

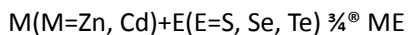
**论文题目： 半导体纳米材料的溶剂热合成、结构与性能研究**

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## 摘 要

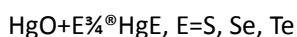
本文旨在探索半导体纳米材料的化学合成新方法。通过大量文献调研，发现在半导体纳米材料的化学合成研究领域中的问题与机遇。提出并建立了溶剂热元素直接反应、有机溶剂室温转化、溶剂热还原、自还原、中温热解催化合成、水热化学反应自控制等六种纳米材料合成新方法，成功地合成出了二十余种半导体纳米材料。

发展了溶剂热元素直接反应合成 II-VI 族半导体纳米晶合成路线



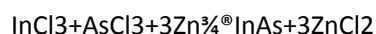
在吡啶溶液中，将等摩尔比的硫粉（或硒粉）与锌粉在 180° C 进行溶剂热反应一定时间后一步可以得到平均粒径为 10nm 的 ZnS 和 15nm 的 ZnSe 纳米晶。实验表明：反应溶剂的配位能力决定目标产物能否形成。反应的温度和反应时间对产物的粒径影响较大。类似地，用金属镉和硫属元素（S, Se, Te）在吡啶和胺类溶剂中直接反应，可以得到 CdE。以 CdS 为例，在吡啶中形成六方相球形 CdS 纳米晶，平均粒径约为 50nm；在 1-6 己二胺中得到的是棒状立方纤锌矿的 CdS；在二乙胺中，得到的是立方和六方的混合相，产物形貌为球形粒子。尺寸在 20nm 左右。在乙二胺中得到的是立方相的 CdS 纳米棒。用 Raman 光谱和 XPS 对所得的 CdS 纳米棒进行表征，结果表明样品纯度高，质量好，CdS 纳米棒的吸收光谱与发射光谱表明：由于形貌和尺寸的变化，与传统体相材料相比，吸收光谱变宽且发生了蓝移。对 CdSe 和 CdTe,也进行了系统的研究 [参见 Inorg. Chem. 38 (1999), 1382]。除了对反应的温度、溶剂以及可能的反应机理进行探讨，我们还提出了纳米棒的可能形成机理，乙二胺、己二胺作为双齿配体可以和金属离子配位，有利于 CdS 在某一结晶面上的聚集和生长，抑制了在其其它方向上的生长，形成纳米棒。[参见 Chem.Mater. 10(9),2301,1998 ]

在制备汞的硫属化合物半导体时，考虑到汞单质较强的毒性和避免使用剧毒性硫属元素氢化物如 H<sub>2</sub>S。我们在乙二胺中将氧化汞和硫属元素直接混合：



在室温下，电磁搅拌反应 7~10 小时，可以分别得到六方纤锌矿的 HgS 和立方闪锌矿的 HgSe 以及 HgTe。分析表明，反应完全，没有 HgO 以及其它杂质。TEM 显示所有产物均为 50nm 球形粒子。成功地建立了有机溶剂室温直接转化法合成半导体纳米晶。[参见 J.Phys. &Chem. Solids, 60(7),965,1999]

III-V 族化合物半导体纳米材料的研究是目前物理，化学，材料以及电子等学科研究的热点。从化学的角度来说，对该类化合物研究主要是集中在（1）传统的高温固相反应；（2）利用金属有机化合物；（3）金属氯化物和磷属元素的钾盐或钠盐的转换反应。由于这些反应所涉及的过程往往比较复杂，实验条件要求较高，试剂昂贵且比较危险。为此发展简便、价廉的合成途径意义重大。本论文提出了溶剂热共还原合成 III-V 族半导体纳米材料新的化学合成路线：



以  $\text{InCl}_3$  和  $\text{AsCl}_3$  为反应物，有机溶剂为反应介质，在还原剂的存在下，合成出了晶粒尺寸为 10nm 左右的立方闪锌矿  $\text{InAs}$  纳米晶。反应的可能机理是金属锌和反应体系中的微量水反应形成活性氢，活性氢再还原  $\text{AsCl}_3$  和  $\text{InCl}_3$  产生具有较高反应活性的 As 和 In 纳米团簇，在反应的温度下，直接化合形成  $\text{InAs}$ 。实验中详细考虑了各种实验条件对产物的形成，颗粒尺寸以及纯度等的影响，发现反应体系中的水的量应合适，太高容易形成氢氧化物杂质，污染  $\text{InAs}$ ；还原剂的还原性应适中，太强或太弱对  $\text{InAs}$  的形成均不利；温度过高（如  $300^\circ\text{C}$ ），反应速度加快，同样不利于形成小粒径的  $\text{InAs}$  纳米晶；在乙二醇体系中，通过乙二醇与反应物之间的配位效应，有效地控制了反应速度；得到了结晶较好的球形产物，而在乙二胺中则有部分一维纳米棒形成。进一步验证了乙二胺的双齿配体对形成一维纳米棒的模板作用 [参见 *J.Am.Chem.Soc.*119(33),7869,1997]。

在上述方法的基础上，发展了溶剂热自还原法制备其它一些 III-VI 族半导体纳米材料，如  $\text{InAs}$ （晶须）、 $\text{InSb}$ 、 $\text{InP}$ 、 $\text{GaSb}$  等。由于在制备过程中避免使用了其它还原剂，为提高产品的质量提供了保障。具体方法为，以  $\text{PCl}_3$ 、 $\text{AsCl}_3$ 、 $\text{SbCl}_3$  为原料，金属铟和镓为还原剂，利用溶剂热方法制备出一些 III-V 族纳米半导体材料。其中  $\text{InSb}$  的液相合成在国际上尚未见报道。关于  $\text{InAs}$  纳米晶须的形成，可以用 Vapour-Liquid-Solid(VLS)生长机制进行解释。

以低熔点的金属（如钠）为熔剂，在一定量的催化剂存在下，进行了  $\text{CCl}_4$  的中温催化还原热解法制备金刚石粉。在有机合成中利用传统的 Wurtz 反应可以使烷烃链长增加。由此启示利用  $\text{sp}^3$  杂化的 C 源，直接制得金刚石。从 XRD 可以清楚地看到（111），（100）和（311）晶面的衍射峰，并用 Raman 光谱对制得的金刚石粉进行了表征 [参见 *Science*,281,783,1998]。

利用水热反应制备出一系列金属氧化物半导体纳米材料

1).  $\text{ZnGa}_2\text{O}_4$  是一种低压荧光半导体材料，可用于场发射显示装置的真空平板阴极射线管，以 Zn 和  $\text{GaCl}_3$  的稀盐酸溶液进行水热合成制备出尖晶石结构的  $\text{ZnGa}_2\text{O}_4$ ，TEM 显示其粒径为 10nm 左右，适宜的合成温度为  $140-170^\circ\text{C}$ ，产率大于 95%。由于反应过程中金属锌可以和稀盐酸反应，控制了  $\text{Zn}^{2+}$  的形成和水溶液体系中 pH 值，对  $\text{ZnGa}_2\text{O}_4$  的形成起到了决定性的作用； [参见 *Chem. Mater.* 1091],17,1998]

2) 以  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  和水合肼为反应物在不同的 pH 值条件下利用水合肼的氧化—还原特性可以获得  $\alpha\text{-Fe}_2\text{O}_3$  和  $\text{Fe}_3\text{O}_4$ ； [参见 *Mater. Res.Bull.*, 33(6),841,1998]

3) 在聚乙二醇的保护下，将  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  在氨性介质中  $150^\circ\text{C}$  进行水热反应，可以得到无团聚、分散好、粒径分布均匀的 3nm 的  $\text{SnO}_2$ ，分别用红外光谱和拉曼光谱对所得的样品进行了

表征:

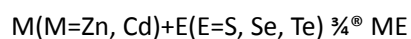
4) 以  $\text{KMnO}_4$  为原料,  $\text{H}_2\text{O}_2$  还原法首先在  $180^\circ\text{C}$  水热条件下处理得到前驱物, 经 1:  $1\text{HNO}_3$  多次洗涤干燥后, 在  $400^\circ\text{C}$  下脱水可以制得  $\gamma\text{-MnO}_2$ , 实验表明, 水热处理后的胶体的静置时间对产物的形貌影响较大, 此外不同的晶化温度可以得到不同的产物,  $400^\circ\text{C}$  是  $\gamma\text{-MnO}_2$ ,  $700^\circ\text{C}$  下是  $\text{Mn}_2\text{O}_3$ ;

5) 在混合溶剂中也可以利用水热法制备出纳米级的  $\text{NiO}$  和  $\text{Co}_3\text{O}_4$ 。

## Abstract

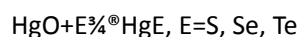
The object of this dissertation is to explore new synthetic methods to nanoscale semiconductors. It is found that, based on the study of so much currently available literatures, there are some challenges existed in the present research of nanoscale semiconductors, especially for the synthetic strategy. Here, solvohermal elemental direct combination, room temperature organic solvent conversion, solvothermal reduction and self-reduction, mild temperature pyrolysis-reduction-catalysis as well as hydrothermal self-regulation process have been proposed and established for the synthesis of nanoscale materials. More than twenty kinds of nanoscale semiconductors have been successfully synthesized by the above mentioned methods or the combination of some of them.

Developing solvohermal elemental direct combination route to II-VI semiconductor nanocrystals



Stoichiometric sulfur (or selenium) and zinc were added to pyridine holden in stainlessness' autoclave with Teflon liner. After reaction at 180°C for a certain duration time, nanocrystalline ZnS and ZnSe with average particle sizes of 10nm and 15nm could be obtained through one-pot synthetic process. The formation of these products depend on the complex ability of the solvents and the particle sizes are determined in a large scale of the reaction temperature and duration time. Similarly, cadmium chalcogenides can be also prepared through the reaction of cadmium and chalcogen in pyridine and some other amine solvents. Take CdS for account, hexagonal spherical CdS with average particle size of 50nm was formed in pyridine, cubic rod-like in 1,6 hexyl diamine, mixtures of cubic and hexagonal spherical particles with 20nm in biethylamine and and cubic nanorods in ethylenediamine. The nanorods of CdS obtained in ethylenediamine were also characterized by Raman and XPS spectroscopy, these results indicate that the product were in high purity and quality. Compared with conventional bulk materials, the absorbance of CdS was broadened and shifted to blue range due to the change of morphology and size. The synthesis and characterization of CdSe and CdTe have been also systematically investigated. More information about this can be seen in detail in [Inorg. Chem. 38 (1999), 1382]. Besides all of these, the possible mechanism for the formation of nanorods in some system was also proposed. It is believed that the formation of nanorods in 1,6 hexylene diamine and ethylenediamine was originated from the bidentric properties of these two solvents. A detailed description concerning this can be found in [Chem.Mater. 10(9),2301,1998].

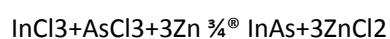
In preparing mercury chalcogenides, in order to avoid the use of toxic mercury and gas such as H<sub>2</sub>S, HgO and chalcogen were mixed together and electromagnetically agitated at room temperature for 7-10 hours



Hexagonal HgS and cubic HgSe as well as HgTe could be conveniently obtained. No impurities

such as HgO and chalcogen could be found in the XRD pattern. TEM showed that all products were spherical with diameters about 50nm. So an organic solvent room temperature direct conversion process has been established for the synthesis of semiconductors. More information can be seen in [J.Phys. &Chem. Solids, 60(7),965,1999].

The research of III-V nanoscale materials has appealed a lot of research interest of physical, chemical, material, and electronic scientist. From the view of chemistry, the research is mainly concentrated on pursuing novel and convenient synthetic process to these materials since the conventional methods such as (1) high-temperature solid state reaction, (2) utilizing organometallic precursors, (3) the metathesis reactions between metal halides and sodium or potassium pnictides, are usually complicated and require extreme experiment conditions. Besides this, the reagent used are usually expensive and dangerous. So it is significant to develop simple and low-cost preparation routine for these compounds. A new solvothermal co-reduction chemical process to III-V group semiconductors was raised here:



With the use of organic solvent as reaction medium, cubic InAs with about 10nm particles size could be synthesized from InCl<sub>3</sub>, AsCl<sub>3</sub> and reductive such as zinc. The process might involve the combination of newly reduced clusters of As and In, which were produced from the redox reactions between AsCl<sub>3</sub>, InCl<sub>3</sub> and reactive atomic hydrogen released from the reaction between zinc powder and the co-existed water in the reaction system. Many factors were considered in this synthesis, for example, the amount of water in the reaction system should not be too much otherwise there would be impurities like In(OH)<sub>3</sub> accompanying the final products. The reducing ability of reductive could not be too strong or weak for it is disadvantage for the formation of InAs at this condition and particles with larger size would be produced if the temperature is as high as 300°C due to accelerated reaction rates. For the ethylene glycol reaction system, the reaction rates can be controlled through the coordination between the reactant and ethylene glycol and spherical particles with good crystallinity was obtained. For the ethylenediamine system, InAs nanorods were obtained, which further supports the bidentric template mechanism of ethylenediamine on the formation of nanorods. [J.Am.Chem.Soc.119(33),7869,1997].

Based on the above established methods, a self-reduction method to other III-V semiconductors nanomaterials was developed, such as InAs (whiskers), InSb, InP, GaSb. Since the use of external reductive was circumvented in the preparation process, it is helpful to improve the quality of the product. In a typical process, some III-V semiconductors are prepared by the solvothermal methods, using PCl<sub>3</sub>, AsCl<sub>3</sub>, SbCl<sub>3</sub> as source materials and metallic Indium and Gallium as reductives. To the best of our knowledge, it is the first time to prepare InSb in the liquid medium. In the case of the formation of nano whiskers of InAs, the Vapour-Liquid-Solid (VLS) growth mechanism was discussed.

Using metal (such as Sodium) with low melting point, the diamond powder was prepared by Pyrolysis-Reduction-Catalysis of CCl<sub>4</sub> at a moderate reaction temperature. The chain increment of alkylane is usually realized by using the Wurtz reaction in organic synthesis. This give a hint

that diamond might be prepared directly from  $sp^3$  hybridized carbon source. XRD pattern clearly shows three typical reflection peaks of (1111), (100) and (311) lattice plane. In addition, the diamond powder was characterized by Raman spectroscopy [Science,281,783,1998]。

A number of metal oxides nano materials have been synthesized through hydrothermal processes:

1) As a low voltage luminescence semiconductor,  $ZnGa_2O_4$  can be employed as vacuum flat cathode ray tubes (CRT) using field emitting display. Nanocrystalline spinel  $ZnGa_2O_4$  with diameter of 10nm was prepared in diluted hydrochloric solution of  $GaCl_3$  with the presence of zinc powder. The favorable reaction temperature range is  $140-170^\circ C$  and the yield is larger than 95%.The formation of  $ZnGa_2O_4$  depends largely on the concentration of  $Zn^{2+}$  and pH value of solution. Since the concentration of  $Zn^{2+}$  and pH value can be regulated through the reaction of zinc and HCl, this process can be viewed as a self-regulated process [Chem. Mater. 1091],17,1998]

2) Nanocrystalline  $\alpha-Fe_2O_3$  and  $Fe_3O_4$  were made from  $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$  and hydrazine by hydrothermal process under various pH, for the redox properties of hydrazine change with the pH value of the reaction solutions.[Mater. Res.Bull., 33(6),841,1998]

3) With the protection of polyglycol, less agglomerated and uniform 3nm  $SnO_2$  was hydrothermally prepared from  $SnCl_4 \cdot 5H_2O$  in amine solution at  $150^\circ C$ .The product was characterized by FTIR and Raman spectroscopy.

4) Under hydrothermal condition, a precursor of  $\gamma-MnO_2$  was reduced from  $KMnO_4$  by  $H_2O_2$  at  $180^\circ C$ . After being washed by 1: 1  $HNO_3$  for several times and desiccated, the precursor was dehydrated at  $400^\circ C$  to form  $\gamma-MnO_2$ . The morphology of final product is influenced by the aging time of the hydrothermally treated precursor. In addition, different products can be obtained at different crystalline temperature, for example:  $\gamma-MnO_2$  at  $400^\circ C$  and  $Mn_2O_3$  at  $700^\circ C$ .

5) Nanoscale  $NiO$  and  $Co_3O_4$  can also be hydrothermally synthesized in mixed solvents.