Materials Science in Semiconductor Processing 39 (2015) 23–29

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Enhanced photocatalytic degradation properties of zinc oxide nanoparticles synthesized by using plant extracts

Manuela Stan [a], Adriana Popa [a,*], Dana Toloman [a], Adriana Dehelean [a], Ildiko Lung [a], Gabriel Katona [b]

[a] National Institute for Research and Development of Isotopic and Molecular Technologies, Donat 67-103, 400293 Cluj-Napoca, Romania
[b] Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 11 Arany Janos Street, 400028 Cluj-Napoca, Romania

ARTICLE INFO

Keywords:
Green synthesis
Zinc oxide nanoparticles
Plant extract
Photocatalytic properties

ABSTRACT

ZnO nanoparticles were successfully prepared by biological synthesis using aqueous extracts of *Allium sativum* (garlic), *Allium cepa* (onion) and *Petroselinum crispum* (parsley). For all ZnO samples, the XRD studies reveal a hexagonal wurtzite structure, without supplementary diffraction lines. The particle size is influenced by the type of plant extract used and varies between 14 and 70 nm. The biomolecules involved in the biosynthetic procedure was evidenced by FTIR spectroscopy. The presence of Mn and Fe in ZnO powders synthesized by using plant extracts was highlighted by ICP-MS. The EPR spectroscopy confirms the presence of Fe^{3+} and Mn^{2+} ions in ZnO samples and its variation depending on the plant extract. Also, Zn vacancy complexes and oxygen vacancies are present in all analyzed samples. A narrowing of the band gap for the ZnO prepared with plant extracts was observed as compared to that of the ZnO, prepared using solely ultrapure water. The photodegradation studies conducted in the presence of UV light irradiation indicated that ZnO nanoparticles prepared using garlic extract exhibit the highest efficiency in the photodegradation of methylene blue dye.

1. Introduction

Nanobiotechnology, presented as the intersection of nanotechnology and biotechnology, is an emerging field dedicated to creation, improvement, and utility of nanoscale structures for advanced biotechnology [1].

The synthesis of nanoparticles by nontoxic and environmentally benign biological methods (using microorganisms, whole plants, plant tissue and fruits, plant extracts and marine algae) is attractive especially if they are purposed for cosmetic, medicinal applications, water depollution [2]. It has been shown that phytosynthesis is truly a "green" synthesis route in comparison to other established methods of nanoparticle synthesis because plants are known to shelter a wide range of metabolites [1]. In the last years, nanostructured semiconductors have attracted considerable interest in many research areas, while increasing interest towards green chemistry and other biological processes has led to the development of an eco-friendly approach for the synthesis of nanoparticles [3]. Zinc oxide nanoparticles (ZnO NPs) have gained considerable attention due to their unique antibacterial, antifungal, UV filtering properties, high catalytic and photochemical activity [4]. Recently, biosynthesis of zinc oxide nanoparticles using extracts of *Aloe vera* [3,5], *Calotropis gigantea* [6], *Citrus aurantifolia* fruits [7], *Coriandrum sativum* [8], *Parthenium hysterophorus* L. [9] or milky latex of *Calotropis procera* [10] have been reported.

* Corresponding author. Tel.: +40 264 58 40 37; fax: +40 264 42 00 42.
E-mail address: adriana.popa@itim-cj.ro (A. Popa).

http://dx.doi.org/10.1016/j.mssp.2015.04.038
1369-8001/

The present work focuses on the study of ZnO nanoparticles synthesized using three types of plant extracts (garlic, onion and parsley). The synthesis mediated by plant extracts is based on the reduction/oxidation reaction. In this reaction, the phytochemicals and enzymes present in biological materials favor the conversion of metal compounds into specific nanoparticles. The bio-reduction of zinc ions into respective nanoparticles mediated by plant extracts is a chemically complex process [11]. Previous studies evidenced that the main phytochemicals present in garlic are carbohydrates, organosulfur compounds, phenolic compounds, proteins and amino acids [12,13]. Carbohydrates are the major chemical constituents of onion, which also contains phenolic compounds, vitamin C etc. [14]. Parsley is a rich source of iron and vitamins (*beta*-carotene, thiamin, riboflavin and vitamins C and E), fatty acids, volatile oils [15]. These bioactive compounds could act both as reducing and stabilizing agents, influencing the synthesis process of the nanoparticles [2,16]. The influence of the plant extract type on the structural, morphological, optical and photocatalytic properties of ZnO nanoparticles was evidenced.

2. Experimental procedure

2.1. Preparation method

The preparation method involved two steps: preparation of vegetable extracts and biosynthesis of ZnO nanoparticles.

The extracts were prepared by two methods, depending on the type of plant material used: the leaf material was extracted with boiling water under reflux and the bulb material by magnetic stirring under heating, respectively. For this purpose, 20 g of fresh leaves of *Petroselinum crispum* (parsley) were extracted in 100 mL ultrapure water by refluxing for 60 min. In addition, 20 g of fresh finely cut bulbs of *Allium sativum* (garlic) and *Allium cepa* (onion) were boiled in 100 mL ultrapure water at 75–80 °C under continuous magnetic stirring at 900 rpm for 20 min. The extracts were cooled down to room temperature, filtered using filter paper and further used for nanoparticle synthesis. The remaining extracts were stored in a refrigerator in order to be used for subsequent experiments.

For the synthesis of nanoparticles, a modified version of the experimental procedure presented by Vidya et al. was used [6]. For this purpose, 20 mL of plant extract was heated at 60 °C under continuous magnetic stirring at 400 rpm, followed by addition of 2 g of zinc nitrate (zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, 99% purity, Lach-Ner company, Czech Republic) and stirring of the mixture for 20 min at the same temperature. The obtained mixture was slowly reduced at 95 °C during 12 h, and the colored paste obtained was further treated in an air heated furnace at 400 °C for 2 h. The dried mass resulted was ground in a mortar-pestle in order to obtain fine powder for further characterization of ZnO nanoparticles. For comparative evaluation, ZnO nanopowder was prepared in ultrapure water following the same experimental procedure presented above. The plant extract mediated synthesized ZnO NPs were abbreviated as follows: ZnO(*g*)–ZnO synthesized with garlic extract, ZnO(*o*)–ZnO synthesized with onion extract, ZnO(*p*)–ZnO synthesized with parsley extract, while ZnO synthesized with water will be referred to as ZnO.

2.2. Characterization methods

X-ray diffraction (XRD) patterns were recorded using a high-resolution Bruker D8 Advance diffractometer with Cu X-ray tube and incident beam Ge (111) monocromator ($k = 1.54056$ Å).

ICP-MS measurements were carried out by the inductively coupled plasma quadrupole mass spectrometry. A Perkin-Elmer ELAN DRC (e) was used with a Meinhard nebulizer, silica cyclonic spray chamber and continuous nebulization. Ultrapure de-ionized water (18.2 MΩ cm^{-1}) from a Milli-Q analytical reagent-grade water purification system (Millipore) and ultra-pure HNO_3 60%, and HF 40% were used. A solution of 10 pbb Mg, Cu, Cd, In, Ba, Ce, Pb, U in 1% HNO_3 (Perkin-Elmer Atomic Spectroscopy Standard Setup/Stab/Masscal Solution) was aspired as external standard. The background signal (blank) was determined with an ultrapure water sample.

The UV–vis absorption spectra were recorded using JASCO V570 UV–vis–NIR Spectrophotometer equipped with absolute reflectivity measurement JASCO ARN-475 accessory. The transformation of reflectance spectra in absorbance spectra were obtained with an intern soft of apparatus.

FTIR spectra were obtained in the 400–4000 cm^{-1} spectral range with a JASCO 6100 FTIR spectrometer by using the KBr pellet technique. The spectral resolution used for the recording of the IR spectra was 2 cm^{-1}.

Morphological studies were performed on transmission electron microscope H-7650 120 kV Automatic TEM, Hitachi, Japan with Olympus KeenView G2 CCD Camera, Resolution 0.20 nm crystal lattice, 0.36 nm point-to-point, Accelerating Voltage 40–120 kV.

EPR measurements of the powder samples were performed with a Bruker ELEXSYS 500 spectrometer in *X*-band (9.52 GHz). The spectra were measured at room temperature using equal quantities of samples. The spectra processing was performed by Bruker Xepr software.

2.3. Evaluation of photodegradation performance

The photodegradation of methylene blue (MB) was carried out in a Laboratory-UV-Reactor system with an UV lamp (30 W) which emits at $\lambda = 365$ nm. The catalyst (10 mg) was suspended in an aqueous solution of methylene blue (1.0×10^{-5} mol L^{-1}, 10 mL), then the mixture was transferred into a beaker and agitated by magnetic stirring in the dark to achieve the adsorption equilibrium on the catalyst surface. Each degradation experiment was continuously conducted for 180 min. The mixture (3.5 mL) was withdrawn for analysis every 30 min. After separating the catalyst from the suspensions by centrifugation, the solution was analyzed by a UV–vis spectrophotometer.