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Facile precipitation synthesis and electrochemical evaluation of Zn_2SnO_4 nanostructure as a hydrogen storage material

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A facile precipitation method with the subsequent thermal treatment has been developed for the synthesis of Zn_2SnO_4 nanostructures in presence of tetraethylenepentamine (TEPA) with long chain as a capping and basic agent. The effects of different parameters such as precursor of Zn, solvent, reaction time and temperature were studied to reach optimum size and morphology conditions. More importantly, through controlling the experimental conditions, three different morphologies of nanoparticle, nanorod and nanoplate Zn_2SnO_4 mesoporous through one reaction were successfully obtained. In this paper, hydrogen storage capacity of Zn_2SnO_4 nanoparticle reported for the first time. Furthermore, the mesoporous of Zn_2SnO_4 nanoparticle showed high electrochemical hydrogen storage capacities at room temperature. After 13 cycles, the discharging capacities of the electrode still remain above 4650 mAh/g. These results indicate that the mesoporous Zn_2SnO_4 nanoparticle may be potentially applied for electrochemical hydrogen storage.

Introduction

Today, environmental pollutions and energy shortages have become two serious crisis for future of the world. So using technology based on renewable and green energy sources to clean up pollution instead nonrenewable fossil fuels is an essential task. For this purpose, Hydrogen with high specific energy content is an ideal energy carrier due to its abundance in world. In recent years, hydrogen storages are attracting universal scientific and technological interest because of their great energy density, renewable and green energy [1]. Although hydrogen storage has been drawn a great consideration for metal hydrides [2] and metal organic frameworks (MOFs) [3], less works have been reported for exploring the hydrogen-storage potential of nanostructured oxide materials. In this work, hydrogen storage of nanostructured oxide materials was investigated. However, considering the fact that nanostructures can strongly impress the thermodynamics and kinetics of hydrogen absorption and dissociation, they can be promising hydrogen storage structure. Beside, nanostructured active materials present a high surface area which raise surface energy associated with particles. The various types of nanostructure materials are available for application as hydrogen storage materials such as: mesoporous nanostructured transition metal hydroxides [4], different oxides [5,6], metal sulfide [7], graphene nanocomposites [8], different alloys [9], CNT materials [10] and

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hydride compounds [2]. Ternary semiconductor oxides are a significant class of materials due to its optical and electronic properties, which are suitable for application as hydrogen storage materials. Among the many possible ternary semiconductor oxide, zinc stannate (Zn_2SnO_4) nanostructures have attracted wide attention due to their superior reversible capacity, facile synthesis, lower cost and especially their various morphologies and sizes [11,12]. Different morphologies of Zn_2SnO_4 including hallow box [13], particle-like nanocrystals [14], single crystal cubes [15], Nanowires versus Nanoplates [16] and hallow fiber [17] have been applied for different applications. So far, many shape and size-controlled synthesis approaches including thermal evaporation [18], hydrothermal [19], co-precipitation [20], microwave-assisted hydrothermal [21] and solid state calcinations [22] have been introduced for the synthesis of Zn_2SnO_4 nanocrystals. In the majority of studies of recent years, Zn_2SnO_4 nanostructures were synthesized via hydrothermal method for different applications such as photocatalysis [23], gas sensor [24,25], li-ion battery [26,27] and dye-sensitized solar cells [28]. Herein, we synthesized Zn_2SnO_4 nanostructures via simple, rapid and cost effective co-precipitation approach with the subsequent thermal treatment. By comparing the available mentioned methods to prepare Zn_2SnO_4 nanostructures with the present method, it is found that this precipitation method has several benefits such as short reaction time, potential for large-scale production and low reaction temperature. In this project, different morphologies and sizes of Zn_2SnO_4 nanostructures were prepared via a facile precipitation method with the subsequent thermal treatment in presence of tetraethylenepentamine (TEPA) as a capping and basic agent. The effects of different parameters such as precursor of Zn, solvent, reaction time and temperature were studied to reach optimum size and morphology conditions. The synthesized Zn_2SnO_4 nanostructure with optimized size and morphology is proposed for the first time as an electrochemical hydrogen storage material. Furthermore, it is also found that these special mesoporous Zn_2SnO_4 nanoparticles exhibited high electrochemical hydrogen storage capacities at room temperature. After 13 cycles, the discharging capacities of the electrode still remain above 4650 mAh/g.

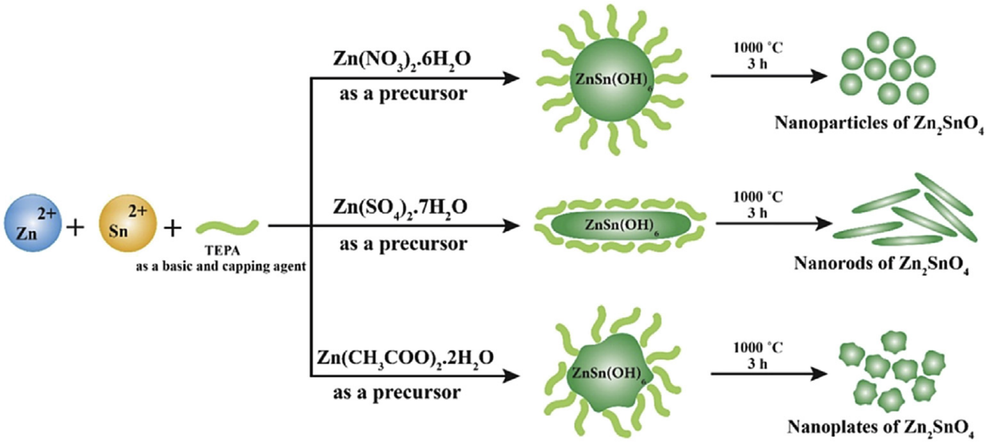
Experimental

Materials and physical measurements

All the chemical reagents for the synthesis of zinc stannate nanostructures such as $Zn(NO_3)_2 \cdot 6H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$, $Zn(SO_4)_2 \cdot 7H_2O$, $SnCl_2 \cdot 2H_2O$, tetraethylenepentamine (TEPA) were commercially available and employed without further refinement. Fourier transform infrared (FT-IR) spectra were detected on Shimadzu Varian 4300 spectrophotometer in KBr pellets. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) image was applied on LEO-1455VP equipped

Table 1 – The reaction conditions for synthesis of Zn_2SnO_4 nanostructures.

Sample no.	Type of amine	Source of Zn	Solvent	Time (h)	Temperature (°C)	Morphology	Particle size (nm)
1	TEPA	$Zn(NO_3)_2 \cdot 6H_2O$	H_2O	1	25	nanoparticle	20–150
2	TEPA	$Zn(CH3COO)_2 \cdot 2H_2O$	H_2O	1	25	Rod-like shape	Length > 500 Diameter > 110
3	TEPA	$Zn(SO4)_2 \cdot 7H_2O$	H_2O	1	25	nanoparticle	80–350
4	TEPA	$Zn(NO_3)_2 \cdot 6H_2O$	Ethylene glycol	1	25	Plate-like shape	Thickness < 50
5	TEPA	$Zn(NO_3)_2 \cdot 6H_2O$	Ethanol	1	25	nanoparticle	30–280
6	TEPA	$Zn(NO_3)_2 \cdot 6H_2O$	H_2O	4	25	nanoparticle	50–300
7	TEPA	$Zn(NO_3)_2 \cdot 6H_2O$	H_2O	1	70	nanoparticle	25–450



Scheme 1 – Schematic illustration for the growth mechanism of different morphologies of Zn_2SnO_4 nanostructures.

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