出的奈米顆粒類似，唯多了一些形狀特殊的顆粒

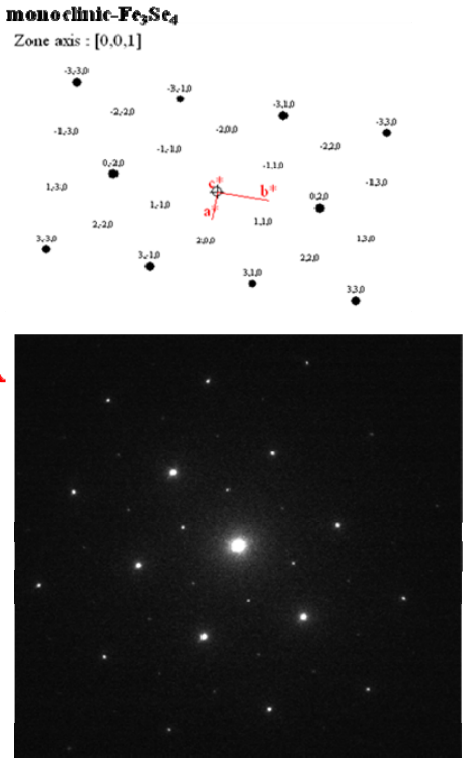




↑參有三角形的顆粒

element	O	Fe	Se	Se/Fe
atomic%	53.25	22.14	24.61	1.11



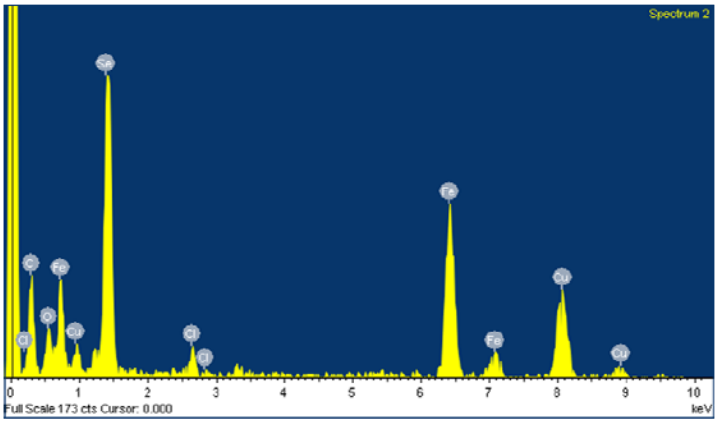


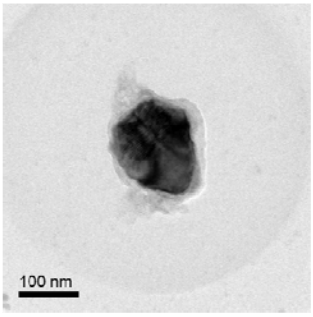
↑參有六角形的顆粒

element	O	Fe	Se	Se/Fe
atomic%	25.48	32.49	42.03	1.29

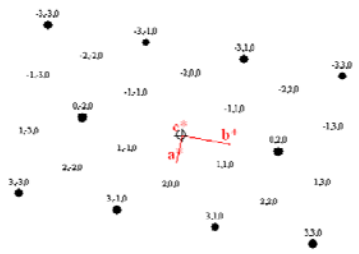
三、實驗③：

反應物 Fe:Se 的比例為 2:1→製出的奈米顆粒大多為 Fe_3Se_4 以及極少數 Fe_1Se_1

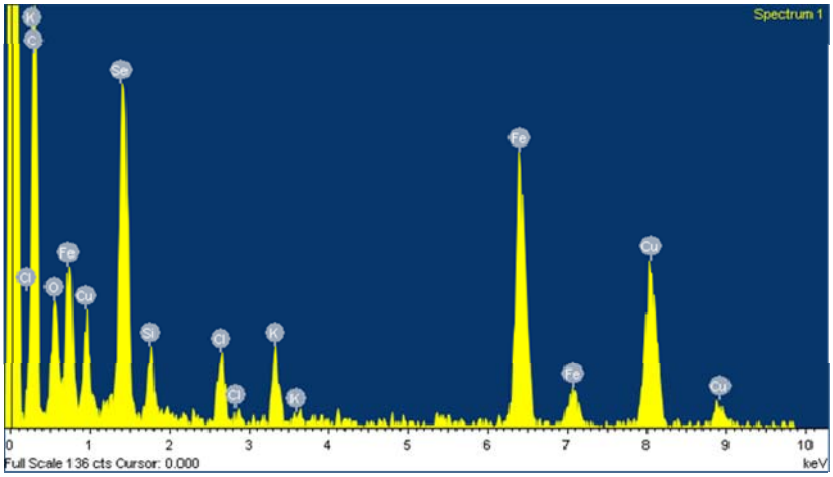




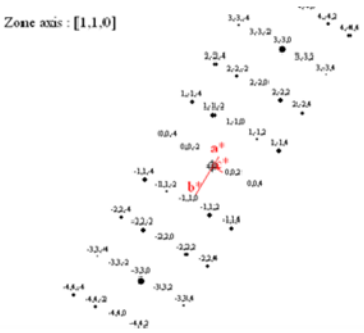
Zone axis : [0,0,1]



element	Fe	Se	$FeSe_x$
atomic%	43.15	56.85	$FeSe_{1.32}$

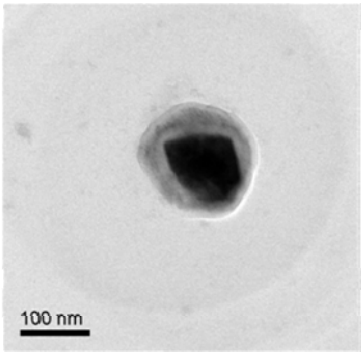


Zone axis : [1,1,0]

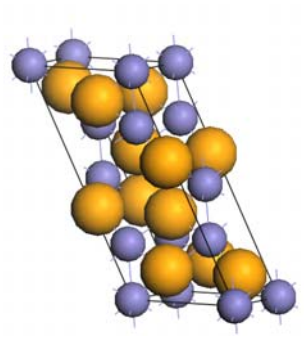
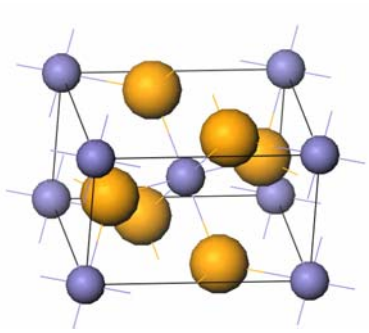
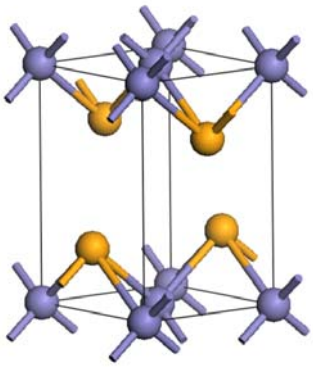
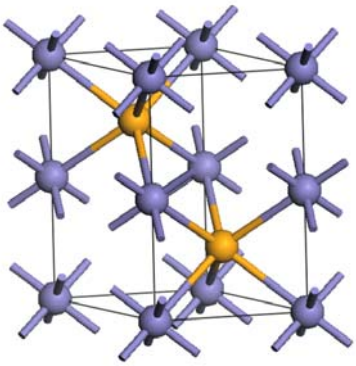


element	Fe K	Se L	$FeSe_x$
atomic%	51.88	48.12	$FeSe_{0.93}$

比例將近1:1

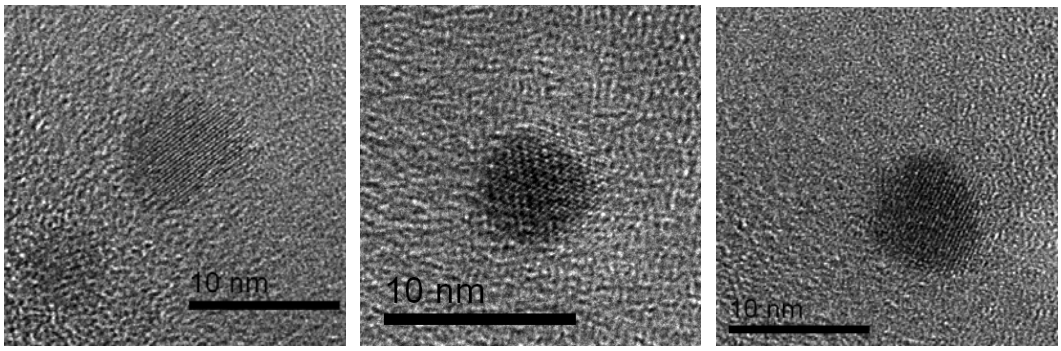


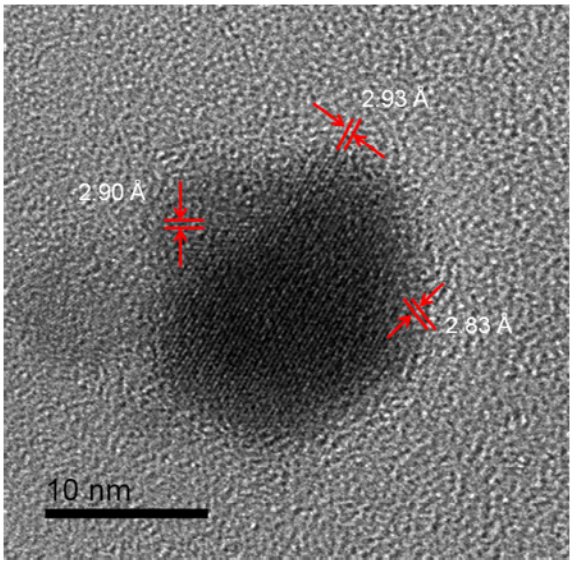
各種 Fe_xSe_y

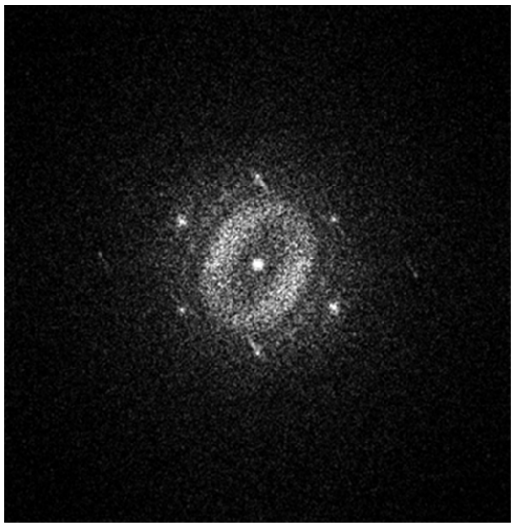
顆粒名稱	顆粒名稱
Fe_3Se_4 Monoclinic 	Fe_1Se_2 Orthorhombic 
Fe_1Se_1 Tetragonal 	Fe_1Se_1 Hexagonal 

四、實驗④：

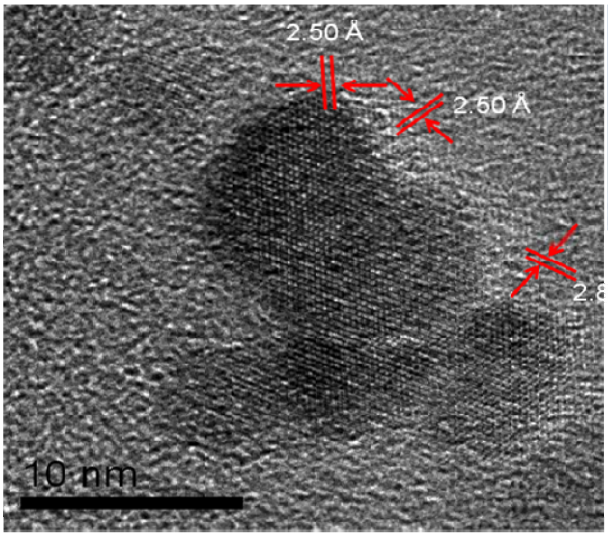
反應物 Fe 改為 $Fe(CH_3CO_2)_2$→製出的奈米顆粒出現 Fe_1Se_1

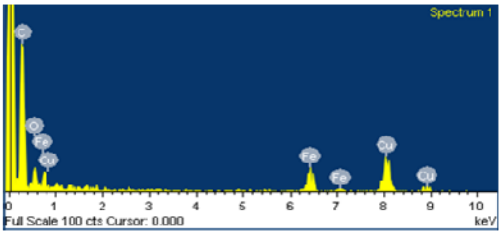




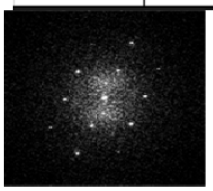


simulated diffractogram



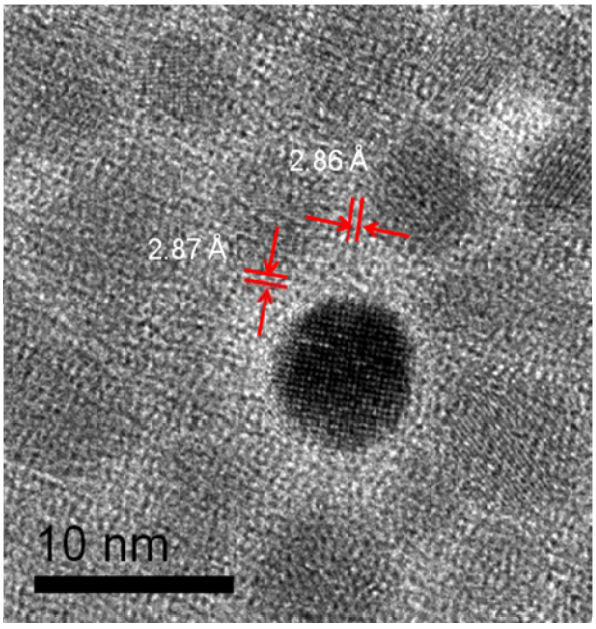


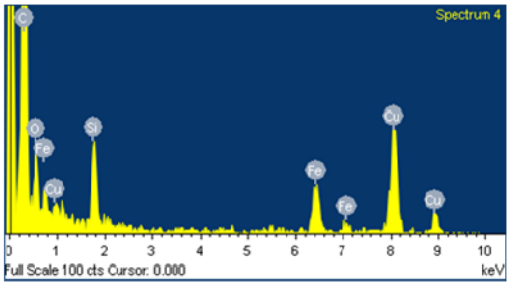
element	Fe K	O K	FeO_x
atomic%	29.26	70.74	$FeO_{2.42}$



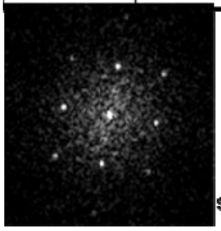
monoclinic-Fe_3Se_4
zone axis: [131]

simulated diffractogram

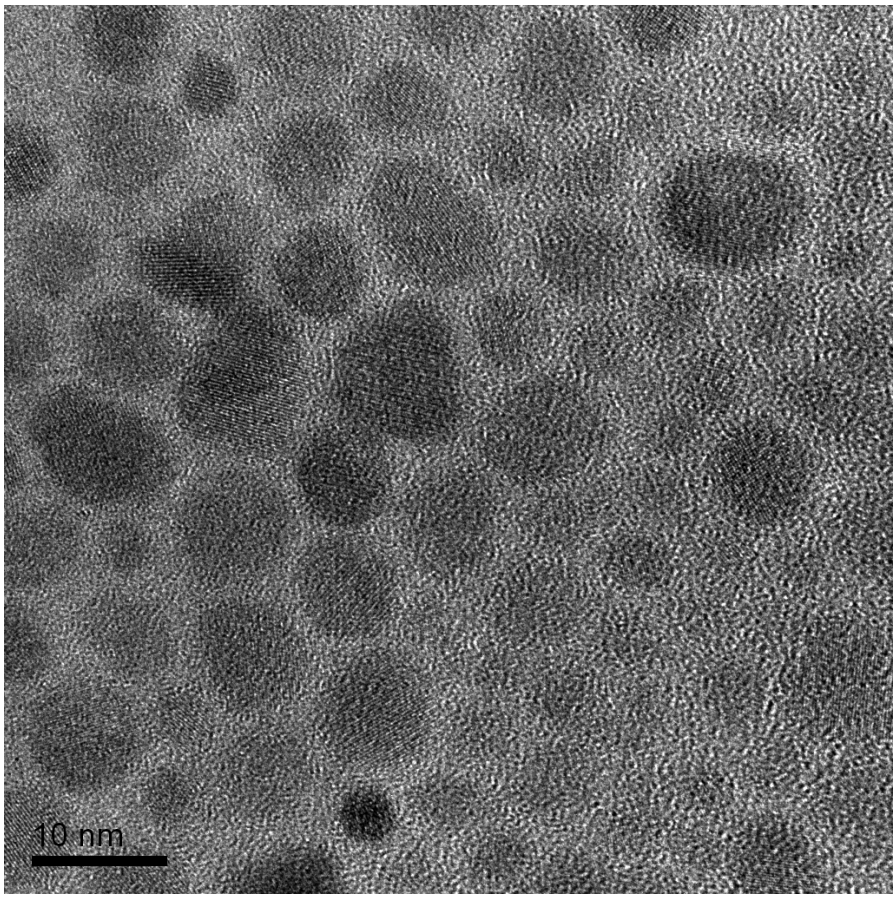


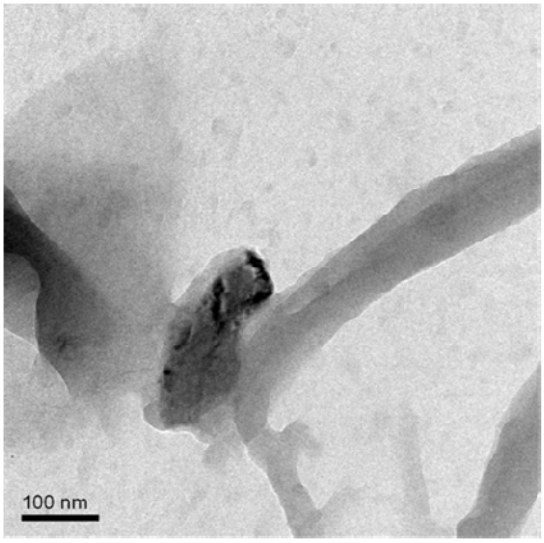


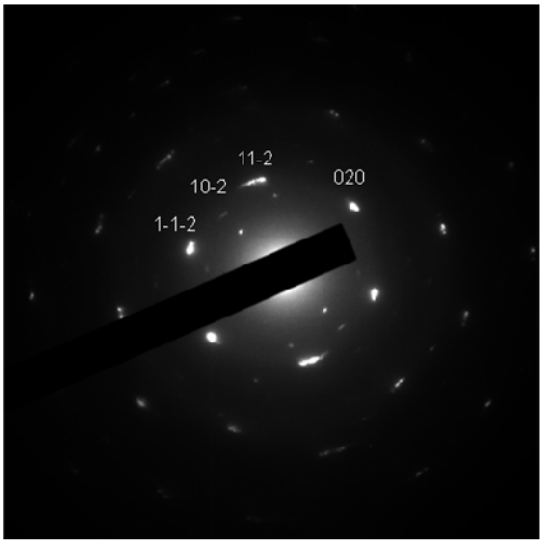
element	Fe K	O K	FeO_x
atomic%	19.56	80.44	$FeO_{2.42}$



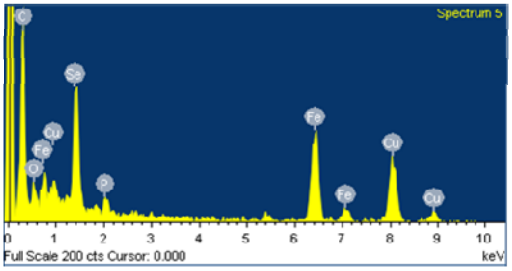
simulated diffractogram



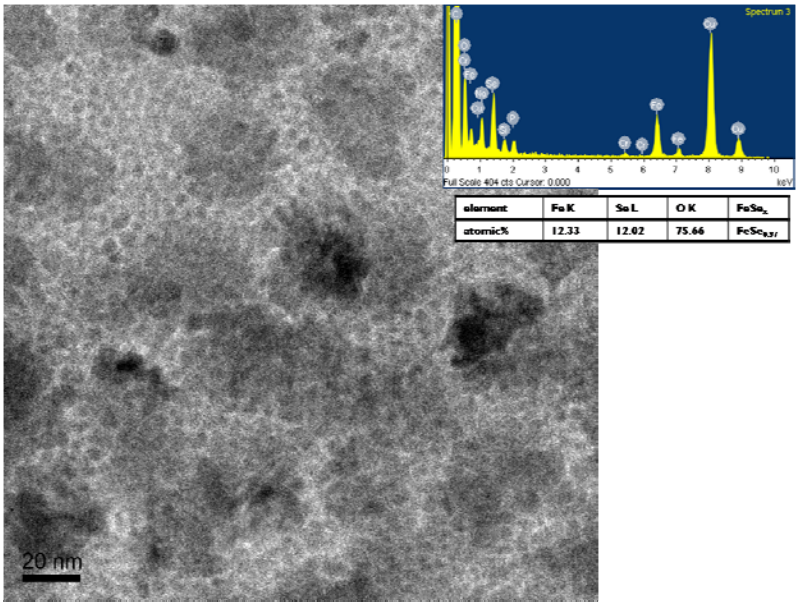


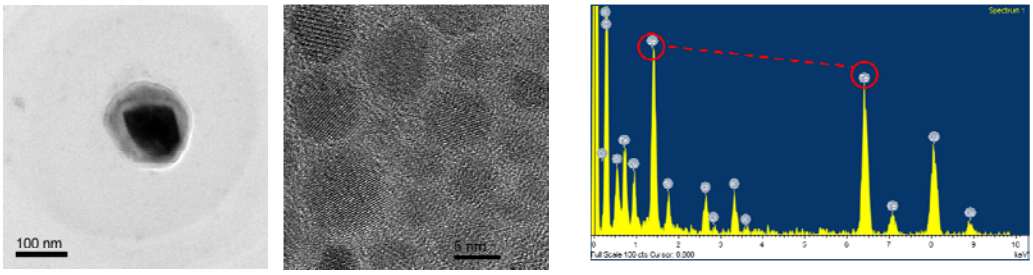


tetragonal-FeSe
zone axis: [201]



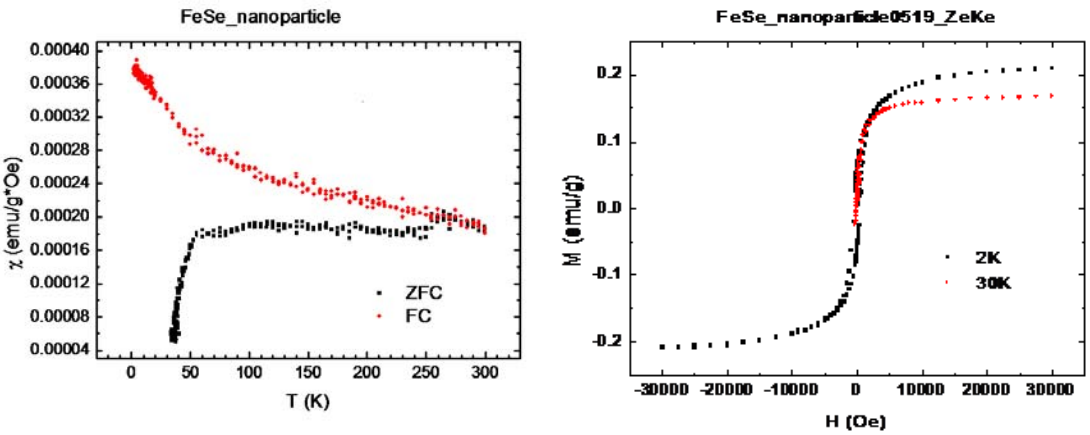
element	Fe K	Se L	O K	$FeSe_x$
atomic%	35.04	33.93	31.03	$FeSe_{0.97}$





element	Fe K	Se L	FeSe$_x$
atomic%	51.88	48.12	FeSe$_{0.93}$

比例將近1:1



由上圖可見由二價鐵所製出的 Fe_1Se_1 在 45K 左右明顯表現出超導特性(抗磁性和零電阻特性)，比塊材的鐵基超導體臨界溫度約提升 10K

陸、討論

一、雖然反應物的 Fe:Se 的比例未必和生成物的 Fe:Se 比例成正比，但兩者間仍具一定相關性。

二、在實驗中，原料 Fe:Se 濃度比逐漸增加過程中，所得到的奈米顆粒中，Fe_3Se_4 占大多數，故推測 Fe_3Se_4 應是其最穩定態。

三、實驗中，原料 Fe:Se 濃度比逐漸增加至 4:1，所得到的奈米顆粒中，Fe_1Se_1 析出的比例越來越多，故推測 Fe 可能比 Se 較難析出。

四、當 Fe:Se 濃度比為 1:1 時，所得到的奈米顆粒，其形狀越來越趨向於 60 度或 120 度，奈米顆粒傾向於形成三角形或六角形，且測量出顆粒大都為 Fe_3Se_4，推測應是其晶體形狀：單斜方導致上述情形。

五、Fe_3Se_4 測出的物理性質中，並不具超導性質，故我們推測奈米顆粒可能也需要如 Fe_1Se_1 塊材相同的結構才具超導性質。

六、這次的實驗中，嘗試了許多方法要析出 Fe_1Se_1 的奈米顆粒，但析出的顆粒大部分都為 Fe_3Se_4 ，我們認為可能與我們之前所使用原料 $Fe(acac)_3$ 的價數有關。

七、二價鐵 $Fe(CH_3CO_2)_2$ 所製出的 Fe_1Se_1 的比例較三價鐵 $Fe(acac)_3$ 多，可知 Fe 原料的價數大幅度影響析出的顆粒。

八、在實驗的過程中，溶液 A 的加入迅速與否似乎也會影響顆粒均勻度，因此實驗時要盡量穩定快速的加入溶液 A，使析出的奈米顆粒均勻。

柒、結論

經過多次實驗我們找出製作 FeSe 奈米顆粒最佳的方法：TOPO-TOP 熱熔法，然而製作出的奈米顆粒 Fe_3Se_4 經過測量不具超導性質。而 FeSe 塊材的結構 Fe:Se=1:1 時，始有超導性質，故我們推測奈米顆粒 Fe_1Se_1 才有超導性質。經過多次實驗，發現反應物 Fe 的比例要較 Se 高，且原料最好選用二價鐵，以利製造

出 Fe_1Se_1。製出的 Fe_1Se_1 在 45K 左右明顯表現出超導特性，比塊材的鐵基超導體臨界溫度約提升 10K。

捌、參考資料

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二、物理雙月刊 2009 年二月　卅一卷一期

三、陳姿蓉 2007 年 Coexistence and Competition between Superconductivity and Spin Polarization in Sn Nanoparticles 其中奈米錫顆粒的超導與自旋極化

四、賴佳伶 2002 年 Penetration depth of superconductor in Pb nano particles 1-1 奈米顆粒的特性&1-2 超導體的特性

五、Brian L. Cushing, Vladimir L. Kolesnichenko, and Charles J. O'Connor　Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana

六、W.-H. Li,1,2, C. C. Yang,2 F. C. Tsao,1 S. Y. Wu,1 P. J. Huang,1 M. K. Chung,1 and Y. D. Yao21　Enhancement of superconductivity by the small size effect in In nanoparticles, Department of Physics, National Central University

Synthesis and Analysis of the New Superconducting Material – FeSe Nanocrystals

Project ID: CH303

Abstract:

According to recent publications, turning superconductors into nanoscale particles might enhance its critical temperature (Tc). Therefore, we tried to find an effective method to synthesize FeSe nanocrystals and analyze their superconducting properties. After performing the experiments several times, we manage to find three effective chemical routes including Hexadecanediol-TOP (trioctylphosphine) hot injection method, Ethylene glycol-TOP hot injection method, and Hexadecylamine-TOP hot injection method to produce FeSe nanocrystals. Among them, the last one is the most effective chemical route in producing FeSe nanocompounds with superconductivity properties. There are several possible crystalline structures that can form in the Fe-Se series, but superconducting screening is observed only in the nanocrystalline tetragonal FeSe. Most importantly, the superconducting critical temperature of nanocrystalline tetragonal $FeSe_{1-x}$ is found to be noticeably higher than that of its bulk counterpart.

Jacqueline Hung and Chi-Chieh, Lin

§ Introduction

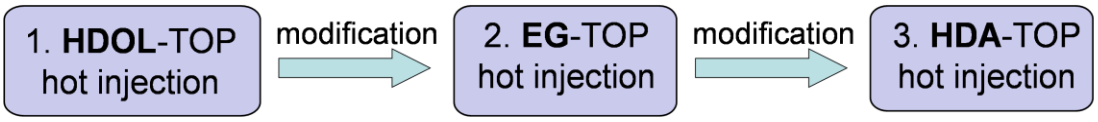
Iron is a ferromagnetic material, but surprisingly, in 2008, scientists discovered iron-based superconductor that shows diamagnetic screening below its critical temperature (Tc). It is known that the diamagnetic and zero-resistance nature of superconductors can greatly reduce the amount of energy lost. It seems to show promise as the next generation of high temperature superconductors. Among the iron-based series, iron-selenium superconductor stands out as a simpler structure and more importantly being not toxic. According to recent publications, reducing superconductors into nanoscale particles might enhance its Tc. Therefore, we tried to find an effective method to synthesize FeSe nanocrystallites and analyze their superconducting properties.

§ Research Goals:

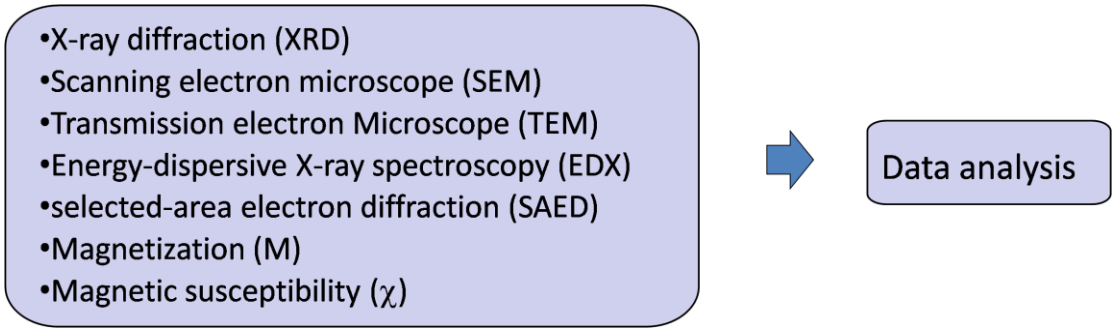
I. To study effective methods to synthesize FeSe nanocrystals with higher Tc.
II. To analyze the superconducting properties of FeSe nanocrystals.

§Flow Chart:

I. Improvement of chemical synthesis:



II. Physical analysis :



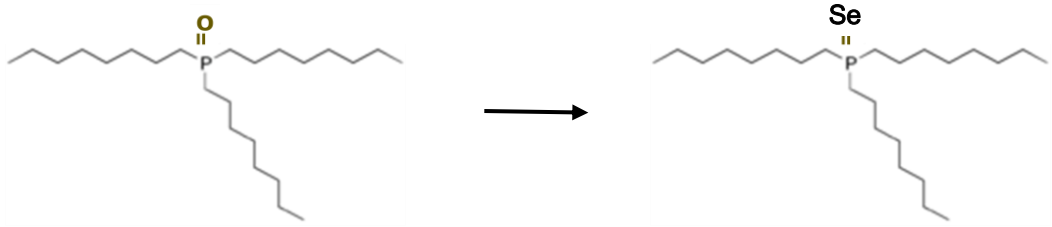
§ Materials and Equipments:

I. Chemicals: Iron(III) acetylacetonate [$Fe(acac)_3$], benzyl ether, selenium powder, TOPO(trioctylphosphine oxide), TOP(trioctylphosphine), hexadecanediol, $Fe(CH_3COO)_2$, $FeCl_2 \cdot 4H_2O$, EG(ethylene glycol), HDA (1-hexadecylamine), HCl and NaOH
Equipments: Three-neck boiling flask, heater, electronic scale, centrifuge, TEM, SEM, EDX, XRD, SQUID

1. XRD (X-ray Diffraction) provides diffraction patterns for analysis and comparison with standard pattern, enabling the determination of crystalline structure and type of resultant compounds.
2. TEM (Transmission Electron Microscope) and SEM (Scanning Electron Microscope) were used to image the nanoparticles products at the microscopic level and under different conditions the FeSe nanocrystallites produced.
3. EDX(Energy-dispersive X-ray spectroscopy) was used for the elemental analysis or chemical characterization of a sample.
4. SAED(selected-area electron diffraction) was performed inside a transmission electron microscope (TEM). The image on the screen of the TEM will be a series of spots—the selected area diffraction pattern, , each spot corresponding to a satisfied diffraction condition of the sample's crystal structure.
5. SQUID (Superconducting quantum interference devices) was used to measure magnetic signals and responses, employing superconducting loops and Josephson junctions.

§ Methods:

We tried to use TOPO for dissolving selenium for improving the growth of nanoparticles, heating the FeSe in an oily environment [2].



The oxygen would be replaced with selenium temporally, and therefore selenium could be dissolved in the solution.

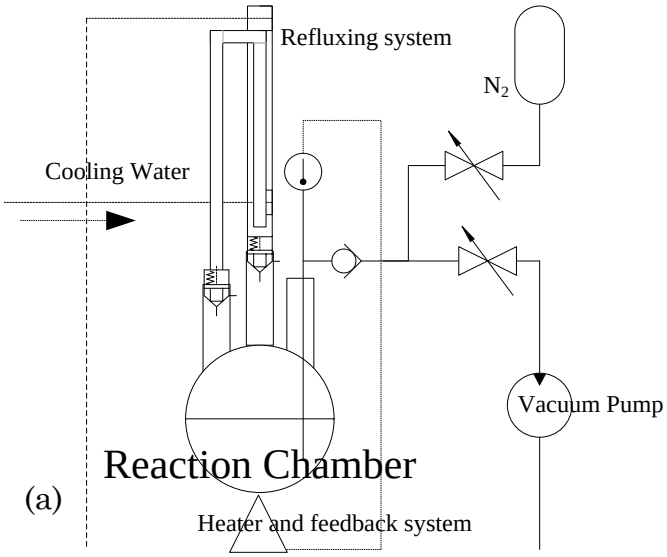
The following reasons are for changing to use TOPO-TOP as solvent for producing FeSe:

I. Preventing from oxidation
II. Successfully dissolving selenium
III. Ensuring the scale of the product

[I.] Method 1: HDOL-TOP hot injection method

Steps:

1. **Solution A**: 1 mmole of Iron(III) acetylacetonate [$Fe(acac)_3$] and 2 ml of benzyl ether
2. **Solution B**: 2 mmole of Se powder and 2 ml of TOP, were added in a 5 ml of TOPO solution.
3. One gram of Hexadecanediol (HDOL), 8 ml of benzyl ether and 7 ml of **solution B** were added into a three-neck boiling flask. Then, we slowly heated it up (~5℃ /min) to 300℃ in a closed system of N_2.
4. After the solution in step 3 reached 300℃, we added in 2 ml of **solution A** and maintained the heat for five min.
5. The products were centrifuged at 6,500 rpm for 10 min after reaction.
6. Analyze the physical properties of the nanocrystallites produced by XRD, TEM, SEM and SQUID.



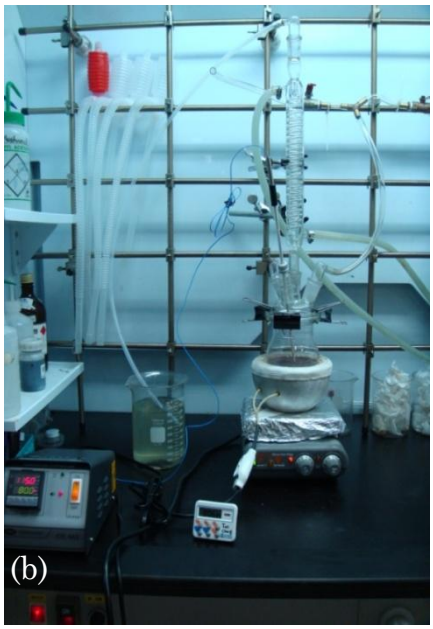


Fig. 1 (a) Design of the experimental device

(b) Photo of the experimental device

[II.] Method 2: EG TOP hot melt method

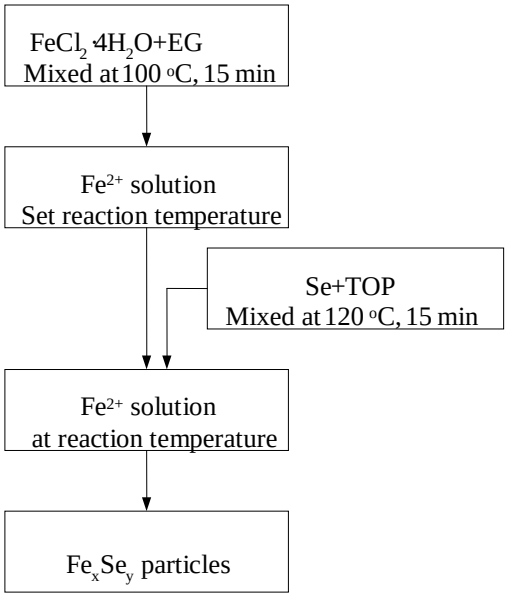
Solvents: Ethylene glycol (EG) : $C_2H_4(OH)_2$

trioctylphosphine (TOP)

: $\{CH_3(CH_2)_7\}_3P$

Reagents: Fe^{2+} source : $FeCl_2 \cdot 4H_2O$

Se source : Se powder



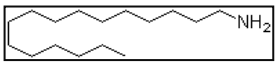
Steps:

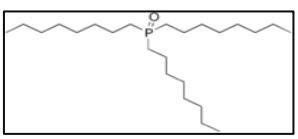
1. **Solution A**: 1 mmole of $FeCl_2 \cdot 4H_2O$ and 5 ml EG (ethylene glycol) were mixed at 100℃.
2. **Solution B**: 0.5 mmole of Se powder and 2 ml of TOP were mixed at 120℃.
3. 5 ml of **solution A** was added into a three-neck boiling flask and slowly (~5℃ /min) heated it up to 200℃ in a closed system of N_2.
4. After the solution reached 200℃, we added in **solution B** and maintained the heat at 200℃ for 2 hours.
5. The products were centrifuged at 6,500 rpm for 10 min after reaction.

Analyze the physical properties of the nanocrystallites produced by XRD, TEM, SEM and SQUID.

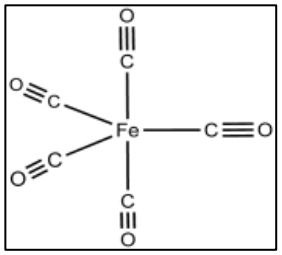
[III.] Method 3: HDA-TOP hot injection method

Solvent:

1-hexadecylamine (HDA) 

trioctylphosphine oxide(TOPO) 

Se source: Se powder



Fe source: $Fe(CO)_5$

Steps:

sol A: HDA 14mmol + TOPO 16mmol
sol B: TOP 3mL + Se 4mmol
sol C: Fe(CO)5 4mmol

1. Heat up the sol A to 160 °C , then add the well-mixed Sol B & C
2. Increase the temperature to 250 °C slowly (~5 °C /min) and keep for 1 hr.
3. Let the solution naturally cool down to 80 °C, then pour the crude solution in to hexane/ethanol.
4. Centrifuge the solution at 6,500 rpm for 10 min, and collected the black precipitation products.
5. Analyze the physical properties of the nanocrystallites produced by XRD, TEM, SEM and SQUID.

§ Results and Discussion:

[I.] Method 1: HDOL-TOP hot injection method

- **Experiment 1:**

At a molar ratio of 1:2 iron to selenium, the reactants produced nanocrystals containing Fe_3Se_4 and $FeSe_2$. XRD pattern of Fe_3Se_4 /$FeSe_2$ showed that we produced a lot of Fe_3Se_4 and $FeSe_2$ by this chemical method.

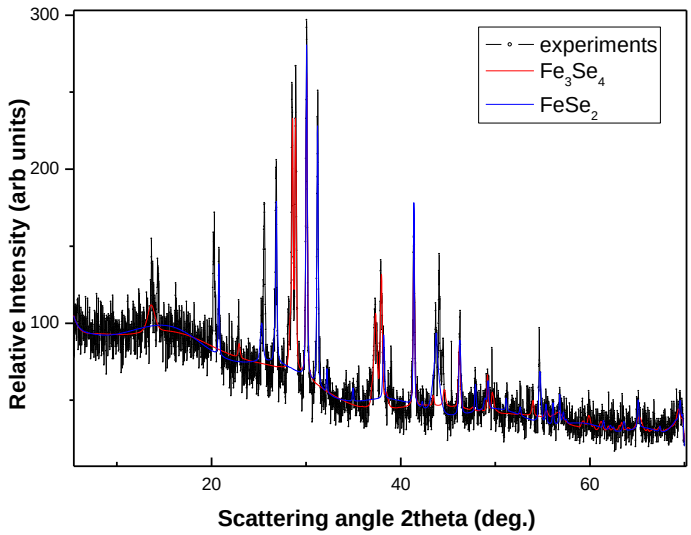
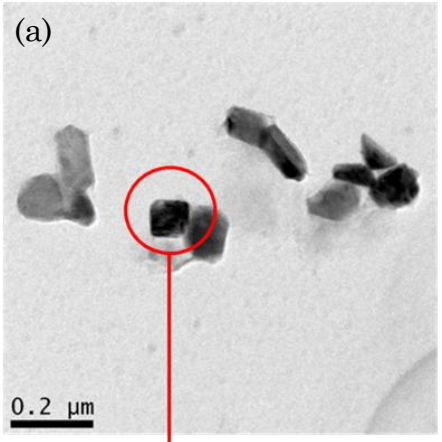
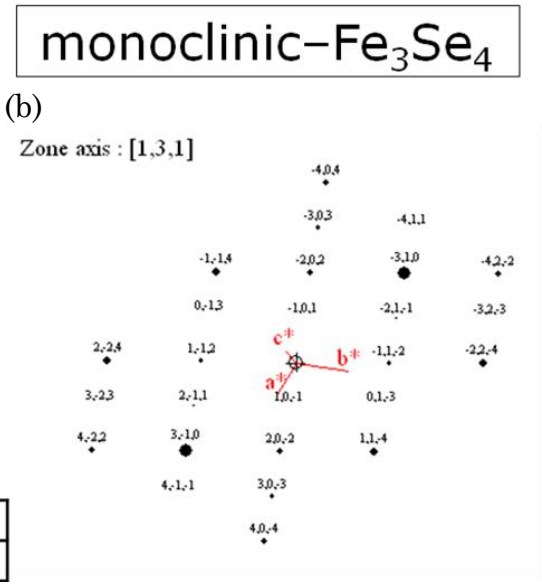


Fig.2 XRD pattern of Fe_3Se_4 /$FeSe_2$

Monoclinic Fe_3Se_4 nanocrystals of particle diameter around 100 nm can be fabricated employing this HDOL-TOP hot injection route, as shown in Fig.3 (a). Detailed transmission electron microscopy is shown in Fig.3 (b). The structure of Fe_3Se_4 nanoparticle is monoclinic in (1,3,1) direction which is revealed by SAED pattern. In Fig.3 (c), it shows that the EDX result from this area and the composition of Fe_3Se_4 nanoparticle is 1 to 1.4.





(c)

element	O	Fe	Se	Se/Fe
atomic%	40.64	24.72	34.64	1.40

Fig. 3 (a) TEM image (b) SAED pattern and (c) EDX result of Fe_3Se_4

Then we analyzed the superconductivity of the monoclinic Fe_3Se_4 and orthorhomb $FeSe_2$, and the results indicate that neither of them show the characteristic of superconductivity.Fig. 4 (a) and (b) indicate that Fe_3Se_4 and $FeSe_2$ show no diamagnetism.

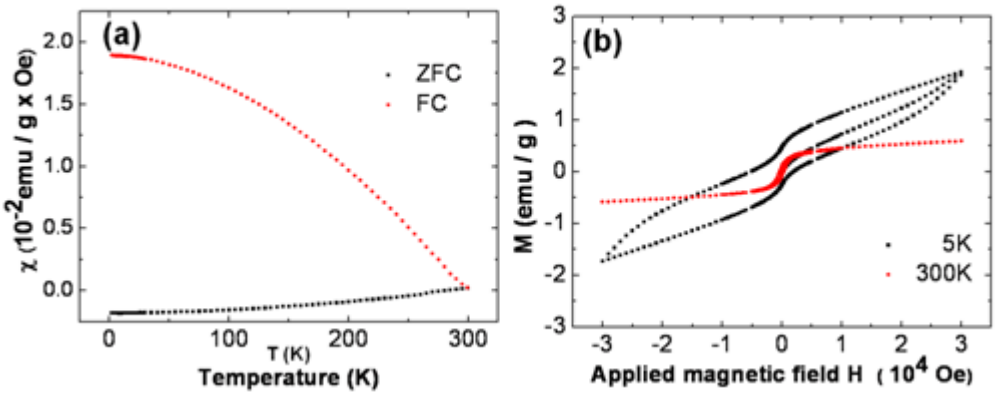


Fig. 4 (a) Temperature dependence of magnetic susceptibility
(b) Magnetization curves of the Fe_3Se_4 /$FeSe_2$ compounds

Based on the bulk materials studied by *Superconductivity in the PbO type structure FeSe*[1], only the tetragonal structure, shown in Fig. 5(c), shows superconductivity. We propose that only nanocrystals with FeSe tetragonal structure could show superconductive qualities.

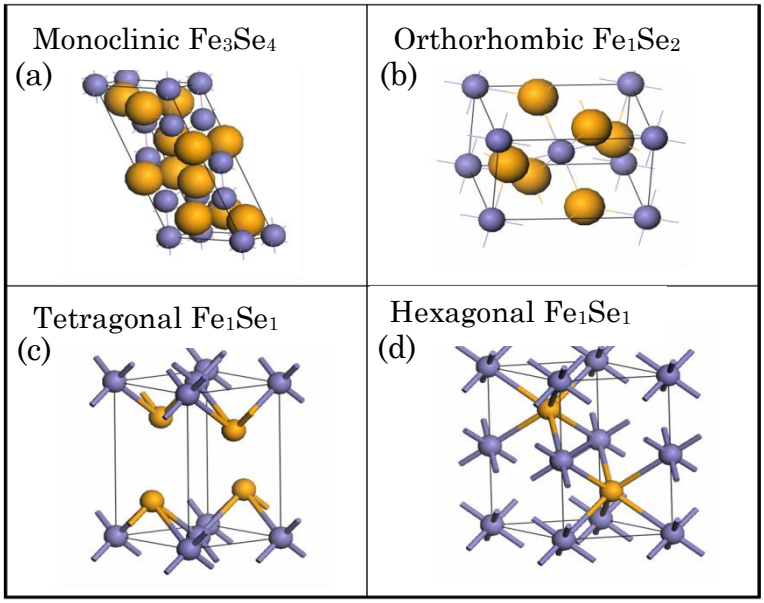


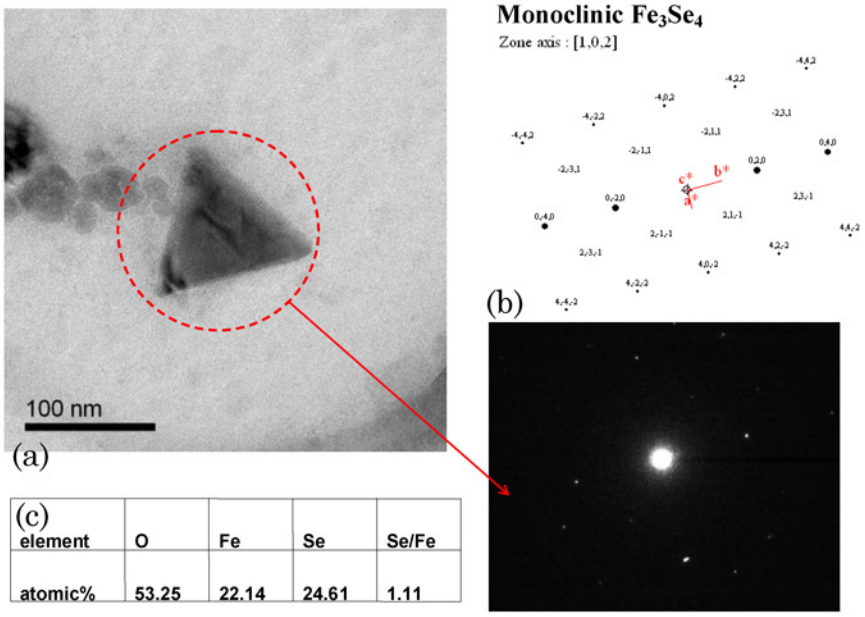
Fig. 5 Crystalline structures of various Fe-Se compounds

- **Experiment 2:**

Since the molar ratio Fe to Se of tetragonal FeSe is 1 to 1 , we tried to produced the tetragonal FeSe nanocrystals by increasing the molar ratio of Fe to Se from 1:2 to 1:1.

However, the majority of nanocrystallites created by increasing the iron: selenium molar ratio to 1:1 was Fe_3Se_4, and the nanocrystallites were similar to those created by Experiment 1. Interestingly,we observed triangular and hexagonal products (Fig.6, Fig.7) and suggested that the products are related to Fe_3Se_4's monoclinic structure, which creates these shapes with 60° and 120° angles.

Detailed transmission electron microscopy is shown in Fig.6 (b). The structure of Fe_3Se_4 nanoparticle is monoclinic in (1,0,2) direction which is revealed by SAED pattern. In Fig.6 (c), it shows that the EDX result from this area and the composition of Fe_3Se_4 nanoparticle is 1 to 1.11.

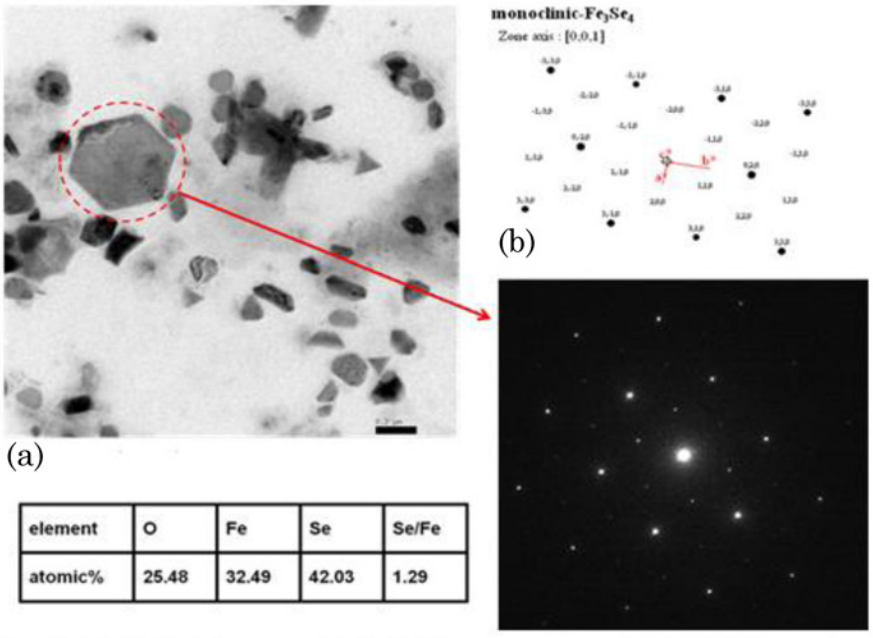


(c)

element	O	Fe	Se	Se/Fe
atomic%	53.25	22.14	24.61	1.11

Fig. 6 (a) TEM image (b) SAED pattern and (c) EDX result of Fe_3Se_4

Detailed transmission electron microscopy is shown in Fig.7 (b). The structure of Fe_3Se_4 nanoparticle is monoclinic in (0,0,1) direction which is revealed by SAED pattern. In Fig.6 (c), it shows that the EDX result from this area and the composition of Fe_3Se_4 nanoparticle is 1 to 1.29.

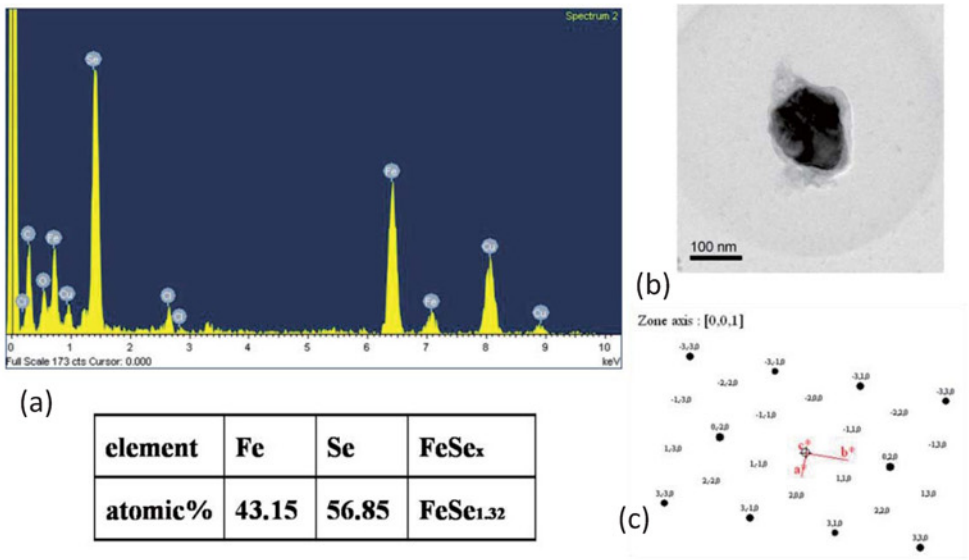


element	O	Fe	Se	Se/Fe
atomic%	25.48	32.49	42.03	1.29

Fig. 7 (a) TEM image (b) SAED pattern and (c) EDX result of Fe_3Se_4

- **Experiment 3:**

Furthermore, we increased the molar ratio of iron to selenium to 2:1.



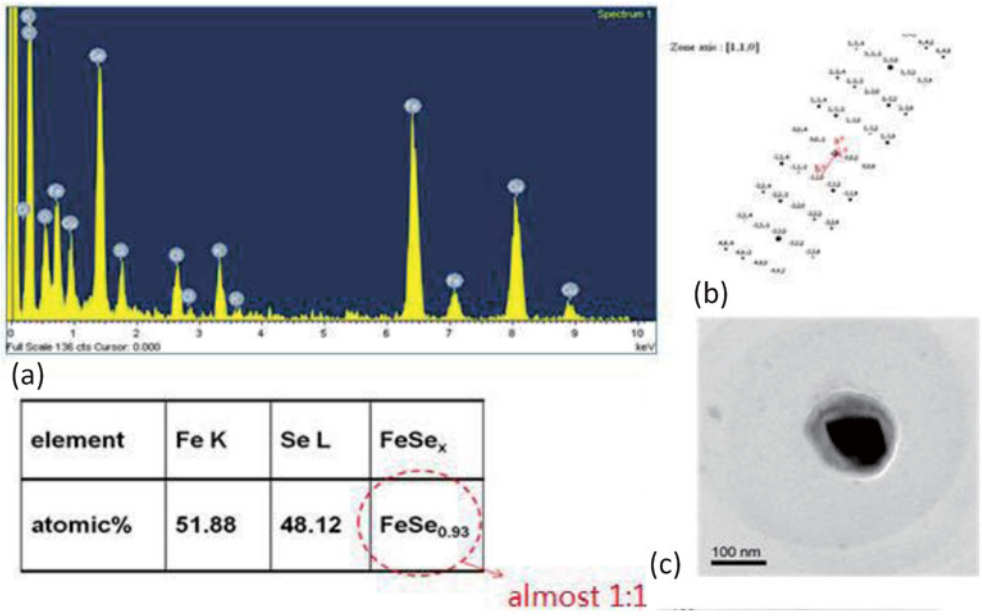
(a)

element	Fe	Se	$FeSe_x$
atomic%	43.15	56.85	$FeSe_{1.32}$

Fig. 8 (a) EDX result (b) TEM image and (c) SAED pattern of Fe_3Se_4

The nanocrystallites produced by this condition were overwhelmingly Fe_3Se_4, which were shown in Fig. 8.

However, we did find small amount of the tetragonal FeSe which was confirmed by EDX (Fig. 9 (a))and TEM (Fig. 9 (b)(c))analysis.



(a)

element	Fe K	Se L	$FeSe_x$
atomic%	51.88	48.12	$FeSe_{0.93}$

Fig. 9 (a) EDX (b) TEM analysis and (c) image of $Fe_1Se_{0.93}$ nanocrystals

We found that the speed at which solution A was added during the experimental process had an effect on the evenness of the distribution of the particles. By

conducting several times of experiments, we found that FeSe is produced rarely, therefore, we tried to change the charge of the iron from +3 to +2.

- **Experiment 4:**

We replaced Fe^{3+} [$Fe(acac)_3$] with Fe^{2+} [$Fe(CH_3COO)_2$] which can skip the first reduction step, and the molar ratio of Fe:Se is 1:1,.

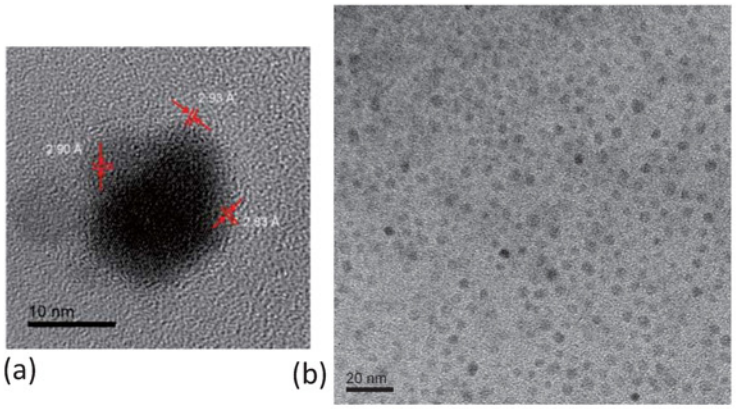
Reaction:

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

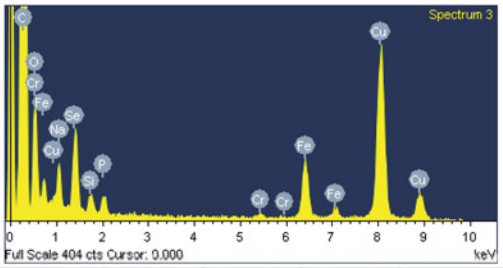
$$Fe^{2+} + 2e^- \rightarrow Fe$$

$$Fe + TOPSe \rightarrow FeSe$$

The results showed that the amount of nanocrystalline tetragonal FeSe produced was increased Particles are smaller and more evenly distributed than in previous experiments [Fig10 (a)and(b)]. The EDX result from this area and the composition of Fe_3Se_4 nanoparticle is almost 1 to 1 [Fig10 (c)] .



(c)



element	Fe K	Se L	O K	$FeSe_x$
atomic%	12.33	12.02	75.66	$FeSe_{0.97}$

Fig. 10 (a)(b) TEM images and (c) EDX result of FeSe nanocrystals

Through measuring the Fe^{+2}-produced nanocrystallites, we found that at 15 K, there is a superconductivity signal, which we infer that its Tc is slightly higher than that of the bulk materials (Fig.11) .

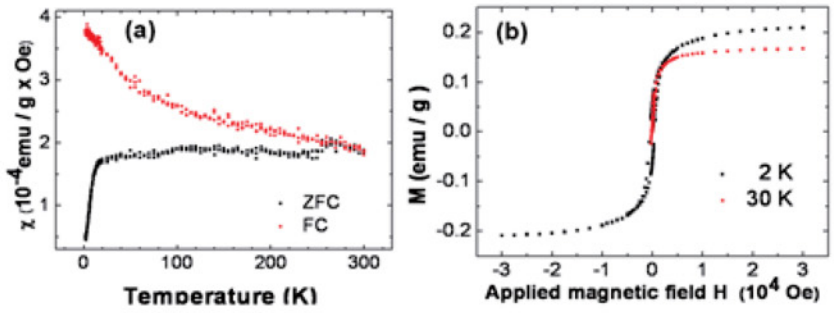


Fig. 11

(a) Temperature dependence of magnetic susceptibility

(b) Magnetization curves of FeSe

[I.] Method 2: EG TOP hot melt method

Nanoparticles produced by HDOL-TOP hot injection method were oxidized easily. Therefore, ethylene glycol was introduced into this method to to cover the particles in order to prevent from oxidation.

Process of Finding the Best Experimental Condition

1. Finding the best reaction temperature:
   - Under N_2
   - Fe^{2+} : Se = 1: 0.50
   - Reaction time: 2 h

   The results indicate that reaction temperature at 200℃ is the best for preparing nanocrystalline tetragonal FeSe particles (Fig.12) .

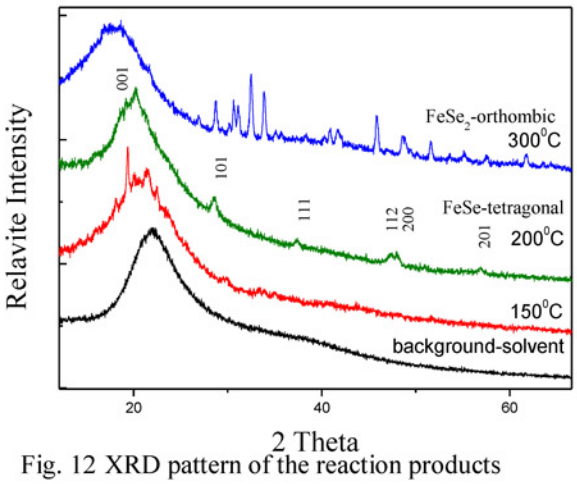


Fig. 12 XRD pattern of the reaction products

2. Finding the best reaction time
   - Under N_2
   - Fe^{2+} : Se molar ratio = 1: 0.50
   - Reaction temp. 200℃

   The results show that reaction time 2~3 h is the best for preparing nanocrystalline tetragonal FeSe particles (Fig.13) .

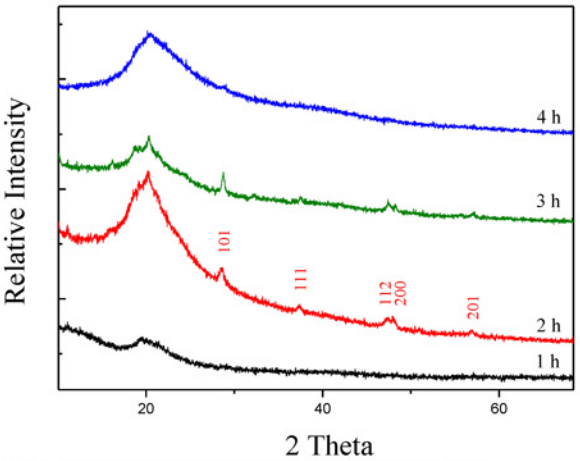


Fig. 13 XRD pattern of the reaction products

3. Finding the best Fe^{2+}/ Se ratio
   - Under N_2
   - Reaction temp. 200℃
   - Reaction time 2h

   The results demonstrate that there was a relationship between the ratio of iron & selenium reactants and the shape of the product. Fe:Se=1:0.50 and Fe:Se=1:0.88, laminar and particle, respectively (Fig.14) .

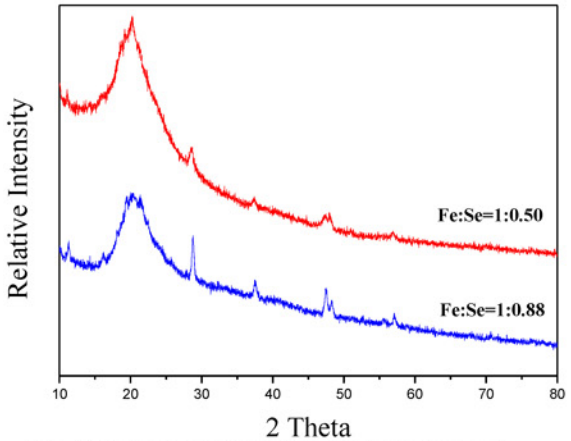


Fig. 14 XRD pattern of the reaction products

4. Purify our reaction products

- Under N_2
- Fe^{2+} :Se ＝1:0.5
- Reaction temp. 200℃
- Reaction time 2h

After purifying the reaction products with hexane and alcohol (3:1) showed clear FeSe peaks(Fig.15).

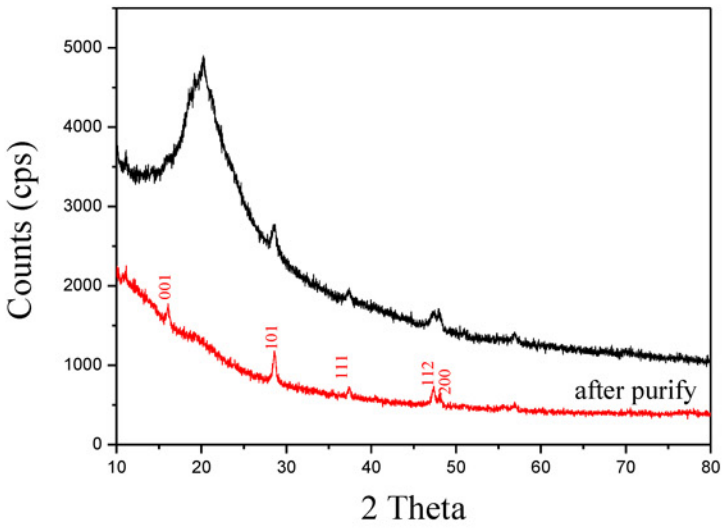


Fig. 15 XRD pattern of the reaction products

5. Oxidation of the reaction products

The reaction products showed significant oxidation after standing at room temperature for two weeks(Fig.16).

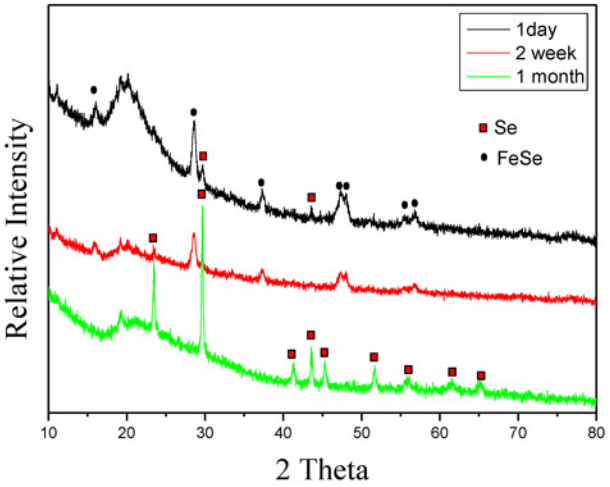


Fig. 16 The effects of incubation time on the oxidation of products.

6. Physical properties of reaction products

After we successfully created FeSe tetragonal nanocrystals by this chemical method, it was found that there was a relationship between the ratio of iron & selenium reactants and the shape of the products. (Table 1.)

Nominal ratio Fe^{2+} / Se	Production form
1 / 0.5	laminar
1 / 0.88	particle

Table 1. Shape of the products obtained at different Fe^{2+}/ Se ratio

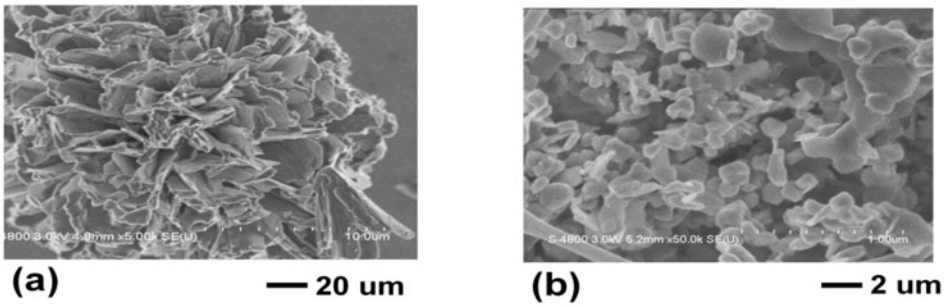
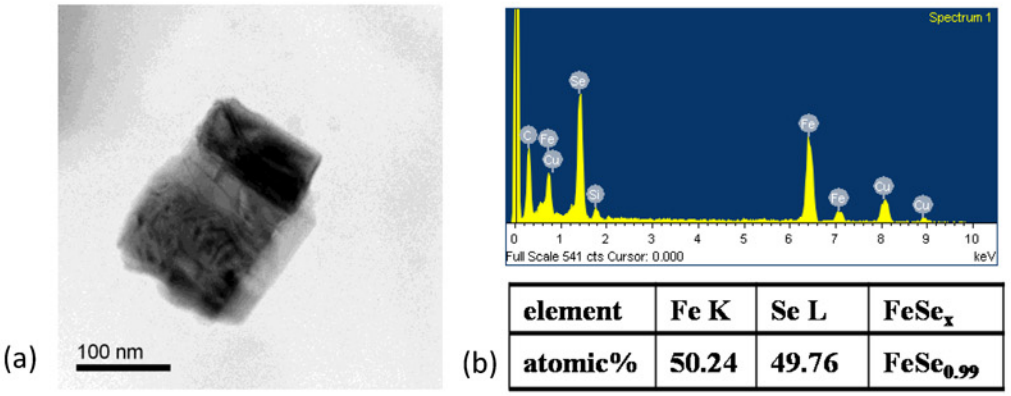


Fig. 17 SEM images of (a) laminar FeSe (b) FeSe particle

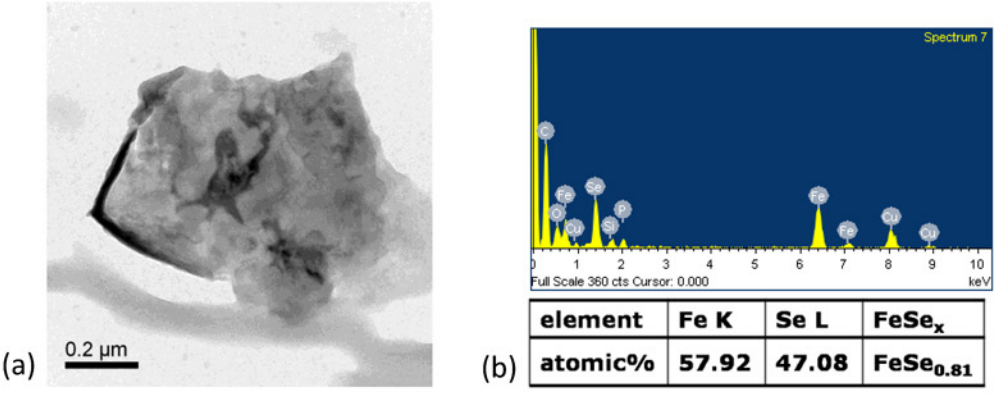
Tetragonal FeSe nanocrystals of particle diameter around 100 nm can be fabricated employing this EG-TOP hot injection route, as shown in Fig.3 (a). In Fig.18 (b), it shows that the EDX result from this area and the composition of FeSe nanoparticle is 1 to 0.99.



element	Fe K	Se L	$FeSe_x$
atomic%	50.24	49.76	$FeSe_{0.99}$

Fig. 18 (a) TEM image and (b) EDX of $Fe_1Se_{0.99}$ nanocrystals

Tetragonal FeSe nanosheets can be fabricated by employing this EG-TOP hot injection route, as shown in Fig.19 (a). In Fig.19 (b), it indicates that the EDX result from this area and the composition of FeSe nanoparticle is 1 to 0.81.



element	Fe K	Se L	$FeSe_x$
atomic%	57.92	47.08	$FeSe_{0.81}$

Fig. 19 (a) TEM image and (b) EDX of $Fe_1Se_{0.81}$ nanocrystals

7. Temperature dependence of magnetic susceptibility of products

Fig. 20 reveals a significant drop of the susceptibility below 7 K. This Tc observed for the laminar FeSe is comparable to its bulk counterpart.

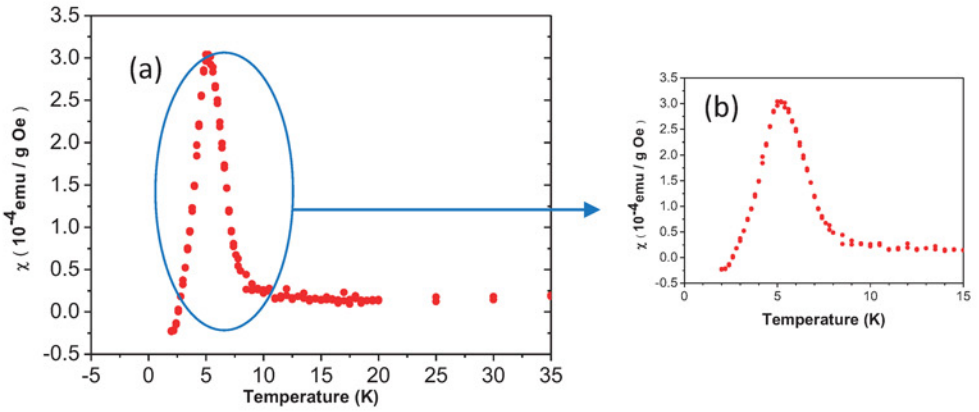


Fig. 20 (a) Thermal profile of magnetic susceptibility of laminar FeSe (b) The enlargement of image (a)

8. Magnetization curves of reaction products

The effects of applied magnetic field on the thermal profile of the magnetic susceptibility shown in Fig. 21 reveal the characteristics of superconductivity being suppressed by the increasing magnetic field, indicating the characteristic of superconductivity. Superconductivity survives even at H=1000 Oe.

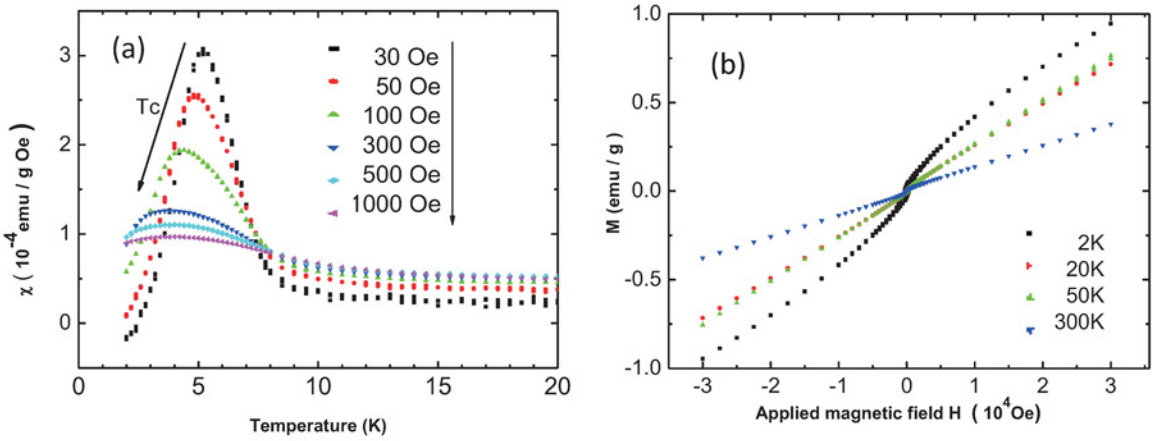


Fig. 21 (a) Temperature dependence of magnetic susceptibility of the FeSe (b) magnetization curves of FeSe

[I.] Method 3: HDA -TOP hot injection method

Tetragonal FeSe nanocrystals produced by EG-TOP hot injection method were more stabilized but larger than we expected. Therefore, HDA was introduced into this third method to serve as the reducing agent and it can control the growth in order to reduce the size distribution of nanoparticles.

Tetragonal FeSe of particle diameter around 8 nm can be successfully synthesized by this HDA-TOP hot injection method, as shown in Fig. 22. However, there are still some unidentified impurities.

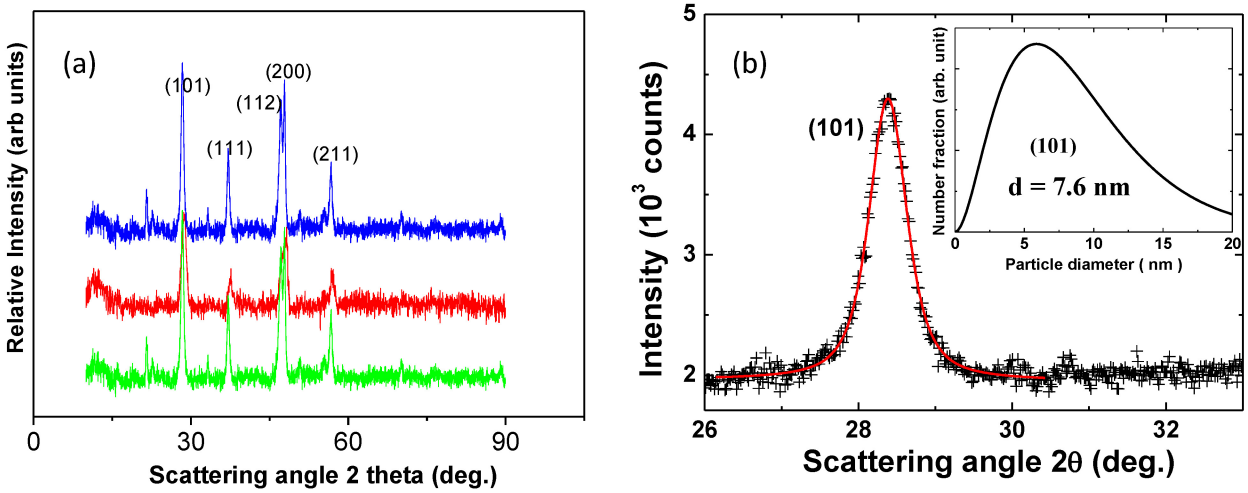


Fig. 22 (a) X-ray diffraction pattern and (b)size distribution of tetragonal FeSe

Detailed transmission electron microscopy is shown in Fig.23 (b)(c). The structure of FeSe nanoparticle is tetragonal which is revealed by SAED pattern.

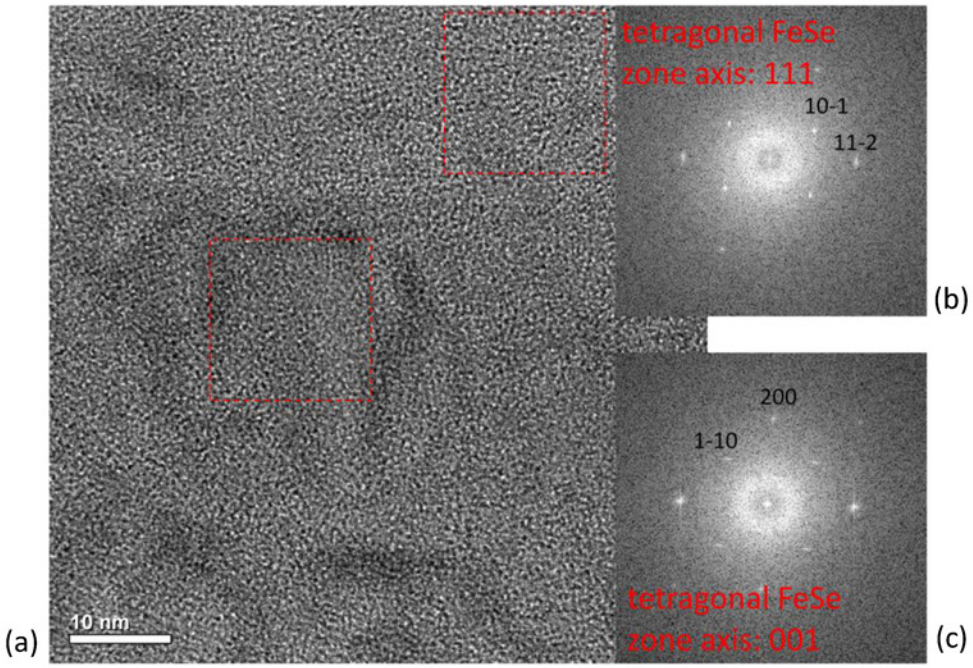


Fig. 23 (a) TEM of the FeSe reaction products and(b) (c) the SAED

Anomalies in magnetic susceptibility are observed at 40 and 120 K. These anomalies can be signs of the occurrences of superconductivity, but further investigation are needed before conclusion can be made. (Fig. 24)

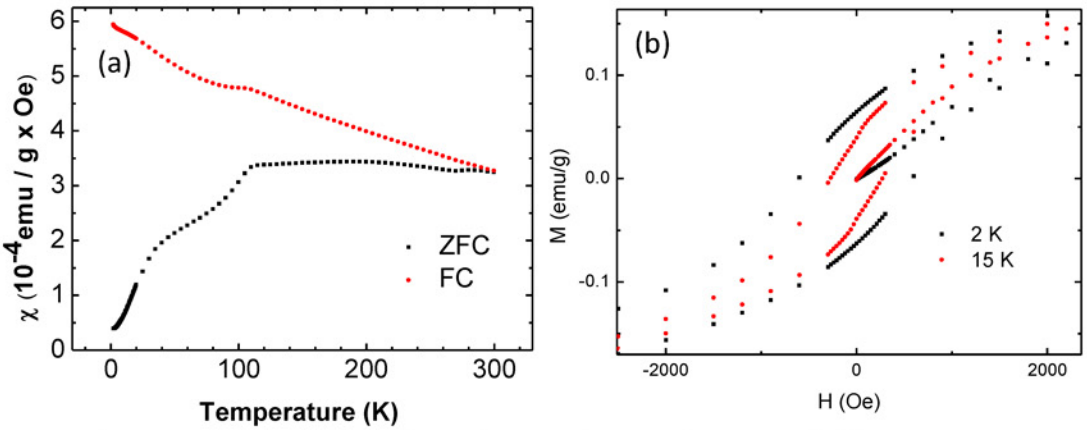
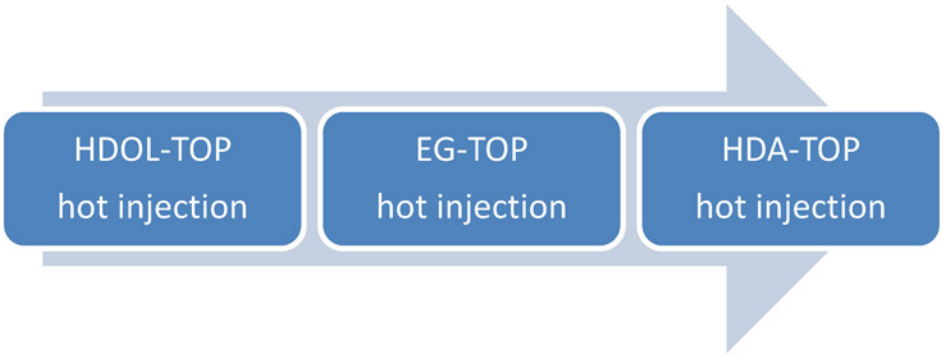


Fig. 24 (a) Temperature dependence of magnetic susceptibility
(b) Magnetization curves of FeSe

Textragonal FeSe nanocrystals produced by HDA-TOP hot injection method were smaller and more purified. Most importantly, the Tc was noticeably higher than that of the FeSe superconductor bulk material.

§ Conclusions:



Nanoparticales produced by the first HDOL hot injection method were oxidized easily. And therefore, ethylene glycol was introduced into the second method to cover the particles and prevent from oxidation. However, the FeSe particles produced by the second method were larger than we expected, so HDA was introduced into the third method. HDA served as the reducing agent and it can control the growth in order to reduce the size distribution of nanoparticles.

I. Three chemical methods have been used to fabricate FeSe nanocrystals, and we found that iron reactants which are more easily to be reduced to iron atoms are effective reagents to produce nanocrystalline tetragonal FeSe. Among them, the HDA-TOP hot injection is the most effective method.

II. According to physical characteristics testing of Fe-Se series bulk materials, FeSe is the only structure that possesses superconductivity. And superconducting screening is observed in nanocrystalline tetragonal FeSe, but not in $FeSe_2$ and Fe_3Se_4.

III. The superconducting critical temperature of nanocrystalline tetragonal FeSe is found to be higher than that of its bulk counterpart.

All TEM photos are taken by the professionals with licenses in Academia Sinica

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