Materials and Design 111 (2016) 230–238

Contents lists available at ScienceDirect

Materials and Design

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

Synthesis and characterization of cross-like Ni-Co-P microcomposites

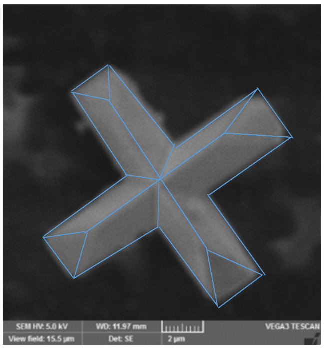
Yuhua Yan [1], Yanping Tian [1], Meifeng Hao, Yuqing Miao *

University of Shanghai for Science and Technology, Shanghai 200093, PR China

HIGHLIGHTS

- Synthesizing the cross-like Ni-Co-P microcomposites by an adapted electroless deposition technique
- Showing the perfect cross-like shape with an approximate stoichiometry of Ni_{12}-Co_6-P_{12}-O_{70}
- Exhibiting the properties of optical absorbance, superparamagnetism and hydrogen evolution

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 July 2016
Received in revised form 27 August 2016
Accepted 31 August 2016
Available online 01 September 2016

Keywords:
Ni-Co-P
Cross-like
Crystalline
Magnetic properties
Electrocatalysts

ABSTRACT

The cross-like crystallines of Ni-Co-P microcomposites were synthesized via a simple hydrothermal method under high pressure and temperature which is adapted from the classical electroless deposition technique for surface modification. Here hypophosphite was employed as reductant and phosphorus resource to prepare the composites of Ni, Co and P elements. The obtain Ni-Co-P microcomposites were characterized in morphology, composition and properties. They show the perfect cross-like shape with an approximate stoichiometry of Ni_{12}-Co_6-P_{12}-O_{70}. The high absorbance in UV area and wide absorbance in vis area are observed. They also exhibit superparamagnetic behavior and hydrogen evolution property.

1. Introduction

The various micro/nano-structured materials based on transition metal elements have attracted great attention due to their unique properties of electricity, optics, magnetics, thermal, catalysis and electrocatalysis [1]. By varying their size and morphology, the significantly improved performance was obtained compared to their bulk counterparts. The materials in micro/nano size with various morphologies have been reported extremely such as particle [2], sphere [3], wire/fibre [4], film [5], cube [6], and hollow or core-shell structures and so on [7–9].

Up to now, these micro/nano-structured materials have been synthesized through many routes such as hydrothermal method [10], solvothermal method [11,12], sonochemistry [13,14], microemulsion [15,16], thermal decomposition [17] and microwave assisted synthesis et al. [18,19] Over the years, the electroless wet-chemical plating techniques have experienced a rapidly increasing demand in a broad spectrum of industrial practices for surface modification [20,21]. It allows the deposition of desired metallic layers on the surfaces of conducting

---

* Corresponding author.
E-mail address: yqmiao@usst.edu.cn (Y. Miao).

[1] Yuhua Yan and Yanping Tian contributed equally to this work and should be considered co-first authors.

http://dx.doi.org/10.1016/j.matdes.2016.08.094

or non-conducting substrates with complex geometries by using the chemical reducing agents, typically hypophosphite, in place of an external electric current. Among various electroless metallic coatings, the alloy films of Ni-P, Co-P or their multinary compounds from the reduction of hypophosphite on the surface of various substrates have attracted a lot of attention due to their unique mechanical and magnetic properties, as well as potential applications in anticorrosion coatings, mechanic and electronic devices [22,23].

Usually, such an electroless process requires a substrate as catalytically active surfaces for metal deposition since the reduction of metal ions to elemental metal by hypophosphite is difficult to occurs directly in bulky solution at common temperature and pressure [24]. All the same, complexing agents and stabilizers are also introduced to prevent the two components from unwanted precipitation due to their possible spontaneous reaction with one another [20].

In the recent years, the techniques of electroless metallic coatings have been adopted and adapted to synthesize some micro/nano materials. As a result, the chemical reaction in electroless deposition was transplanted from the interface of solid/liquid to the bulky solution to prepare metal nanomaterials. For this purpose, crystal seeds or micro/nano sized supports were often employed to initiates a redox reaction around them [25]. Otherwise, the conditions like high temperature, high pressure, ultrasonication or microwave should be provided to meet the need of external energy to drive the reaction. By controlling the ratio of hypophosphite and the other reaction condition, the micro-/nano materials of Co, Ni, Bi or their compound based alloys were synthesized with particle, spherical, dendrite or porous shapes [18,26].

Herein, the cross-like Ni-Co-P microcomposites were synthesized by adapting the conventional electroless deposition technique in the hydrothermal method with high temperature and high pressure. The high crystallized Ni-Co-P microcomposites were yielded in bulky solution, exhibiting a geometrical figure consisting of two bars perpendicular to each other, dividing two of the bars in half. Their morphology, composition, optics, magnetics and electrochemistry were studied also.

2. Experiments

2.1. Reagents

Nickel sulfate heptahydrate ($NiSO_4 \cdot 7H_2O$), sodium tartrate dibasic dihydrate ($Na_2C_4H_4O_6 \cdot 2H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and sodium hypophosphite (NaH_2PO_2) were purchased from Aladdin Reagent Database Inc. (Shanghai, China). All chemicals were of analytical grade and used without further purification. The ultra-purified water purified by a Milli-Q system (Millipore, Milford, MA) was used in all experiments.

2.2. Preparation of the cross-like Ni-Co-P microcomposites

In a typical procedure, the cross-like Ni-Co-P microcomposites were synthesized as followed. 10 mL of 80 mM NaH_2PO_2 was dropwise added into 20 mL aqueous solution dissolved with 10 mM $NiSO_4$, 10 mM $Na_2C_4H_4O_6$ and 2.5 mM $CoCl_2$ under violently stirring. Then the mixed solution was transferred into an autoclave. After sealed, it was heated to 180 °C from room temperature within 1 h and maintained at 180 °C for 24 h or 48 h and then naturally cooled to room temperature. The precipitation was obtained at the bottom of the autoclave. It was centrifuged and washed for several times with deionized water and absolute ethanol to remove the remaining reactants. Finally, the precipitation was dried at 40 °C for 10 h. The ash black power was obtained and denoted as Ni-Co-P. For comparison, Ni-P and Co-P were synthesized also with similar reaction condition.

2.3. Instruments and methods

The morphology of the cross-like Ni-Co-P microcomposites was examined at 5.0 KV with a MIRA3 XMU/XMH scanning electron microscope (SEM, TESCAN), followed by the determination of the local elemental composition with an SYSTEM 7 energy dispersive X-ray spectrometer (EDXS, Thermo Fisher).

The phase identification was characterized by X-ray diffraction (XRD) with a Bruker D8 Advance X-ray diffractometer using Cu Kα

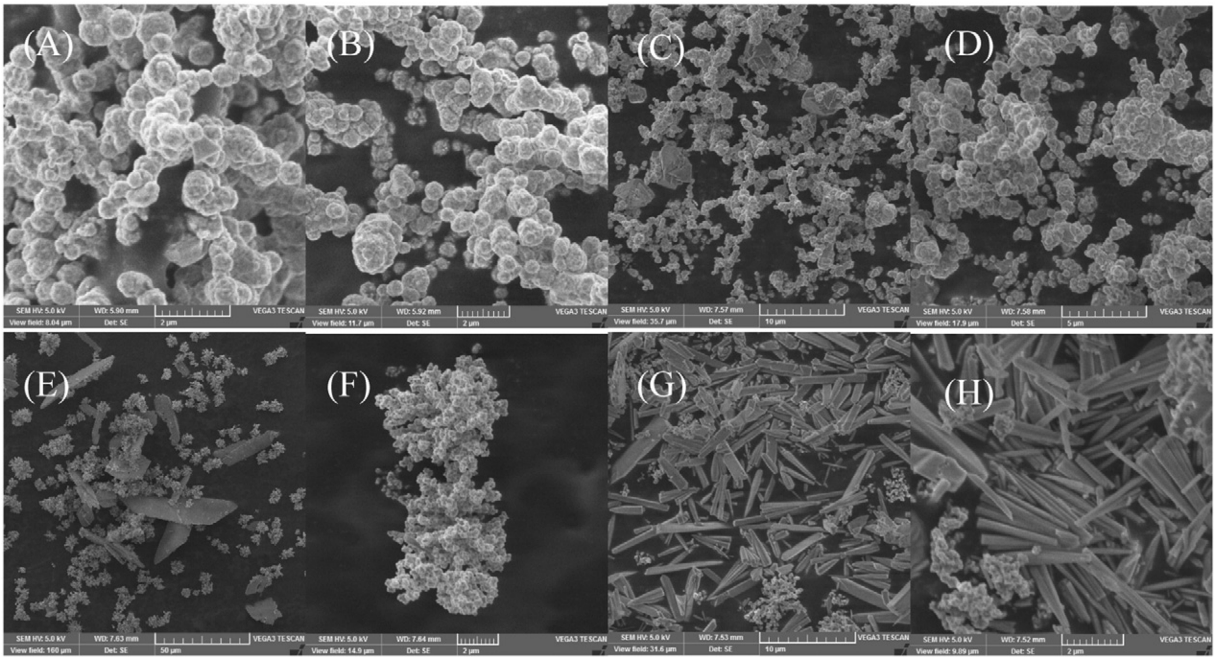


Fig. 1. SEM micrographs of Ni-P (A, B) from 24 h constant temperature reaction, Ni-P (C, D) from 48 h constant temperature reaction, Co-P (E, F) from 24 h constant temperature reaction and Co-P (G, H) from 48 h constant temperature reaction.