



Preparing ultrafine PbS powders from the scrap lead-acid battery by sulfurization and inert gas condensation



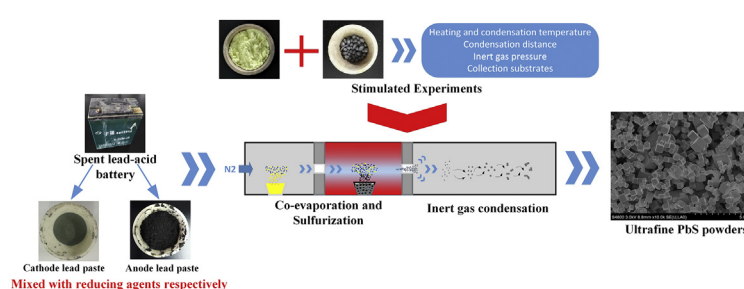
Huipeng Xia, Lu Zhan^{*}, Bing Xie

Shanghai Key Lab for Urban Ecological Processes and Eco-Restoration, School of Ecological and Environmental Science, East China Normal University, 500 Dong Chuan Road, Shanghai, China

HIGHLIGHTS

- Ultrafine PbS powders were prepared via sulfurization combined with inert gas condensation.
- Critical factors of ultrafine PbS powders preparation were intensively studied.
- Ultrafine PbS powders with a high purity can be successfully prepared from the lead paste of scrap lead-acid batteries.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 October 2016

Received in revised form

2 December 2016

Accepted 9 December 2016

Keywords:

Sulfurization

Inert gas condensation

Recycle

PbS ultrafine powders

Spent lead-acid battery

ABSTRACT

A novel method for preparing ultrafine PbS powders involving sulfurization combined with inert gas condensation is developed in this paper, which is applicable to recycle Pb from lead paste of spent lead-acid batteries. Initially, the effects of the evaporation and condensation temperature, the inert gas pressure, the condensation distance and substrate on the morphology of as-obtained PbS ultrafine particles are intensively investigated using sulfur powders and lead particles as reagents. Highly dispersed and homogeneous PbS nanoparticles can be prepared under the optimized conditions which are 1223 K heating temperature, 573 K condensation temperature, 100 Pa inert gas pressure and 60 cm condensation distance. Furthermore, this method is successfully applied to recycle Pb from the lead paste of spent lead acid battery to prepare PbS ultrafine powders. This work does not only provide the theoretical fundamental for PbS preparation, but also provides a novel and efficient method for recycling spent lead-acid battery with high added-value products.

© 2016 Published by Elsevier B.V.

1. Introduction

Lead-acid batteries are widely used as a vital power supply device, which is much more evident in the developing countries, because of the advantages of low price, stable performance, and a wide range of operation temperature [1–3]. In China, lead-acid

batteries account for more than 95% of all electric vehicles [4]. As a result, large amounts of spent lead-acid batteries containing lead oxides and sulfates are replaced every year, which prompts spent lead-acid batteries to be the dominant resource of secondary lead nowadays [5,6]. However, outdated recycling technologies and poor managements for the scrap lead-acid batteries might bring potential Pb contaminations to human beings and the environments [7,8]. Thereby, how to better recycle and utilize the waste lead-acid batteries is a grand challenge and opportunity for us, not

^{*} Corresponding author.

E-mail address: lzhan@des.ecnu.edu.cn (L. Zhan).

only in terms of lead pollution control but also from the perspectives of resource conservation and economic growth.

At present, the spent lead-acid batteries are mainly used to recycle the metallic lead [5]. However, some studies have shown that the highly purity lead oxide (PbO) can be directly recovered from the waste lead paste and lead grids of spent-acid batteries [1,9], which is more valuable and useful than the metallic lead. Thus, exploiting high value-added products through a novel method from the waste lead-acid batteries could make better use of the potential resource.

Lead sulfide, a rock salt crystal structure and an important binary IV-VI semiconductor, has attracted significant attention for its fascinating properties, especially small direct band-gap energy (0.41 eV, in bulk form at 300 K) and a large exciton Bohr Radius (18 nm) [10]. Moreover, as demonstrated by recent studies, the adsorption edge of lead sulfide shows a large blue-shift by forming nanoclusters [11]. These vital features render PbS nanoparticles to be highly useful in efficient electroluminescent devices, such as tunable near-infrared detectors [12,13], hybrid solar cells [14,15], and solid state laser [16]. Various approaches have been exploited to prepare PbS ultrafine particles. However, few reports referred to the gas-phase route [17], let alone using the scrap lead-acid battery as raw materials. Presently, much attention has been paid to the method using vacuum evaporation combined with inert gas condensation to separate and prepare the products with high added values from the solid wastes [18,19]. The method is not only an environment-friendly approach without secondary pollution for the sealed system, but also can produce ultrafine particles with the free surface and controlled chemical purity [20].

In this paper, a simple and precisely controllable method of sulfurization coupled with inert gas condensation was employed to prepare lead sulfide (PbS) ultrafine powders. The effects of preparation parameters on the size and morphology of PbS nanoparticles were systematically determined, including the heating and condensation temperature, the dynamic inert gas pressure, the condensation distance and the different substrates. Moreover, under the optimized preparation condition, attempts had been made to recycle Pb from the lead paste of spent lead-acid batteries and to prepare the high added-value PbS ultrafine powders by this method. It can provide a novel and efficient approach for spent lead-acid battery recycling.

2. Materials and methods

2.1. Materials

Initially, the pure metallic Pb particles (AR grade, Sinopharm Chemical Reagent Co., Ltd) with the diameter of about 4 mm and the pure sulfur powders (AR grade, Shanghai Shangsi Elaboration Chemical Industry Co., Ltd) were adopted to study the sulfurization process and growth mechanism of PbS ultrafine powders by co-evaporation coupled with the inert gas condensation.

Then, the scrap lead-acid batteries containing six cells provided by a local recycling agency were adopted in the practical application experiments to check the validity of preparing the PbS ultrafine powders from the scrap battery. Fig. S1 shows the sample diagram of the scrap lead-acid battery for the experiments. The scrap lead-acid battery is mainly composed of electrolyte (sulfuric acid), anode and cathode plate, baffle plate or baffle membrane, electrolytic cell, terminal block, vent holes and plastic housing. Each electrolytic cell has four anode plates and five cathode plates. Approximately 100 g anode paste and 70 g cathode paste can be scratched from each anode and cathode plate, respectively.

2.2. Apparatus

A self-designed vacuum furnace setup was manufactured and employed for all experiments (Fig. S2). The system was mainly consisted of three components which were nitrogen input system, tube furnace and vacuum pump team. The tube furnace had three chambers, where the temperature could be separately controlled and adjusted below the maximum temperature of 1273 K. A flexible thermal couple was equipped to detect the temperatures of different locations in the furnace. The water cooling jacket coupled with a filter was designed to prevent nanoparticles from entering into the pump oil and polluting the pump team. The pump team containing an oil diffusion pump and a mechanical pump can achieve a vacuum level of about 1×10^{-3} Pa.

2.3. Experimental procedure

Firstly, a quartz tube with the length of 1500 mm, outer diameter of 100 mm was placed in the middle of the tube furnace. Then, about 5 g of lead particles or lead paste (anode, cathode) loaded with a corundum crucible was placed in the center of heating room. Placing two plugs on each side of the heating zone aimed to eliminate the impacts of thermal diffusion from the heating room to the subsequent condensation room. The two plugs (diameter of 95 mm and thickness of 40 mm) are made of aluminium oxides (Al_2O_3) with a 10 mm diameter hole in the center through which the nitrogen gas could pass. The appropriate amount of sulfur powders loaded with corundum crucibles was placed on the upstream of the left plug. Substrates used to collect final products were positioned at different distances (40 cm, 60 cm and 80 cm) away from the heating zone in the condensation zone. The dynamic vacuum (100 pa, 1000 pa and 5000 pa) was maintained by means of simultaneously adjusting pumping and the gas inputting according to the pressure controller. The pure nitrogen (N_2 , 99.99%) was flowed into the quartz tube to keep a steady nitrogen gas pressure of desired values. Finally, the heating room and condensation room were heated to the preset temperature respectively at the rising rate of 10 K/min and eventually maintained for a specific time.

2.4. Analysis

The synthesized PbS ultrafine particles were preserved in a dry environment for further analysis. The morphologies of the products were characterized by scanning electron microscopy (SEM, S-4800, HITACHI, Japan), transmission electron microscopy (TEM, HT7700, HITACHI, Japan), and high-resolution transmission electron microscopy (HRTEM, HT7700, HITACHI, Japan). For TEM and HRTEM characterization, the products were ultrasonically dispersed in ethanol, and then a drop of the suspension was placed on the Cu grids coated with carbon film. The phase composition and phase structure were characterized by X-ray diffraction (XRD-6100, SHIMADZU, Japan) with Cu $K\alpha$ radiation, operated at 40 kV and 30 mA at a rate of 2° per minute over an angle range of $10^\circ < 2\theta < 80^\circ$.

3. Results and discussion

3.1. Theoretical feasibility

As shown in Fig. 1a. There are two dominant processes involved in PbS ultrafine powders preparation, namely sulfurization and growth process. During the sulfurization process, the sulfur and the lead are firstly co-evaporated into the gaseous phase. Then, the sulfur vapor carried by N_2 flows into heating zone where the PbS sulfurization reaction rapidly takes place. Subsequently, the newly

Download English Version:

<https://daneshyari.com/en/article/5149763>

Download Persian Version:

<https://daneshyari.com/article/5149763>

[Daneshyari.com](https://daneshyari.com)