



Synthesis and microstructural properties of zinc oxide nanoparticles prepared by selective leaching of zinc from spent alkaline batteries using ammoniacal ammonium carbonate



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ABSTRACT

Two different precursors of zinc oxide were prepared via the ammoniacal ammonium carbonate leaching of the black mass obtained during the recycling of alkaline batteries. For a concentration of 0.1 mol/L of ammonium in the leaching solution, zinc basic carbonate, was obtained, while for higher ammonium concentrations (0.5 and 1 mol/L), zinc ammonium carbonate was the final product. These precursors were characterised by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA/DTG) and Scanning electron microscopy (SEM), and calcined to obtain ZnO. Raman spectroscopy, X-ray diffraction and Transmission electron microscopy (TEM) analysis of the resulting zinc oxide samples indicated a wurtzite hexagonal lattice with *a* parameter values ranging from 3.23 Å to 3.30 Å, and *c* parameter values from 5.18 Å to 5.21 Å (values close to typical). The room temperature photoluminescence spectra of the zinc oxide samples showed two main bands: a high energy UV-blue band centred at either 412 or 382 nm (depending on the NH₃ concentration of the leaching solution used), and a green band centred at 527 nm. These emission bands are comparable to those reported for pure zinc oxide.

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1. Introduction

ZnO is one of the most widely studied semiconductors due to its excellent properties for many technological applications. ZnO has attracted much attention as a component of ultraviolet and optoelectronic sensors (Chou et al., 2006), UV lasers (Tang et al., 1998), light emitting diodes (Tsukazaki et al., 2004) and solar cells (Keis et al., 2002), etc., a consequence of its high refractive index and large exciton binding energy (60 meV) at room temperature. ZnO crystallites can be obtained by different chemical and physical synthesis methods involving nanowires, nanobelts or nanorods. Other, more complex ZnO morphologies can be produced that expand its application range (Djurišić et al., 2010).

Several synthesis routes have been developed in order to

manufacture or extract pure ZnO, mainly involving synthetic materials as precursor materials (Kołodziejczak-Radzimska and Jesionowski, 2014). One widely used method is the thermal decomposition of different zinc compounds and salts. For example, Audebrand et al., 1998 obtain zinc oxide powders by thermal decomposition of four different precursors (hydroxide nitrate, oxalate, hydroxide carbonate, and acetate); Baskoutas et al., 2007 by thermal decomposition of zinc alginate gels and finally, Khalil et al., 2014, by thermal decomposition of a binuclear zinc (II) curcumin complex.

The most common precursors used in thermal decomposition for obtaining ZnO are the basic zinc carbonate forms Zn₅(OH)₆(CO₃)₂, Zn₄CO₃(OH)₆·H₂O and Zn₃CO₃(OH)₄·2H₂O. The Zn₅(OH)₆(CO₃)₂ is of particular interest given its low decomposition temperature (Tsukazaki et al., 2004). Basic zinc carbonates can be synthesized from zinc acetate dehydrate (Zn(CH₃COOH)₂·2H₂O) and urea (NH₂CONH₂) via the sol-gel method (Wahab et al., 2008), by the dissolving of Zn(NO₃)₂·6H₂O and urea in milli-Q water (Bitenc et al., 2008), and from ZnSO₄ solution using (NH₄)₂CO₃ as a

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precipitating agent followed by thermal treatment (Li et al., 2005), among others.

On the other hand alkaline batteries (which account for some 85% of all those manufactured (Deep et al., 2011)) have four main components: MnO_2 (the positive electrode), Zn (the negative electrode), electrolytes (KOH or $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$), and steel (the battery casing). Together, these make up some 93% of the average battery. The collection of spent portable primary and rechargeable batteries in Europe is mandated by Directive (2013/56/EU (European Parliament and the Council, 2013), which required Member States to achieve a collection rate of 25% by 2012 and 45% by 2016. Around 214,000 tonnes of portable batteries (around 10.2 billion batteries) entered the market of the EEA+Switzerland in 2014, and around 85,000 tonnes of spent batteries were collected (European Portable Battery Association, 2015).

A number of pyro- and hydrometallurgical processes have been developed for the treatment of these batteries which allow recovering the main components of these, Zn and Mn. Both types of processes require the grinding and milling of the batteries, followed by the magnetic separation of all their steel components plus the removal of all their plastic and paper parts, to obtain a product known as “black mass”. i.e., a black mixture of carbon, ZnO, Zn/Mn oxides, and the battery's electrolytes.

Pyrometallurgical treatment involves the recovery of Zn from this black mass via the Waelz process (Serbent et al., 1980) of carbothermic reduction in a rotary furnace. There are, however, several hydrometallurgical methods for recovering the Zn from alkaline batteries. One of these, leaching with H_2SO_4 , allows some 95% recovery of the Zn, but it also simultaneously recovers some 45% of the Mn (Salgado, 2003); the leachates produced therefore have to be treated to separate these metals. Although most of the iron in batteries is removed during the magnetic separation step, its elimination is not complete. Hence, leaching the black mass of batteries with acid, has the drawback that the leachate is contaminated by iron. To overcome this problem, leaching with NaOH (Senanayake et al., 2010), and ammoniacal- $(\text{NH}_4)_2\text{CO}_3$ solutions have been studied. Zn forms stable complexes in the Zn– CO_2 – NH_3 system, allowing the final recovery of Zn in the form of ZnO via ZnCO_3 intermediates (Buzatu et al., 2013). Leaching with ammoniacal NH_4Cl solution has also been studied; Zn forms stable complexes in the Zn–Cl– NH_3 system (Nogueira and Margarido, 2015).

The present work explores the production of ZnO via the thermal decomposition of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ obtained from the ammoniacal- $(\text{NH}_4)_2\text{CO}_3$ leaching of the black mass extracted from alkaline batteries. The ZnO recovered was characterised, and its photoluminescent behaviour at room temperature in the visible and infrared ranges examined.

2. Experimental

2.1. Black mass starting material: characterisation

Black mass starting material from the recycling of Zn–C and alkaline batteries was obtained from Envirobat España S.L. (Guadalajara, Spain). Collected batteries were ground in a mill under an N_2 atmosphere. The steel components were then magnetically separated, and the plastic and paper components removed. The resulting black mass had a grain size of <0.83 mm. The chemical composition of the black mass was determined by X-ray fluorescence using a PANalytical Axios wavelength dispersive spectrometer (4 kW). The mineralogical composition of the black mass was determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer equipped with a Cu anode (Cu $K\alpha$ radiation) and a LiF monochromator.

2.2. Production of ZnO

ZnO was produced from the black mass in three steps: (i) leaching of the black mass with ammoniacal $(\text{NH}_4)_2\text{CO}_3$; (ii) evaporation of the leachate under vacuum, and (iii) calcination of the post-evaporation product.

- (i) *Leaching*: The black mass was leached with 1.72 mol/L $(\text{NH}_4)_2\text{CO}_3$ (final black mass pulp concentration 100 g/L) at room temperature for 60 min, agitated at 1800 rpm. The concentration of NH_3 added to the leaching solution varied from 0.1 to 1 mol/L. The suspension obtained was filtered under vacuum and the resulting solution (leachate) kept for further processing. An aliquot of the leachate was used for the determination of its Zn and Cu content by atomic absorption spectroscopy.
- (ii) *Evaporation*: representative samples (0.5 L) of the leachate obtained with each leaching solution (i.e., with the different NH_3 concentrations) were evaporated in a Buchi R-100 Rotavapor under a pressure of 34 bars. The resulting solid (termed 'precursor') was dried in an oven at 80° C for 6 h. A sample of each of the precursors obtained was characterised as described below.
- (iii) *Calcination*: The different precursors were calcined at 800° C for 5 h in a Heraeus Model 10003 furnace to obtain ZnO.

2.3. Structural analysis of the precursors and the ZnO obtained from them

All precursor and ZnO samples were characterised by scanning field emission electron microscopy (SFSEM) using a HITACHI S-4800 instrument, and by XRD using a Siemens D-500 X-ray diffractometer.

The precursors were also subjected to Fourier-transformed infrared spectroscopy (FTIR) using a Varian 670 FTIR spectrometer (spectral range 4000–400 cm^{-1} , spectral resolution of 4 cm^{-1}) in transmittance mode. This analysis was performed using a pellet (made following the KBr pellet technique [precursor = 1 wt%]) of each precursor produced. In addition, the precursors were subjected to thermogravimetric decomposition analysis, performed using 12 mg samples in a SETARAM Sensys Evolution 1500 instrument (microbalance sensitivity ± 0.1 μg) at temperatures up to 650 °C. All analyses were performed under a constant flow of Ar (20 ml/min). Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric Analysis (DTG) curves were prepared under non-isothermal conditions and the decomposition interval of the precursors determined.

The different ZnO samples were also characterised by transmission electron microscopy (TEM) using a JEM2100 HT transmission microscope. In addition, visible photoluminescence (PL) and micro-Raman spectra were obtained using a confocal Horiba Yvon instrument using excitation wavelengths of 325 nm and 633 nm respectively. For the latter two analyses, the ZnO samples were compacted into pellets, by pressing the powders under 1T pressure.

3. Results and discussion

3.1. Characterisation of the black mass and synthesis of the precursors

The black mass was mainly composed of Mn (36.8 wt%) and Zn (23.7 wt%) with some C (6 wt%) (Table 1). Around 50% of the Zn was in the form of ZnO and 50% in the form of $\text{Zn Mn}_2\text{O}_4$.

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