Journal of Molecular Structure 1099 (2015) 232–238

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Electrochemical synthesis and characterization of zinc carbonate and zinc oxide nanoparticles

Seied Mahdi Pourmortazavi [a,*], Zahra Marashianpour [b], Meisam Sadeghpour Karimi [b], Mohammad Mohammad-Zadeh [c]

[a] Faculty of Material and Manufacturing Technologies, Malek Ashtar University of Technology, Tehran, Iran
[b] Faculty of Chemistry & Chemical Engineering, Malek Ashtar University of Technology, Tehran, Iran
[c] Department of Physiology & Pharmacology, School of Medicine, Sabzevar University of Medical Sciences, Sabzevar, Iran

ARTICLE INFO

Article history:
Received 31 January 2015
Received in revised form
12 June 2015
Accepted 13 June 2015
Available online 18 June 2015

Keywords:
Electrosynthesis
Zinc carbonate
Zinc oxide
Nanoparticles
Taguchi robust design

ABSTRACT

Zinc oxide and its precursor i.e., zinc carbonate is widely utilized in various fields of industry, especially in solar energy conversion, optical, and inorganic pigments. In this work, a facile and clean electrodeposition method was utilized for the synthesis of zinc carbonate nanoparticles. Also, zinc oxide nanoparticles were produced by calcination of the prepared zinc carbonate powder. Zinc carbonate nanoparticles with different sizes were electrodeposited by electrolysis of a zinc plate as anode in the solution of sodium carbonate. It was found that the particle size of zinc carbonate might be tuned by process parameters, i.e., electrolysis voltage, carbonate ion concentration, solvent composition and stirring rate of the electrolyte solution. An orthogonal array design was utilized to identify the optimum experimental conditions. The experimental results showed that the minimum size of the electrodeposited $ZnCO_3$ particles is about 24 nm whereas the maximum particle size is around 40 nm. The TG-DSC studies of the nanoparticles indicated that the main thermal degradation of $ZnCO_3$ occurs in two steps over the temperature ranges of 150–250 and 350–400 °C. The electrosynthesized $ZnCO_3$ nanoparticles were calcined at the temperature of 600 °C to prepare ZnO nanoparticles. The prepared $ZnCO_3$ and ZnO nanoparticles were characterized by SEM, X-ray diffraction (XRD), and FT-IR techniques.

1. Introduction

Nanomaterials are of increasing attract due to their special properties and potential applications in various fields ranging from mesoscopic researches to the development of nano-devices used in science and technology [1,2]. Particularly, the preparation and characterization of nano-scale materials with specific structure and/or special morphology are of critical concern with respect to understanding the properties of materials originating from their size, shape, dimensions and aggregation form [3–6]. Nowadays, multiple synthetic techniques such as sol–gel, hydrothermal, supercritical fluid micronization, template-engaged, micro-emulsion, biomimetic and electrochemical processes have been utilized for the preparation of nanomaterials [7–13]. Among these methods, electrodeposition is a facile and cost-effective technique for production of nanoparticles which are insoluble in aqueous or non-aqueous electrolytes [12,13]. The main advantages of the electrodeposition procedure which make it attractive for the preparation of nano-sized powders and films are including simplicity, low temperature operation, and feasibility of commercial productions [14]. Optimization of experimental parameters is a critical stage in developing a synthesis route for the fabrication of nanoparticles. Regularly, two systematic procedures are used for the optimizations, which are simultaneous and sequential methods. Drawbacks of sequential methods, for example slow convergence at complex response surface and difficulty regarding to the response surface with high dimensionality, caused the simultaneous optimization to be more engrossed [15]. In the simultaneous optimization method, as a well-established orthogonal array designs, the orthogonal arrays are utilized to assign process parameters to a series of experiments combinations whose results may then be analyzed through a general mathematical way [16]. In fact, arranging experiments orthogonal permits separation of different effects. As results, this advantage being curiously noteworthy when complex experiments are being planned [16–20].

* Corresponding author. P.O.Box 16765-3454, Tehran, Iran.
E-mail address: pourmortazavi@yahoo.com (S.M. Pourmortazavi).

http://dx.doi.org/10.1016/j.molstruc.2015.06.044
0022-2860/

Table 1
OA_9 (3^4) experimental design and average particle size of electrodeposited zinc carbonate as results.

Trial no.	[Carbonate] (M)	Voltage (V)	Stirring rate (RPM)	Solvent (°C)	Particle size (nm)
1	0.01	3	200	100%Water	33
2	0.01	6	400	75:25W:EthoH	40
3	0.01	9	600	50:50W:EthoH	34
4	0.05	3	400	50:50W:EthoH	24
5	0.05	6	600	100%Water	30
6	0.05	9	200	75:25W:EthoH	37
7	0.1	3	600	75:25W:EthoH	34
8	0.1	6	200	50:50W:EthoH	31
9	0.1	9	400	100%Water	35

It is noteworthy that zinc carbonate as an inorganic salt is commonly used as a catalyst in organic synthesis reactions. Furthermore, this inorganic is an appropriate precursor for the fabrication of zinc oxide particles [21,22]. Zinc oxide nanoparticles are used widely in various fields of industry, i.e., in the conversion of solar energy [23], non-linear optical [24], catalysts [25], and the inorganic pigments [26]. This nanomaterial is a significant semiconductor material with a wide band gap and hence it has a suitable potential to use in different areas, i.e., UV laser, UV light emitting diodes, photo-catalyst, photovoltaic devices, and gas sensors [27–30]. Meanwhile, ZnO is a typical photochemical and electrochemical semiconductor which is used in different fields [31–33].

The aim of this work was focused on the optimization of electrodeposition process parameters in order to electrochemical preparation of zinc carbonate nanoparticles without any template, catalyst, or surfactant. Therefore, the effect of numerous process parameters, i.e., applied voltage for electrosynthesis, the electrolyte (sodium carbonate salt) concentration, stirring rate of the electrolyte solution and the solvent composition on the size of resulted product was investigated by Taguchi robust design as a statistical route [16,18]. The micro-structure of the electrodeposited zinc carbonate nanoparticles was characterized by the SEM. Also, the electrosynthesized zinc carbonate samples were subjected to recording their thermal behavior and determining the appropriate conditions for its calcination in order to produce ZnO nanoparticles. To the best our knowledge, several reports could be found on the synthesis of zinc carbonate microparticles and nanoparticles [34,35]; but, there is no information on the synthesis of zinc carbonate nanoparticles by electrodeposition route in the literature.

2. Experimental

2.1. Materials and procedure

The chemical reagents were prepared by the Merck Company (Germany). The electrolyte solutions were prepared by dissolving sodium carbonate in the mixture of deionized water/ethanol. Prior

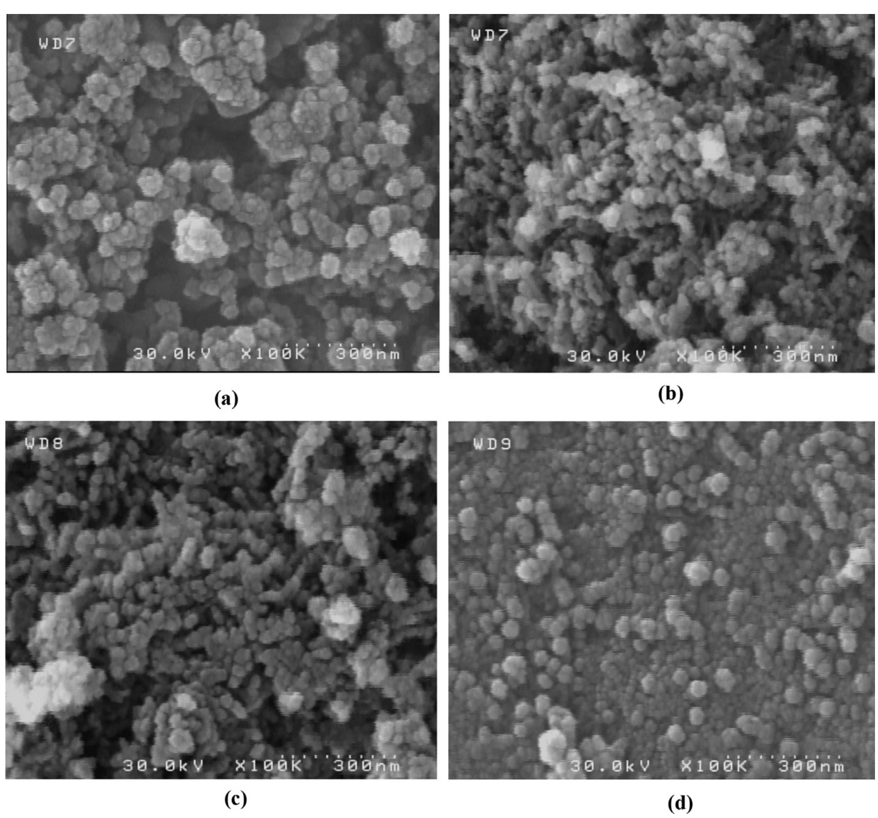

Fig. 1. SEM images of $ZnCO_3$ nanoparticles obtained at different runs (a) run 2, (b) run 4, (c) run 7 and (d) run 8.