ORIGINAL RESEARCH ARTICLE

Solvent Thermal Method to control Lead Sulfide Nano/Micron Crystal and Its Ni/PbS Composites

Yajia Ding,Bing Bai,Jianan Peng

Key Laboratory of Nanometer Materials, University of Architecture and Technology, Fujian, China

ABSTRACT

Lead sulfide (PbS) is an important IV-VI semiconductor material with narrow bandwidth and wide wave width, which attracts people's attention. Nano-level PbS has many novel optoelectronic properties and has a wide range of applications in the field of optoelectronics, such as infrared optoelectronic devices, photovoltaic devices, light-emitting devices and display devices. In this paper, Pbs is produced by solvent thermal method by using lead acetate as lead source, sulfur power as sulfur source, ethylene glycol as solvent, and acetic acid to provide acidic environment. The reaction acidity, type of lead source, amount of sulfur source and other aspects will be explored. The products obtained under different conditions were characterized by X-ray diffraction (XRD), optical microscopy and scanning electron microscopy (SEM). The results showed that PbS produced at 140°C for 24 hours, using 14mL ethylene glycol and 1.2mL acetic acid has the best morphology. It has a non-planar six-arm symmetrical structure. Finally, we prepare the lead sulfi de composite Ni/PbS, and characterized it.

KEYWORDS: PbS; solvent heat; nanomaterials; composites

1. Introduction

1.1. Nanomaterials

1.1.1 Introduction to Nanomaterials

Nano-materials[1], also known as ultra-fi ne particles, are composed of nanoparticles. Nanoparticles, also known as ultrafi ne particles, generally refer to particles in the range of 1 to 100 nm which are in the transitional region between atomic cluster and the macroscopic object boundary. Such a system is neither typical in the general point of view of microcosmic and macroscopic system. This system is a typical mesoscopic system with surface eff ect, small size eff ect and macroscopic quantum tunneling eff ect. When subdividing macroscopic objects into ultrafi ne particles (nanoscale), it will show many properties namely optical, thermal, electrical, magnetic, mechanical and chemical properties, and has signifi cant diff erences when compared to its large solid phases.

Nanoparticles are composed of a limited number of atoms or molecules, able to maintain the chemical properties of the original material and maintain in a metastable atomic group or molecular group. When the linearity of the material decreases, the relative proportion of the number of atoms on the surface increases, so that the surface energy of the single atom can increase rapidly. To the nano-scale, the changes in this form refl ect on the material structure and performance, and will show unique eff ects which can be divided into the following basic characteristics [3].

(1) Small size effect [4, 5]

When the volume of a substance is reduced to a size equal to or smaller than the size of the physical characteristic of light wavelength, Deborah wavelength, coherence length or transmittance depth of superconductivity, the periodic boundary conditions of the crystal will be destroyed which lead to a great change in magnetism, internal pressure, light absorption, thermal resistance, chemical activity, catalytic activity, melting point, etc. when compared to ordinary crystal. This is the volume effect of nano-materials. When the crystal is in the nano-scale category, the average free path of free electrons in the metal will be reduced resulting in a decrease in conductivity which may cause the original material to convert from metal conductor to an insulator. The stress-strain of a material in nano-scale will change from Hall-Petch effect to anti-Hall-Petch effect. For example, under normal conditions the melting point of gold is 1337 K,

while the melting point of 2 nm gold particles is 600 K, and the melting point of nano silver can be reduced from 1173 K to 373 K.

(2) Surface effect

The surface effect of nano-materials is the abrupt increase on ratio of the number of atoms on the surface of the nanoparticles to the total number of atoms with the change of the particle size, which leads to the change of the material properties. It is well known that the specific surface area of the material is inversely proportional to the size of the material. As the size of the material decreases, the number of atoms in the surface area and surface atoms will increase significantly. The increase in the number of atoms on the surface causes a lack of surface atomic coordination and high surface energy, these atoms combine easily with other atoms and stabilize, which has a high chemical activity. It can be widely used in catalysis, adsorption and other fields. The ratio of the number of surface atoms to the total number of nanoparticles increases sharply with the decrease of particle size. When the particle size is reduced to 1 nm, the proportion of the number of atoms on the surface has reached 99% and the atoms are almost all concentrated on the surface of the nanoparticles. The increase in the number of atoms on the surface causes a lack of surface atomic coordination and high surface energy, these atoms combine easily with other atoms and stabilize, which has a high chemical activity [6, 7]. This causes the change of surface electron spin conformation and electron spectrum, and the change of atomic transport and configuration on the surface of nanoparticles.

(3) Quantum size effect

When the particle size drops to a certain value, the electron energy level near the Fermi level is reduced from quasi-continuous to discrete energy levels, conductive nano particles have discontinuous highest occupied molecular orbit and lowest unoccupied molecular orbit, band gap widening and other phenomena, are known as quantum size effect [8] . The band theory suggests that the electron level near the Fermi level is generally continuous, which is only true at high temperature or macro size. For ultrafine particles with only a limited number of conductive electrons, in low temperature energy level is discrete; for macroscopic material which contains infinite atoms, by the Kubo formula:

$$\delta = (4/3)\ EF\ /\ N \tag{1-1}$$

It can be seen that the energy level spacing is $\delta \rightarrow 0$. Which means that the spacing of large particles or macroscopic objects is almost zero; and for nanomaterials, the number of contained atoms is limited, N value is very small, and caused a certain value to δ. The separation of energy level causes the Kubo effect.

When the energy level is greater than the cohesive energy of thermal energy, magnetic energy, magnetostatic energy, electrostatic energy, photon energy, or superconductivity, quantum size effects must be taken into account. This can lead to significant difference between nanoparticle magnetism, light, sound, thermoelectric, superconductivity and macroscopic characteristics.

(4) Macro quantum tunneling effect

The tunneling effect is one of the basic quantum phenomena. When the total energy of the microscopic particles is less than the barrier height, the particles can still pass through the barrier. In recent years, it has been found that some macroscopic quantities such as the magnetization of ultrafine particles and the magnetic flux in quantum coherent devices also have tunneling effects which can change through the potential well of the macroscopic system, known as the Macroseopie Quantum Tunneling [9]. Many of the magnetic electrons in the atom (referring to the electrons in the 3d and 4f shells) pass through the barrier in a tunneling manner, resulting in a change in magnetization which is a magnetic macroscopic quantum effect. It can be used to explain the phenomenon where nano-particles at low temperature remain Superparamagnetic. The study of macroscopic quantum tunneling is of great significance to basic research and application, which limits the time limit of information storage of magnetic tape and disk. The quantum size effect and the macroscopic quantum tunneling effect will be the foundation of future microelectronic devices which establishes the limits of further miniaturization of existing microelectronic devices. When the microelectronic devices are further refined, the above-mentioned quantum effects must be considered.

 (5) Volume effect

Due to the small size of the nanoparticles, the number of atoms contained is very small. Therefore, many phenomena such as adsorption, catalysis, diffusion, sintering and other physical and chemical properties related to the interface state will be significantly different from those of the large particle conventional materials, and can not be explained by the nature of the bulk material which is usually infinitely atomized. This particular phenomenon is often called the volumetric effect [10].

(6) Dielectric limit effect

The dielectric confinement is the phenomenon that the nanoparticles are dispersed in the heterogeneous medium due to the dielectric enhancement of the interface caused by the interface. This dielectric enhancement is usually called the dielectric limit, mainly derived from the enhancement of the surface and the internal of the particles. When the refractive

index of the medium is larger than the refractive index of the microparticles, the refractive index boundary is generated which leads to the enhancement of the field strength of the particles and the internal field. The enhancement of the local field strength is called dielectric limited field. Generally, transition metal oxides and semiconductor microparticles may produce dielectric limiting effects. The dielectric confinement of nanoparticles has an important effect on light absorption, photochemistry and optical nonlinearity. Therefore, when we analyze the optical phenomenon of a material, it is necessary to consider the quantum size effect and dielectric limit effect.

1.2.   Hydrothermal / Solvent thermal method

1.2.1 Definition of hydrothermal method / solvent thermal synthesis

In hydrothermal method, a water solution is used as a reaction medium in a specially made closed reactor to create a high temperature and high pressure reaction environment by heating the reaction vessel so that the normally insoluble material dissolves and recrystallizes. The hydrothermal reaction can treat some organic reaction or treat organic wastes that endanger our environment, as well as sintering ceramic materials at relatively low temperatures. However, the process of hydrothermal preparation of nanocrystals using water as solvent reaction is subjected to certain restrictions such as reactants decomposition or some reaction are unable to occur. For example: carbides, nitrides, phosphides and silicides. Therefore, by replacing water with non-aqueous solvent such as ethanol, methanol, benzene etc. as a solvent, and by replacing hydrothermal reaction with solvothermal reaction, a large amount of precursors to water-sensitive nanocyrstaline compound.

Solvent thermal reaction is in the lime light in recent years. Solvent thermal reaction is the development of hydrothermal reaction, which is different from hydrothermal reaction where an organic solvent is used rather than water. Compared with other preparation method, the main characteristic of solvent thermal reaction is very mild reaction conditions (such as the preparation of diamond), stabilizes phase, prepares new substances, develop new preparation routes and more. In the solvent thermal reaction process, the chemical component involved in the reaction acts as a solvent, mineralization accelerator, and also transmission medium for pressure. Solvent thermal reaction is mainly researched and developed by research group lead by Mr Qian Yitai. The most widely used solvent is ethylenediamine. In ethylenediamine system, in addition to being a solvent, ethylenediamine is also a complexing agent or chelating agent. Ethylenediamine as a bidentate ligand, due to the strong chelating effect of N, together with ion precursor become stable complex ion, where the complex ion then react with reactants to produce products. The reduction properties of methanol, ethanol, etc. in addition to solvent can also be used as a reducing agent. It can be seen, that solvent thermal reaction greatly expands the field of nano-functional materials synthesis. The method is simple and convenient. As long as the suitable solvent is found, the development and application of solvent thermal reaction will have broad prospects.

1.2.2 Characteristics of hydrothermal / solvent thermal method

(1) Advantages and disadvantages of hydrothermal method:

(a) Hydrothermal method uses medium temperature in liquid phase control. Energy consumption is relatively low and has wide applicability.

(b) Raw material is relatively cheap and easy to obtain, quickly convection in the liquid phase reaction, high yield, uniform phase, high purity, good crystallization, and controllable shape and size.

(c) In hydrothermal process, the purpose of effective control of reaction and crystal growth can be achieved by adjusting the reaction temperature, pressure, treatment time, solution composition, pH value, the type of precursor and mineralizer.

(d) Reaction is carried out in a closed vessel and the reaction atmosphere can be controlled to form a suitable redox reaction condition, and obtain some special phases, which is particularly advantageous for the synthesis reaction in a toxic system and minimizes environmental pollution.

Limitations of hydrothermal method: This method is only applicable to the preparation of oxides or a few water-insensitive sulfide semiconductor nanomaterials. In this context, researchers design solvent thermal synthesis in new solvent system, expanding the application of hydrothermal method.

(2) Advantages and disadvantages of solvent thermal synthesis method

In hydrothermal synthesis, water is the medium to transfer pressure and also played the role of mineralizer. Replacing water with a non-aqueous solvent also has the same effect and additional effects. At high temperature and high pressure, the solvent of the synthesis reaction is in critical or near-critical state. The physical and chemical properties of the reactants in the solvent have a great change, and the thermochemical reaction of the solvent is much different from normal. The functional materials and crystal has its own excellent characteristics in terms of its nature. Therefore, the solvent thermal reaction is an effective method for the synthesis of chalcogenides.

Solvent thermal methods have the following advantages over other methods:

(a) Solvent thermal method may replace the solid phase reaction and the difficult synthesis reaction due to the change in the reactivity of the reactants under solvent thermal conditions and the improvement of the activity.

(b) As intermediate state, steady state, and specific phase is relatively easy to be generated, the synthesis and development of a series of special metastable structure and special condensed products can be produced.

(c) Able to crystallize compound with low melting point, substance that is non-liquid in high vapour pressure condition, and high temperature decomposition phase.

(d) Low temperature, isobaric, are solution conditions of the solvent thermal method, are beneficial due to less defects, perfect crystals with good orientation, synthesis of high crystallinity and easy to control the crystal particle size.

(e) As the atmosphere under solvent thermal method is easily adjustable, it is beneficial for the formation of compounds in low valence state, intermediate state and special valence state, doping is uniformed, and beneficial to the synthesis of new structures.

Although the solvent thermal synthesis of nano-materials has the above advantages, this method has some shortcomings as following:

(a) The solubility of the solvent and the rate of crystal growth are unpredictable.

(b) It takes a long time to grow crystals of the appropriate size.

(c) the influencing factors are more complex and have no mature theoretical causality.

1.2.3 Advances in hydrothermal / solvent thermal processes

Reaction systems in hydrothermal synthesis are usually the following: water, inorganic ammonia, inorganic strong complexing agent system, organic amine, organic alcohol, organic alkane, other organic solvent system. Various reaction systems have their own characteristics and properties.

Over the past decade, hydrothermal (solvothermal) synthesis has made considerable progress in the preparation of chalcogenide nanomaterials. The conditions of synthesis of chalcogenide nanomaterials under hydrothermal (solvothermal) were studied in detail, and various binary and ternary chalcogen compounds were synthesized. The results show that the hydrothermal (solvothermal) method is simple and effective for nanocrystalline morphology control and phase control.

1.3. Nano lead sulfide

Lead sulfide is a cubic rock salt structure semiconductor material with narrow band gap (0,41 eV) and a large Bohr exciton radius (18 nm) [16]. PbS nanocrystals have a strong quantum confinement effect, and their cubic nonlinear optical properties are about 30 times that of GaAs and 1000 times of CdSe. They are potential application in infrared communication, photon switch, thermal and biological imaging, optoelectronic devices and solar cells. Recently, the generation of effective polychromes has been detected in PbS quantum dots, making it the most promising highly efficient photovoltaic conversion material [17-23].

As an important member of the IV-VI semiconductors, lead sulfide has a small band gap and a larger Bohr radius, and the nanoscale PbS band moves from near-infrared blue to the visible region, showing special optical properties and electrical properties [24], and thus, it has been extensively studied in nonlinear optical devices, infrared detectors and the application of solar receivers. The properties of PbS nanomaterials are directly related to their microstructure.

2. Experimental Part

2.1. Experimental reagents and instruments

2.1.1 Experimental reagents

Table 2-1-1 List of reagents used in the experiment

Drug name	Product purity	Manufacturer
High - purity lead acetate	Analytical	No. 230 Shuguan Dao, Hebei District, Tianjin City
Sublimation of Sulphur	Chemical	Chongqing Oriental Reagent Factory
Ethylene glycol	Analytical	Tianjin Ke Miou Chemical Reagent Co., Ltd

Glacial acetic acid	Analytical	Kaifeng Chemical Reagent Factory
Lead Nitrate	Analytical	Tianjin Chemical Reagent Factory
Anhydrous Ethanol	Analytical	Anhui Ante Biochemical Co., Ltd
Distilled water	Analytical	University of Information Materials Research Institute
Hydrated Nickel Chloride	Analytical	Tianjin Ke Miou Chemical Reagent Co., Ltd
Hydrate Hydrazine	Analytical	Tianjin Zhiyuan Chemical Reagent Co., Ltd.
Sodium Hydroxide	Analytical	Zhengzhou Paini Technology
Cetyltrimethylammonium Bromide	Analytical	Tianjin Ke Miou Chemical Reagent Co., Ltd
Thioacetamide	Analytical	Tianjin Ke Miou Chemical Reagent Co., Ltd

Note: Of all reagents used in the experiment, sublimation of sulfur as pure chemical and the others are analytical. Glass equipment used are washed with tap water, rinsed with distilled water, and rinsed with industrial alcohol and dried before use. Reactor lining is soaked in water, washed with tap water, rinsed with distilled water, and rinsed with industrial alcohol and dried before use.

2.1.2 Experimental apparatus

Table 2-1-2 List of experimental instruments

Instrument Name and Model	Manufacturer
Electric Mixer	Shanghai Pudong Physics Optical Instrument Factory
Electronic Balance	Beijing Sartorius Instrument System Co., Ltd
Electric Constant Temperature Blast Drying Oven	Shanghai Yiheng Instruments Co., Ltd.
D/max-2200PC X-ray Diffraction (XRD)	Japanese Science
DGG-9246A Electric Constant Temperature Blast Drying Oven	Shanghai Qi Xin Scientific Instrument Co., Ltd
DMS-653 Optical Microscope	Boyu Instrument
85-2 Digital Thermostat Magnetic Stirrer	Shanghai Pudong Physics Optical Instrument Factory
KH 2200 Ultrasonic Cleaner	Kunshan Wo Chong Ultrasonic Instrument Co., Ltd
800B Centrifuge	Shanghai Anting Scientific Instrument Co., Ltd.

2.2.   Experimental steps

2.2.1 Preparation of PbS nanocrystals / micrometer crystals

(1) 1 mmol (0.379 g) of lead acetate was added to a polytetrafluoroethylene lined stainless steel kettle, and 10 ml of ethylene glycol was added as a solvent to stir the mixture on a magnetic stirrer.

(2) 1.5 mmol of the recovered sulfur powder was added to the kettle of (1), and the mixture was sufficiently stirred to disperse.

(3) 1.5 ml of glacial acetic acid was added to the solution using a pipette and stirring was continued.

(4) When the sulfur powder was dispersed uniformly, 4 ml of the ethylene glycol solution was finally added, and the mixture was stirred till sufficiently dispersed.

(5) Kettle was sealed and placed into the oven. In the constant temperature of 240°C for 24h, after the end of the reaction, let the reactor naturally cooled to room temperature.

When cooled to room temperature, the black product is poured out by filtration, repeatedly washed with alcohol until the filtrate become colorless. A small amount of product is observed under optical microscope and recorded. All the black powder was then dried in a vacuum oven at 60°C. The product is collected for further characterization.

2.2.2 Preparation of Ni-coated PbS heterogeneous materials

(1) 0.2 mmol (0.048 g) of lead sulfide, 0.4 mmol of nickel chloride hydrate and 8 mmol of hydrazine hydrate were added to a mixed solvent of ethylene glycol / water (30 ml of ethylene glycol, 6 ml of water).

(2) 1 ml, 2 ml, and 4 ml of 1 M NaOH were each added to the above solution and stirred at room temperature for 30 min on a magnetic stirrer.

(3) Kettle was sealed and placed into the oven, at 140°C for 12h. After the reaction has completed, let the reactor naturally cooled to room temperature.

After cooled, the product is poured out, filtered, and repeatedly washed with alcohol. A small amount of the product is observed under optical microscope and recorded. Use magnet to verify whether the outside of the sulfur has been coated with metal Ni, and use the magnetic size to judge the coverage condition under different variables. The black powder was then dried in a vacuum oven at 60°C. The product is collected for further characterization.

2.3. Characterization method

The phase and purity of the product were measured by a Japanese Rigalcu D/Max-3c X-ray powder deffractometer (XRD) using Cu Kα (λ = 1.5418Å), a test voltage of 40 kV, and a measurement angle of 2θ 10 to 80°; the morphology and size of the product were observed using an optical microscope and a Quanta 200 Environmental Scanning Electron Microscope (ESEM, FEI Company).

3. Results and discussion

3.1. Characterization of PbS nanocrystals / micrometers

3.1.1 Product phase and purity analysis

The phase and purity of the product were examined by XRD. Figure 3-1-1 shows the X-ray diffraction spectrum of the product obtained when the molar ratio of lead acetate and sulfur powder is 2: 3, 14ml ethylene glycol is used as solvent and 1.5ml acetic acid is added. It can be seen from the figure: the purity of lead sulfide is relatively high. The diffraction peak is strong and sharp, and all the diffraction peaks can be indexed into cubic phase PbS with a unit cell parameter a = 5.936Å which is consistent with the reported literature (JCPDS card value 05-0592). XRD does not detect impurity peaks such as S, PbSO4, PbO, which indicates that the purity and crystallinity of the product are relatively high.
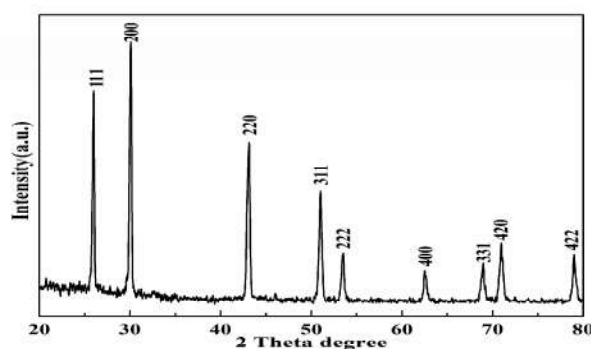

Figure 3-1-1 shows the XRD pattern of the product at 140°C for 24 hours

3.1.2 Morphological analysis of products

The morphology of the product was observed by SEM. Figure 3-1-1 shows the molar ratio of lead acetate and sulfur powder of 2: 3, with 14ml of ethylene glycol as solvent, adding 1.2ml of acetic acid, at 140°C for 24 hours.

Figure 3-1-1a is the overall topography of the product at low magnification. As can be seen from the figure, the product is mostly tree-like six-arm symmetrical structure and some crystal arm has small bifurcation and some did not. Its size is relatively uniform, arm length of about 5 μm. In addition, some six-arm structure is broken, indicating that the tree-like PbS is not easy for long-term ultrasonic dispersion. Figure 3-1-1b is a SEM image of a single tree structure at high magnification. The structure of the lead sulfide micrometer crystal can be clearly seen from the figure. A single lead sulfide tree structure consists of six different orientations of arms, each arm size is more uniform, the orientation distribution is also more uniform, but they are not in the same plane. In addition, each arm is distributed with fine bifurcation, they are arranged more uniform, the overall structure is like a symmetrical branch. By the figure, each small bifurcation is about 1μm, each arm is about 5μm, each crystal is about 10μm, so we consider it more suitable for micron crystal. Figure 3-1-1c is another six-arm lead sulfide structure we have obtained. Compared to the six-arm structure in Figure 3-1-1b, its surface is relatively smooth, there is no small bifurcation, but its overall shape and the former is basically the same, the size is similar with the former.

Figure 3-1-1 PbS sample obtained from molar ratio of lead acetate to sulfur powder of 2: 3, reaction at 140°C for 24 h

3.1.3 Effect of sulfur content on product morphology

Experiments show that the amount of sulfur powder on the product morphology has a greater impact. In this regard, we analyze them through SEM image. Figure 3-1-3 is the SEM image of the product with different amounts of sulfur powder.
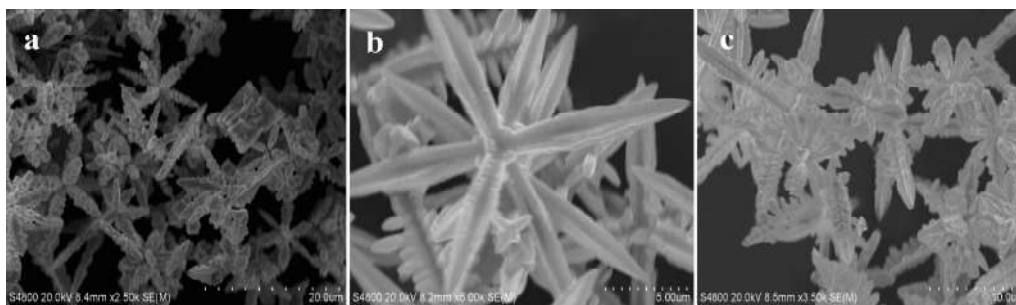

Figure 3-1-3 SEM images of PbS with different amounts of sulfur powder (Figure a, b, c uses 1mmol, 1.5mmol, 2mmol of sulfur powder, respectively)

It can be seen from the figure, when the other variables are the same (lead acetate 1mmol, acetic acid 1.2ml, ethylene glycol 14ml, reaction time 24 hours, temperature 140°C), when the sulfur powder is 1mmol, the product morphology is more messy, there are flower-like structure, there are square-shaped structure, but less non-planar six-arm structure; when the sulfur powder is 1.5mmol, the product morphology is very uniform, more than 80% non-planar six-arm structure, the size is relatively uniform, the symmetry is also very good, and the results are ideal; when the sulfur powder is 2mmol, although there are still non-planar six-arm structure, but there are also other structures, and the six-arm structures are not very regular, the size is not very uniform. This shows that the amount of sulfur powder has a certain role on the product structure, morphology of the regularity, and the size of uniformity. Sulfur powder dosage should not be too less or too much, from the experimental results we know that sulfur powder 1.5mmol is more appropriate.

3.1.4 The effect of acetic acid on the morphology of the product

Experiments show that the amount of acetic acid also has a great impact on the appearance of lead sulfide. Likewise, we analyze the impact through SEM image. Figure 3-1-4 is the SEM image of lead sulfide obtained with different amounts of acetic acid.

It can be seen from the figure, when the other variables are the same (lead acetate 1mmol, sulfur powder 1.5mmol, ethylene glycol 14ml, reaction time 24 hours, temperature 140°C), when acetic acid dosage is 1ml, its morphology is more messy and the size of each petal is not uniform; when the amount of acetic acid is 1.2ml, the product morphology is very uniform, more than 80% of non-planar six-arm structure, the size is also more uniform, the symmetry is also very good, and the results are ideal; when the amount of acetic acid is 1.5ml, the product is mostly six-arm structure, there are flower structure and other cluttered structure, and size is also different; when the amount of acetic acid is 2ml, there are very few six-arm structure, arm lengths are different, mostly are flower structure and cubic block structure, the shape and size is not regular. It can be seen that the preparation of lead sulfide microstructure requires appropriate acidic conditions, where the increase in the amount of acetic acid is conducive to the product to the uniform morphology changes. However, the acidity cannot be too strong; otherwise it is not conducive to the formation of uniform morphology products. From the results, a usage of 1.2ml acetic acid is more appropriate.

3.1.5 Effect of lead source on product morphology

When different lead sources are used, the morphology of the resulting products is also different. Figure 3-1-5 is an image observed under optical microscope of the product obtained using lead acetate and lead nitrate, respectively, as lead sources.
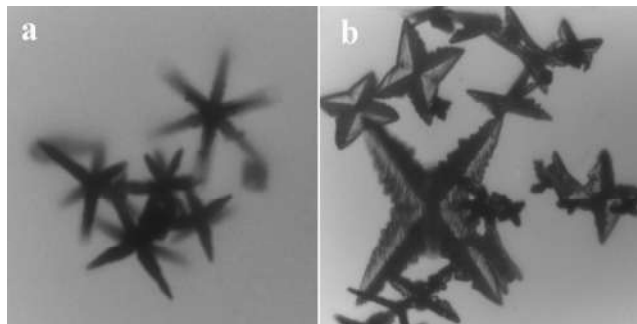

Figure 3-1-5 Image observed under optical microscope of product obtained under different lead sources (Figure a and b are lead acetate and lead nitrate, respectively)

It can be seen from the figure that when the other variables are the same (acetic acid amount, solvent, sulfur source, reaction time, reaction temperature), when lead acetate is used as lead source, the product has a non-planar six-arm structure with uniform size, looks more regular, and has a good symmetry; and when the use of lead nitrate as a lead source, the product has a large size four corner spindle structure, its shape is also more structured but the size is not uniform. When observed by the naked eye: PbS products made with lead acetate are darker, and is of black powder, and PbS prepared by using lead nitrate is of gray powder.

At the same time, we tried to use lead chloride as a lead source but failed to get the product. The specific reason is unclear.

3.2. Characterization of Ni / PbS Composites

3.2.1 Product phase and purity analysis

The phase and purity of Ni/PbS composites were observed by XRD. Figure 3-2-1 shows the X-ray diffraction pattern of the product obtained by coating 0.2 mmol of PbS with nickel at 140°C for 12 hours with polyethylene glycol and water as a composite solvent. In this case, we compare the spectra of lead sulfide with the products obtained with different amounts of 1 mol/L NaOH in the same spectrum. It can be seen from the figure: the resulting PbS (05-0592) diffraction peak is strong and sharp, indicating that its purity and crystallinity are relatively high. When NaOH is added (under alkaline conditions, the reduction of hydrazine hydrate is enhanced and nickel chloride is more easily reduced to elemental nickel), the strength of the peak varies with nickel, and with the addition of different amount of NaOH, the change is not the same. Secondly, the product is not of pure Ni/PbS composite, from the figure we can clearly see the diffraction peak of Ni3Pb2S2 (26-1287) indicating that in the coating process, bimetallic sulfide is produced. In addition, with the increase in the amount of NaOH, the peak of bimetallic sulfide has weakened, while the peak of metal nickel initially enhanced and then weakened. When adding 2ml of NaOH, nickel peak is the strongest, indicating that at this time there is more Ni/PbS heterogeneous materials.
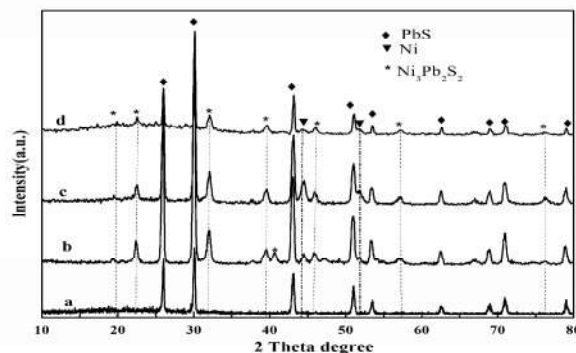

Figure 3-2-1 XRD pattern of the product obtained at 140°C for 12h (a is the XRD pattern of PbS, b, c, d is the composite product obtained by adding 1, 2, 4ml 1mol/L NaOH, respectively)

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3.2.2 Morphological analysis of products

The morphology of the composite product was observed by SEM. Figure 3-2-2 shows SEM image of the product obtained by coating 0.2 mmol of PbS with nickel at 140°C for 12 hours with ethylene glycol and water as a complex solvent (Vethylene glycol: Vwater = 5: 1).
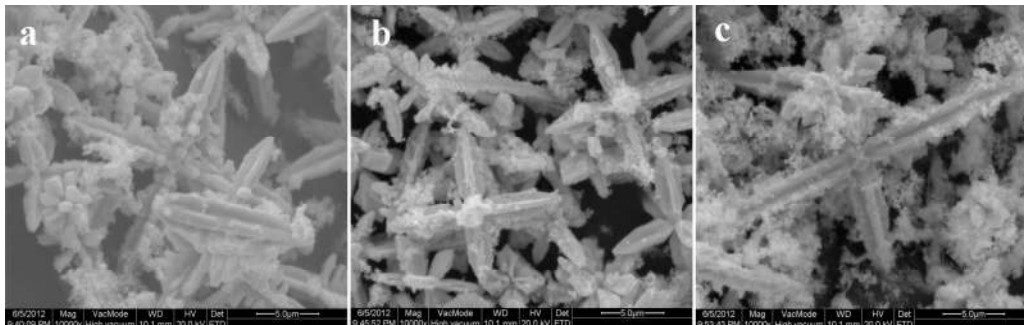

Figure 3-2-2 SEM image of products obtained at 140°C for 12 h (Figure a, b, c were added with 1, 2, 4ml 1mol/L NaOH, respectively)

It can be seen from the figure: When NaOH is added to the lead sulfide, the six-arm structure of lead sulfide can still maintain its original state. When adding 1ml of NaOH, the six-arm structure surface is coated with many small particles, while the surrounding is also scattered with some particles, they are not evenly distributed, and in addition to six-arm structure, there are other clutter structure; when adding 2ml of NaOH, the distribution of small particles is more uniform, well coated on the surface of lead sulfide, it has similar properties as a 'binder'; when adding 4ml of NaOH, the are very thick layer of small particles stuck to the six-arm structure, surrounded by a large number of scattered particles, and the overall phenomenon of agglomeration is very serious, which may be due to slightly stronger alkaline and reaction was too fast. It can be seen, when coating lead sulfide, 2ml of NaOH is more appropriate. When NaOH is less, there were more impurities, more reactions which is too fast, and not conducive to dispersion.

4. Conclusions

In this experiment, the nano-crystal materials with uniform morphology (non-planar six-arm structure) were successfully synthesized at the appropriate temperature by the compound solvent method, and the effects of various factors (acetic acid dosage, sulfur content and lead source) are studied. The XRD, SEM and microscopy were used to characterize them. Finally, nickel-coated lead sulfide heterogeneous materials were prepared.

(1) The amount of sulfur powder on the product morphology has a greater impact. When the amount of sulfur powder is too much or too little, it will affect the regularity and uniformity of the product morphology. Different amounts of sulfur powder may be produce different products. The appropriate amount of sulfur powder is 1.5mmol.

(2) The amount of acetic acid is another factor affecting the product morphology. The preparation of lead sulfide requires proper acidity, and the increase in acetic acid is beneficial to the uniformity of the product. However, the acidity shall not be too strong; otherwise it is not conducive to the formation of uniform morphology. From the results: 1.2ml acetic acid is more appropriate.

(3) Different lead sources also affect the product. When using different lead sources, not only the product's color and sedimentation capacity is different, the product also shows a completely different morphology and the size is also very different.

(4) When coating with nickel, the amount of NaOH used gives a great impact. Its amount will not only affect the speed of the coating, but also affect the purity of the composite material, and product dispersion. The results show that the amount of 2ml is more appropriate.

In this experiment, different variables were studied and observed using XRD, SEM and microscopy. The target products were the non-planar six-arm structure. The optimal reaction conditions were as follow: 1.2ml acetic acid, 1mmol lead acetate, 1.5mmol sulfur powder, reaction temperature 140°C, reaction time 24 h, 14ml ethylene glycol as solvent. For coating, 2ml of NaOH is more appropriate.

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