



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

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

Straightforward ultrasound-assisted synthesis of bismuth oxide particles with enhanced performance for electrochemical sensors development



Roberto María-Hormigos, M^a Jesús Gismera^{*}, M^a Teresa Sevilla

Departamento Química Analítica y Análisis Instrumental, Facultad de Ciencias, Universidad Autónoma de Madrid, Avenida Francisco Tomás y Valiente, 7, 28049 Madrid, Spain

ARTICLE INFO

Article history:

Received 4 February 2015

Received in revised form

13 May 2015

Accepted 20 May 2015

Available online 14 June 2015

Keywords:

Bismuth oxide

Particles

Sensors

Sonochemical synthesis

ABSTRACT

Solid-state, wet-chemical and sonochemical routes of synthesis were assayed to obtain Bi₂O₃ particles. X-Ray powder diffraction (XRD), scanning electron microscopy (SEM) and dynamic light scattering (DLS) were applied to characterize the obtained particles. Then, they were evaluated as electrode materials to develop sensor devices. The best electrochemical behavior was obtained for electrodes modified with Bi₂O₃ particles obtained by sonochemical synthesis route.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Bismuth oxide is a semiconductor material with excellent optical and electrical properties that has been used for different applications including development of sensor devices. In fact, bismuth has emerged as a promising electrode material to replace mercury-based electrodes. Bismuth-based electrodes are environmentally-friendly and show comparable performance to mercury electrodes in electroanalysis [1–4]. Bi₂O₃ particles can be used to prepare bulk-modified bismuth electrodes or modify bare electrodes with composites containing these particles, in a simple way.

Six polymorphs of Bi₂O₃ (α -, β -, γ -, δ -, ϵ -, and ω - phases) have been reported in the literature [5,6], being the α - monoclinic form the room temperature stable phase. Different methods for synthesis of Bi₂O₃ have been described [7–11], and particles of different phase, morphology and size are obtained. Synthesis of different materials using high intensity ultrasound has received considerable attention because products with improved characteristics can be obtained without using bulk high temperatures, high pressures, or long reaction times [12,13].

In this work Bi₂O₃ particles were synthesized, characterized and evaluated to be used as electrode materials of sensing devices. Solid-state, wet-chemical and sonochemical routes of synthesis

were assayed to choose the most adequate Bi₂O₃ particles for electrochemical sensors development. For this purpose, the particles were incorporated into composite materials used as sensing membranes of electrodes for heavy metals determination.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used without further purification. Bismuth nitrate, Bi(NO₃)₃ · 5H₂O (Carlo Erba), sodium hydroxide (Merk) and urea (Merk) were used to synthesize Bi₂O₃ particles. Composites for electrode modification were prepared, according to our previously published method [14], from aqueous dispersions containing adequate amounts of poly(sodium-4-styrene-sulfonate) (PSS) powder (average *M_w* 70,000, Sigma-Aldrich) and carbon nano-powders (CnP) (particle size < 50 nm, Sigma-Aldrich).

2.2. Methods for Bi₂O₃ synthesis and characterization

Bi₂O₃ particles were synthesized by four different procedures. The particles denoted by **P1** were obtained by hand-mixing in solid-state of 0.98 g of Bi(NO₃)₃ · 5H₂O and 8.88 g of NaOH in a ceramic mortar until a yellowish-white powder was formed. The mixture was air-exposed at room temperature for three hours.

^{*} Corresponding author.

E-mail address: mariajesus.gismera@uam.es (M.J. Gismera).

Then, it was suspended in ultrapure water to eliminate NaNO_3 and Bi_2O_3 particles were isolated by centrifugation and decantation. Particles denoted by **P2** were synthesized mixing a bismuth nitrate solution (9.97 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 30.0 mL of 0.05 M HNO_3) with 20.0 mL of Tween 85[®], used as surfactant, and 50.0 mL of 4 M NaOH solution under vigorous mechanical stirring at 1000 rpm. The reaction mixture was heated at 90 °C for 2 h in continuous stirring. Particles named **P3** were synthesized in solution similarly to **P2**, but using ultrasound (Elmasonic P30H model ultrasonic bath, at 100 W 80 KHz) for heating and mixing. Different temperatures, between 25 and 80 °C, and a reaction time of 60 min were assayed. Bi_2O_3 particles denoted by **P4** were synthesized by dropwise addition of 30 mL of 0.1 g L⁻¹ urea solution to 20 mL of 0.5 g mL⁻¹ $\text{Bi}(\text{NO}_3)_3$ solution in 0.065 M HNO_3 . The reaction was heated under reflux with mechanical stirring for 24 h. After that, concentrated NaOH solution was added under vigorous stirring until a yellow precipitate was formed. **P2**, **P3** and **P4** particles were isolated from the reaction medium by centrifugation and decantation. All the synthesized Bi_2O_3 particles were rinsed successively with ultrapure water and ethanol and then, they were dried out in an oven at 60 °C.

The crystal structure of the particles was characterized by XRD with a X'Pert PRO PANalytical diffractometer using $\text{Cu K}\alpha$ $\lambda=1.5406$ Å radiation. Data for structural refinement were taken in the 2θ range 5–100°, with the step of 0.0167° and scanning time of 100 s per step. Bi_2O_3 particles morphology was studied by SEM using the scanning electron microscope Hitachi S-3000N with Oxford Instruments X-ray analyzer. Particle characteristics were also studied by laser diffraction using a Mastersizer 2000 equipped with Hydro 2000MU accessory (Malvern Instruments) and a Vasco-1 (Cordouan Technologies) instruments.

2.3. Electrodes preparation and electrochemical measurement procedures

The Bi_2O_3 particles were incorporated into PSS–CnP composites for electrode modification. PSS–CnP– Bi_2O_3 suspensions were prepared mixing 30.0 mg of Bi_2O_3 particles, 30 mg of CnP, 1.0 mL of 300 g L⁻¹ PSS solution and 9.0 mL of ultrapure water in an ultrasonic bath. Then, commercial screen-printed carbon electrodes (SPCE) (DRP-110, DropSens) were modified putting 4 μL of PSS–CnP– Bi_2O_3 aqueous suspension onto the working electrode of the SPCE. Finally, electrodes were dried at 30 °C overnight.

The $\mu\text{STAT-400}$ portable bipotentiostat (DropSens) was used to perform electrochemical measurements. The silver and carbon electrodes incorporated in the commercial SPCE device were used as reference and counter electrodes, respectively. Differential pulse anodic stripping voltammetric (DPASV) studies were carried out to evaluate electrochemical performance of the PSS–CnP– Bi_2O_3 modified SPCEs. The DPASV measurements were performed in lead and cadmium solutions using 0.2 mol L⁻¹ acetic acid–sodium acetate buffer solution at pH 4.5 as supporting electrolyte, by applying a -1.2 V potential for 420 s and then, a reoxidation sweep from -1.2 V to 0.2 V (50 mV s⁻¹ scan rate, 2 mV potential step, 5 ms pulse time and 100 mV pulse amplitude).

3. Results and discussion

The crystalline phase of **P1**, **P2**, **P3** and **P4** particles was determined by XRD and the obtained patterns are shown in Fig. 1. All particles showed the same diffraction pattern, which matches the reported one for the monoclinic $\alpha\text{-Bi}_2\text{O}_3$ phase (JCPDS No. 41-1449). It could be deduced that crystal structure of the particles is not influenced by temperature applied in the synthesis since the $\alpha\text{-Bi}_2\text{O}_3$ form was obtained at 20–25 °C (**P1** and **P3** particles), or

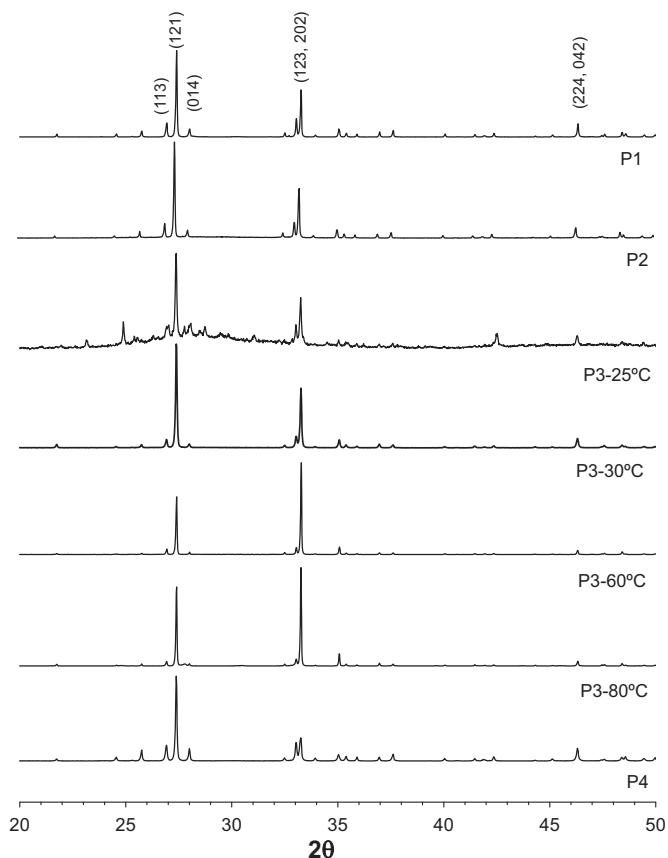


Fig. 1. XRD spectra of **P1**, **P2**, **P3** at 25 °C, **P3** at 30 °C, **P3** at 60 °C, **P3** at 80 °C and **P4** Bi_2O_3 particles.

80–90 °C (**P2**, **P3** and **P4** particles).

The intensity ratio between peaks at 27° and 33° is higher than 1 for **P1**, **P2**, **P4**, and **P3** particles synthesized at low temperatures, whereas for the **P3** particles synthesized at 60 °C and 80 °C this ratio is lower than 1. This fact could be attributed to a special orientation of the crystals obtained by the sonochemical synthesis route using high temperatures. This behavior has not been observed in a reported synthesis method carried out using high-intensity ultrasound [13] and performed without temperature control. The diffractogram of **P3** particles synthesized at 25 °C shows a lower crystallinity than **P3** particles obtained at 30 °C, 60 °C and 80 °C.

The morphology of the particles was studied by SEM. As can be seen in Fig. 2, all particles have oblique prism shape and are heterogeneous in size. Particles **P1**, **P2** and **P4** form aggregates with shape of bunches. **P3** images show morphology mainly of isolated needles and scarce aggregates due to sonochemical synthesis hinders the aggregation process [12]. For **P3** particles synthesized at low temperatures more aggregates with shape of bunches were observed than for particles obtained at high temperatures. Particles synthesized at 60 °C or 80 °C were mainly displayed as isolated needles of oblique Bi_2O_3 prisms. The size of the needles was estimated from SEM images as it shows in Fig. 2-P3-30 °C-zoom image. The estimated sizes for these particles are between 150 and 400 nm in width. The particle sizes observed by SEM for all the synthesized particles are reported in Table 1.

Bismuth oxide particles were studied by DLS using two experimental procedures. In method 1, measurements were performed with a Mastersizer 2000 instrument equipped with a manual wet dispersion accessory used to prepare aqueous suspension of the particles. In this case the obtained information may

Download English Version:

<https://daneshyari.com/en/article/1642425>

Download Persian Version:

<https://daneshyari.com/article/1642425>

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