Chemical Engineering Journal 304 (2016) 271–281

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

$AgPb_mSbTe_{m+2}$ microspheres comprised of self-assembled nanoparticles driven by inhomogenous co-doping synergetic induced dipoles and their thermoelectric and electrochemical Li-storage properties

Qun Wang [a,b], Yuanyuan Fang [b], Jia Zhou [b], Guangjun Zhang [a,*], Lu Yang [b], Hua Huo [b,*]

[a] State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China
[b] School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

HIGHLIGHTS

- Quaternary $AgPb_{10}SbTe_{12}$ microspheres comprised of tiny nanoparticles were successfully prepared by a hydrothermal method.
- Ag and Sb atoms tend to segregate into Ag-rich and Sb-rich regions, creating substantial inhomogeneity on the nanoscale.
- Theoretical calculations confirm the co-doping synergetic dipole-driven aggregation mechanism forming the microsphere.
- The inhomogeneous local structure has a high impact on their thermoelectric and electrochemical properties.

ARTICLE INFO

Article history:
Received 20 March 2016
Received in revised form 19 May 2016
Accepted 8 June 2016
Available online 11 June 2016

Keywords:
Quaternary
$AgPb_{10}SbTe_{12}$
Co-doping
Dipole
Properties

ABSTRACT

Design and fabrication of low-cost, high efficient and robust three-dimensional (3D) microspherical materials for energy conversion and storage is of paramount importance. Here, we first reported a template-free and efficient hydrothermal method to synthesize quaternary $AgPb_{10}SbTe_{12}$ ($AgPb_mSbTe_{m+2}$, m = 10) microspheres comprised of tiny nanoparticles driven by co-doping synergetic dipole-driven aggregation. Due to the effect of site blocking, Ag and Sb atoms tend to segregate into Ag-rich and Sb-rich regions, creating substantial inhomogeneity on the nanoscale. Theoretical calculations confirm the dipole-field-driven mechanism forming the microsphere structure. The inhomogeneous local structure has a high impact on the physical properties of the synthesized compounds: the local Ag/Sb ordering and multiple nanoscale interfaces result in the improved thermoelectric performance and cycling stability during the lithiation/delithiation process in Li ion battery compared to their binary or ternary compounds.

1. Introduction

Recently, Buonsanti et al. reported co-doping can be indeed considered the next major synthetic challenge in controlled nanocrystal (NC) doping [1]. Doping that involves intentional incorporation of specific atoms into host lattices of nanocrystals to generate materials with desirable functions is a widely applied technological process to control and manipulate the properties of semiconductors. Unlike doping bulk materials, it is well known that the most common way to dope nanomaterials is to include impurities in precursor solutions, but it is not always successful due to the “self-purifcation” mechanism and requires much fine-tuning of reaction reactivity [1,2]. On the other hand, in fact, some literatures demonstrated foreign metal ions can induce the morphology transformation process of colloidal semiconductor nanoparticles, which caused the electron charge density of the crystal surface variation [3]. For instance, Milliron et al. described the cooperative effect of trivalent dopants, gallium and antimony, on the shape of complex compound chalcogenide (CIS-based) NCs [4]. Guria et al. investigated the Ag dopant-controlled enhancement of the rate of the chemical selenization reaction of Pd nanocrystals and the consequent effect on the shape evolution of the nanostructures [5]. Despite these efforts, interactions between dopant ions and host lattices during the growth of doped nanocrystals have not been well understood.

Thermoelectric materials can directly convert waste heat to electricity. Since the discovery of an enhanced thermoelectric performance on lead-antimony-silver-telluride (LAST) alloys

---

* Corresponding authors.
E-mail addresses: wangqun5992@hit.edu.cn (Q. Wang), zhanggj@hit.edu.cn (G. Zhang).

http://dx.doi.org/10.1016/j.cej.2016.06.049

(conventionally denoted as $AgPb_mSbTe_{m+2}$) in 2004 [6], a series of PbTe-based ternary and quaternary nanocrystalline $Pb_mSb_{2n}Se(Te)_{m+3n}$ and LAST-m have been fabricated by the Kanatzidis's research group through solution synthesis route [7–9]. In our previous work, $AgPb_mMTe_{m+2}$ (M = Sb, La, Bi) one- and two-dimensional (1D, 2D) nanostructures have been fabricated by a solvothermal method [10]. However, the simple and efficient sloution route to synthesize three-dimensional (3D) hierarchial $AgPb_mSbTe_{m+2}$ microsphere still remains a great challenge because of the limited availability of suitable and compatible precursors in the reaction medium.

On the other hand, rechargeable lithium batteries can reversely transform chemical energy into electric energy. The capacity and performance of a specific battery system are directly linked to the chemical reactions occurred in the active electrode materials. Currently, considerable investigations related to binary metal telluride (M_xTe_y) have been performed due to different lithium-ion storage mechanisms depending on the type of metal. Reversed electrochemical lithium intercalation and de-intercalation processes can occur in $Bi_2Se_{0.3}Te_{2.7}$ with layered lamellas (called quintuples) [11]. In contrast, non-layered metal telluride compounds including copper telluride ($Cu_{2-x}Te$), zinc telluride (ZnTe), lead telluride (PbTe) have been proposed to follow two types of lithium ion storage mechanisms induced by reversible decomposition of Li_2Te and M-Li alloying [12–15]. Moreover, Mullins's research group showed PbTe nanoparticles for potential use in low-power applications such as cell phones [15]. As we all known that design of innovative electrode materials for practical applications must take full consideration of high gravimetric and volumetric density, superior power rates, long cycle life, low cost and good safety, and well balance of them. However, from the fundamental research point, regardless of the cost and toxicity, it is still meaningful to probe electrochemical behavior of multinary lead telluride (PbM_xTe_y). To the best of our knowledge, widely study on electrochemical properties of ternary and quaternary PbTe-based compounds is still quite limited so far. Herein, we have presented synthetic details and thermoelectric and electrochemical performance for Ag, Sb-codoped PbTe (defined as $AgPb_{10}SbTe_{12}$) microspheres with Ag,Sb-rich nanoinclusions by solvothermal method for the first time. Furthermore, the co-doping synergetic dipole-driven aggregation mechanism for the formation of microsphere composed of nanoparticles was proposed on the basic of a series of experimental results and confirmed by theoretical calculations.

2. Experimental details

2.1. Materials and preparation procedures

All reagents were analytical grade and used without further purification. Lead acetate ($Pb(CH_3COO)_2{\cdot}3H_2O$, 99.5%), sodium selenite (Na_2TeO_3, 97%), silver nitrate ($AgNO_3$, 99.9%), antimony potassium tartrate ($K(SbO)C_4H_4O_6{\cdot}0.5H_2O$), acetone, deionized water, potassium hydroxide (KOH, 99.9%), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 80%), sodium oxalate ($Na_2C_2O_4$, 99.9%), sodium dodecyl benzene sulfonate (SDBS, 99.9%), and ethanol (CH_3CH_2OH, 99.7%) were purchased from the Shanghai Chemical Company.

In the typical procedure, the mixed solvent of water and acetone was added into a beaker on the plate of a magnetic force stirring device. The potassium hydroxide (KOH, 0.86 g), hydrazine hydrate 80% ($N_2H_4{\cdot}H_2O$, 2 mL), lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$, 1.20 mmol), sodium tellurite (Na_2TeO_3, 1.44 mmol), ($K(SbO)C_4H_4O_6{\cdot}0.5H_2O$, 0.12 mmol), silver nitrate ($AgNO_3$, 0.12 mmol), and sodium oxalate ($Na_2C_2O_4$, 0.166 g) were added in turn under constant stirring with a magnetic bar at room temperature. After being stirred for 15 min, the mixture was transferred into a 15 mL stainless Teflon-lined autoclave at 180 °C for 4 h. Then the autoclave was cooled to room temperature naturally. The black specimen was poured into a clean beaker, and the samples were washed five times with water and ethanol, and the final product was dried in a vacuum oven at 60 °C for 3 h.

2.2. Characterization

The X-ray diffraction (XRD) patterns were collected at room temperature from 20° to 80° with a step of 0.02° and scanning rate of 5°/min on a Rigaku D/max-2000 diffractometer equipped with Cu Kα radiation. The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM, Quanta 200F FESEM), transmission electron microscopy, and high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai G2). In addition, energy-dispersive X-ray spectroscopy (EDX) implemented by FESEM was used to analyze the chemical composition of the prepared products. For typical SEM sampling, 1 mg product was added into 5 mL of absolute ethanol and then sonicated for 10 min to achieve a homogeneous suspension. The suspension can stay stable for several days without obvious settling at the bottom of the container. The suspension was then dropped onto a smooth silicon wafer substrate using a pipet for SEM measurement and onto carbon coated 200 mesh Cu grids for TEM, HRTEM and EDX characterization. BET specific surface areas and pore volumes were calculated from nitrogen adsorption-desorption isotherms determined at 77 K using an AUTOSORB-1-MP surface analyzer (the sample was outgassed under vacuum at 200 °C).

2.3. Thermoelectric transport properties

In current research work, the black powder of $AgPb_{10}SbTe_{12}$ and PbTe products fabricated in similar chemical synthesis system were integrated pressed into a bar with a rectangular shape of about $10 \times 4.6 \times 1.0\ mm^3$ with a special mold by cold pressing under a high pressure of 20 MPa for electrical property measurements. Silver pastes were used as electrical contacts. The electrical conductivities of the samples were measured by a DC four-probe technique using a 2400 sourcemeter (Keithley 2400, Keithley Instruments Inc., America) under an argon atmosphere from room temperature to 600 °C, in order to avoid possible oxidization at high temperature. To obtain the Seebeck coefficient, a microheater that created a temperature difference of about 3–15 K between the cool and hot ends of the specimen was applied. A temperature gradient was established in the samples when the electrical power was applied by a thermoelectric pile. The two thermocouples were contacted with the surface of the samples to detect the temperature drop (DT). The temperature and temperature differences (ΔT) were determined by calibrated nickel chromium-nickel silicon thermocouples, while the corresponding thermally induced voltage ΔV was recorded by the voltage probes. Then the Seebeck coefficient can be obtained by the formula, $S = -\Delta V/\Delta T$. The thermal conductivity was calculated from $\kappa = D{\cdot}C_p{\cdot}\rho$, where the thermal diffusivity coefficient D was measured using the laser flash diffusivity method on a Netzsch LFA457 (Netzsch, Selb, Germany) instrument. The temperature dependence of the heat capacity (C_p) was measured by a relaxation method using a Quantum Design physical properties measurement system (PPMS). Here, ρ was measured by the Archimedes method. The figure of merit was then obtained from the transport property measurements above.

2.4. Electrochemical characterization

Electrochemical measurements were performed using CR2025-type coin cells assembled in an argon-filled glove box (China,