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The role of the temperature in the morphology and properties of zinc oxide structures obtained by electrosynthesis in aqueous solution

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HIGHLIGHTS

- ZnO micro and nanostructures were synthesized by an electrochemical method.
- Increasing the applied current and synthesis temperature augments the specific energy consumption.
- The amount of ZnO phase increases as the temperature of the synthesis augments.
- ZnO products demonstrate a high photocatalytic degradation ability toward organic dyes.

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ABSTRACT

Herein, ZnO micro and nanostructures were synthesized by an electrochemical method in aqueous solution employing NaCl as the electrolyte. Different parameters influencing the synthesis process, i.e. current intensity, reaction time and temperature, were investigated. From this, it was concluded that the productivity of the reaction increases with longer reaction time, whereas the use of higher current intensity augments the specific energy consumption. On the other hand, the increase in temperature seems to exert a negative effect. The characterization of the resulting materials by scanning electron microscopy, X-ray diffraction and thermogravimetric analysis demonstrated that a mixture of $Zn(OH)_2$ and ZnO crystalline structures is formed directly from the synthesis procedure. The content of $Zn(OH)_2$ phase in the sample decreases as the temperature of the synthesis increases, this fact indicates that the low productivity obtained at higher temperatures is related to the nature of the resulting material. Thermal annealing of the samples containing both phases prepared following synthesis allows the phase transformation from $Zn(OH)_2$ to pure ZnO structures. The band gap energies of the ZnO materials were determined by diffuse reflectance measurements according to the Kubelka Munk theory, revealing low values in all the cases which were highly dependent on the size of crystals within the materials. The photocatalytic properties of the pure ZnO samples post calcination were investigated by the decomposition of an organic dye under UV light irradiation. The results show the beneficial photocatalytic properties of the samples that had undergone calcination, these were superior in comparison to those prepared at room temperature which mainly consisted of $Zn(OH)_2$.

1. Introduction

The application of zinc oxide (ZnO) nanomaterials is continuously expanding due to their excellent physicochemical, electrical piezo-electrical properties and optical properties. These materials have found a niche of applications in some conventional uses such as electronic devices, light emitting diodes, photo-catalysts, within solar cells, sensors or even as antimicrobial agents [1–5]. ZnO is an important *n*-type semiconductor that is highly stable, with an elevated excitation binding energy of 60 meV at room temperature and a wide bandgap of 3.1–3.4 eV [6]. Alongside these properties, a variety of morphologies can be obtained of ZnO nanoparticles including spheres, rods, needles, tubes, flowers, among others. The development of these morphologies can be precisely controlled via the synthesis methods and treatments used to fabricate them [7]. The properties of ZnO nano and microparticles are significantly

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influenced by these morphologies, along with other factors such as their crystalline density, crystal size and porosity; which can also be tuned by the preparation method employed. Hence, there has been a considerable amount of interest regarding the synthesis methods used to formulate ZnO materials and nanomaterials in order to control their properties; also to find new synthetic strategies that are efficient, productive, environmentally friendly and attractive for industry.

Numerous methods have been previously investigated to synthesize ZnO, examples include: hydrothermal synthesis [8], sol-gel [9], solvothermal process [10], precipitation routes [11] and microemulsion methods [12]. In recent years, electrochemical methods have accumulated great interest regarding the synthesis of a variety of metal oxide nanoparticles and films [13–15] as they are simple, low cost methods that usually require low temperatures and aqueous conditions, thus they are very attractive for commercial fabrication. This approach has been utilized for the preparation of ZnO nanoparticles in both organic and aqueous media, using zinc sheets as a working electrode to generate Zn^{2+} within the solution [16–20]. However, synthesis in particularly aqueous solution has not been extensively investigated despite the current increase in interest in this green strategy. Most of the studies in this area employ either alkaline or slightly acidic conditions for the electrolyte at different concentrations, investigating its influence of the synthetic process. Other parameters such as the current density, insufflated gas and temperature have been shown to have a clear effect on the final properties of the nanoparticles [21,22].

In this current work, we explore the electrosynthesis of ZnO nanoparticles in an aqueous solution using NaCl as the electrolyte, which leads to a non-toxic and cheap approach that is easily scalable. The influence of different experimental parameters including current intensity, reaction time and temperature on the synthesis process were carefully studied and optimized in order to increase the overall productivity of the reaction. In particular, the effect of temperature during the synthesis process was carefully analyzed demonstrating that a further calcination step is normally required to form pure ZnO nanoparticles.

2. Experimental part

2.1. Synthesis procedure

Zinc oxides nano and microstructures were synthesized through an electrochemical process followed by thermal treatment. The electrolyte aqueous solution was prepared by dissolving NaCl salt (purchased from Aldrich), in deionized water at a concentration of 40 mM. The electrolyte solution was placed into a Pyrex electrochemical cell. A foil of zinc (99.9%, Goodfellow) was used as an anode (2 cm^2 of effective area) whilst an iron electrode (99.5%, Goodfellow) with a double effective area was used as cathode. Both electrodes were immersed into the cell, parallel to each other, with a distance of 1 cm between them. The current was then adjusted using an AMEL model 549 potentiostat/galvanostat along with the reaction time and temperature of the solution; these parameters were also varied in an effort to control the synthesis processes. Table 1 shows the specific experimental parameters of each of the performed tests. A magnetic stirrer within the cell preserved the speed of agitation within the solution at 1100 rpm. Following each experimental run, the resulting suspensions were centrifuged at 1000 rpm to separate the white product. The product was washed further with distilled water, then centrifuged once more at the same rate. Subsequent to centrifugation, the compound was collected and dried under vacuum at 60 °C for 5 h. The white powder produced was weighed to determine the mass of nanoparticles and fully characterized. A portion of the sample was calcined at 200 °C, 400 °C, 600 °C and 800 °C under static air atmosphere during a 2 h period to investigate the influence of the thermal treatment on the crystallinity of the structures.

Table 1
Experimental conditions used in the electrochemical synthesis of ZnO particles.

Run	Reaction time (min)	Current (mA)	Temperature (°C)
1	5	100	25
2	10	100	25
3	20	100	25
4	30	100	25
5	40	100	25
6	20	20	25
7	20	50	25
8	20	150	25
9	20	100	5
10	20	100	35
11	20	100	50
12	20	100	60
13	20	100	80

2.2. Characterization

The analysis of the crystalline phase and the size of the crystals of the obtained nanoparticles was performed by X-ray diffraction (XRD) in a PANalytical X'Pert PRO diffractometer with a theta/2theta primary monochromator and a fast X'Celerator detector. The patterns were collected at room temperature in the range of 10° to 80° with a scan rate of 4° min^{-1}, the diffractograms were analyzed using the Fullprof suite based on the Rietveld method.

Field emission scanning electron microscopy (FE-SEM) on a Philips XL30 S-FEG was used for the analysis of the morphology of the prepared samples.

The porous structure of the ZnO samples was characterized by means of nitrogen adsorption–desorption isotherms at −196 °C using a Micromeritics apparatus (Tristar II 3020 model). The samples were previously outgassed at 100 °C and a residual pressure lower than 10^{-3} Pa was used. The BET equations was applied to obtain the BET surface area (A_{BET}).

Thermogravimetric analyses (TGA) of runs 1–13 were carried out in a Mettler Toledo Instrument (TGA/SDTA851e model) under air at a heating rate of 10 °C min^{-1}. The accuracy of temperature and mass measurements was 0.1 °C and 10^{-3} mg, respectively. A dynamic method was used within a temperature range from 35 to 900 °C at a heating rate of 10 °C min^{-1} while purging with 50 ml min^{-1} of air. The mass of the samples in the TGA runs was between 4 and 12 mg. Aluminium pans with a capacity of 70 μL were always used.

The analysis of the band gap energies of the samples was conducted using a UV-VIS spectrophotometer fitted with a diffuse reflectance accessory (Perkin-Elmer Lambda 35 spectrophotometer).

The photocatalytic activity measurements of the samples towards the degradation of methyl orange dye (Aldrich) was carried out in a Pyrex flask type reactor under UV illumination using a Hg lamp of 150 W under refrigeration. The Zn based particles were dispersed into an aqueous solution containing 6.10^{-5} M of methyl orange in a concentration of 0.16 mg mL^{-1}. Prior to UV illumination, the suspension was stirred under dark conditions during a 1 h period to reach adsorption equilibrium. Subsequently, the mixture was exposed to UV light illumination under constant stirring and aliquots were periodically withdrawn. Finally, the absorption spectrum of each aliquot was collected using a Perkin-Elmer