Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Facile green synthesis of zinc oxide nanoparticles by *Eucalyptus globulus* and their photocatalytic and antioxidant activity

Siripi Balaji Reddy, Badal Kumar Mandal *

Trace Elements Speciation Research Laboratory, Department of Chemistry, School of Advanced Sciences, VIT University, Vellore 632014, India

ARTICLE INFO

Article history:
Received 11 February 2016
Received in revised form 2 September 2016
Accepted 22 November 2016
Available online xxxx

Keywords:
Eucalyptus globulus
ZnO NPs
Photocatalytic and antioxidant activity
DPPH

ABSTRACT

Eucalyptus globulus leaf extract mediated synthesis of spherical zinc oxide nanoparticles (ZnO NPs) was carried out under ambient conditions. UV–Visible studies of the synthesized nanoparticles revealed the characteristic peak at 361 nm indicating the formation of ZnO nanoparticles. Powder X-ray Diffractometric (XRD) study showed the strong, intense and narrow-width diffraction peaks indicating the formation of crystalline nanoparticles with most stable hexagonal phase. Field emission-scanning electron microscopy (FE-SEM) and high resolution-transmission electron microscopic (HR-TEM) results confirmed the formation of spherical ZnO NPs with mean particle size of 11.6 nm which is in close agreement with XRD pattern. Further, energy dispersive X-ray diffraction analysis (EDAX) revealed the formation of highly pure ZnO NPs with the peaks of Zn and O atoms. ZnO NPs exhibited effective photocatalytic activity in degrading Methylene blue and Methyl orange with maximum degradation efficiency up to 98.3% at 30 mg of catalyst doses. In addition, ZnO NPs exhibited high antioxidant activity against DPPH free radicals scavenger.

1. Introduction

Most dyes released by the industries such as plastic, leather, paint, food, tanneries, pharmaceutical, cosmetic and textile industries belong to mainly synthetic organic compounds. During last decades the discharge of effluents from industries containing intractable pollutants causes severe concern and challenge to our environment. The color content in dye absorbs and reflects sunlight radiation by inflowing polluted water, thereby hindering photosynthesis and interfere the development of aqua species [1]. Dyes contain different functional groups like acidic, basic, azo, anthraquinone and metal complexes. Most of the dyes cause a major health problem in humans including mutagenic and carcinogenic effects. These organic pollutants may induce skin irritation, a blood disorder, liver and kidney damage with the poisoning of the central nervous system in humans and animals [2,3]. Dyes cannot be degraded readily by predictable methods such as coagulation, flocculation, adsorption on activated carbon and membrane filtration. Conversion of these compounds to non-toxic compounds is difficult due to complex structures and higher stability. In order to overcome these difficulties researchers are favoring green synthesized metal oxide NPs for the degradation of organic contaminants as a green catalyst [4] due to the involvement of environmentally non-toxic reactants, solvents and without any unwanted byproducts during synthesis [5]. In addition, for safe operation, energy saving and avoiding the use of organic solvents, the development of suitable processes for the degradation of organic dyes in aqueous solutions under the mild condition is still in demand for both industrially and environmentally. Since the conventional methods involve toxic chemicals and produce toxic intermediates which are hazardous to the environment, green methods promote the researchers to minimize the usage of toxic chemicals and reduce waste generation by doing operations in aqueous medium [6]. Among different metal oxides NPs ZnO NPs has gained lot of importance due to its versatile properties. ZnO NPs exhibits hexagonal phase, wurtzite structure with a wide band gap of 3.37 eV and n-type semiconductor [7]. ZnO nanostructures are used in optoelectronic devices such as liquid crystal devices, solar cells, piezoelectric, metal insulator-semiconducting diodes and catalytic applications [8,9]. The fabrication of ZnO NPs is dominated by various physical and organic methods such as thermal evaporation, pulsed layer deposition, molecular beam epitaxy and chemical vapor condensation (CVC) [10–12]. Generally, these methods consuming supplementary energy and obligatory high vacuum, whereas chemical methods such as chemical vapor

* Corresponding author. Fax: +91 4162243092.
E-mail addresses: badalmandal@vit.ac.in, badalkmandal@gmail.com (B.K. Mandal).

http://dx.doi.org/10.1016/j.apt.2016.11.026
0921-8831/

deposition (CVD), sol-gel, hydrothermal, spray pyrolysis, sono-chemical and electro-deposition methods are costly and harmful mass production methods [13,14].

Biological fabrication of ZnO NPs by using plants, microorganisms, algae and enzymes are ecologically favorable and sustainable compared to physical and chemical approaches [15]. Although significant works had been reported on using various plant-based extracts to formulate several metal oxide nanoparticles, the use of *Eucalyptus globulus* (*E. globulus*) plant extract mediated biosynthesis of ZnO nanoparticles explicitly is not seen in literature. *E. globulus* (Blue gum) is an evergreen tree native to Australia and also found in other southeast countries. *E. globulus* leaves are widely used in Ayurveda and general public community due to its divergent health promoting medicinal activity effects against respiratory and cold infections [16–18].

Present work reports the green synthesis of ZnO NPs by using *E. globulus* as green reducing and capping agent for the first time to our knowledge. The crystal structure, surface morphology, and sizes are characterized by using UV–Visible spectroscopy, PXRD, FE-SEM, HR-TEM, DLS techniques. The efficiency of ZnO nanoparticles as photocatalyst for the degradation of various organic dyes like methylene blue and methyl orange and their antioxidant activity by DPPH assay are studied (see Table 1).

2. Experimental section

2.1. Materials

Fresh leaves of *E. globulus* were collected in the early morning during the month of March 2015 in the University of Hyderabad (UOH) Campus, Hyderabad [19]. Zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] and required organic solvents were purchased from Sigma-Aldrich, India. De-ionized Milli-Q water was used throughout the experiments.

2.2. Preparation of extract

Freshly collected leaves were washed 2–3 times under running tap water and sanitized with Milli-Q water 2–3 times and dried at room temperature in dust free condition for one week. Fully dried leaves were crushed into powder form by using an electrical mixer. About 20 g of leaf powder was added to 100 ml of de-ionized water and kept for boiling at 80 °C for about 1 h. The appearance of the light black color solution was observed which settled down at room temperature. The formed precipitate was filtered and the obtained supernatant was stored at 4 °C in the refrigerator for further use.

Table 1
Catalytic doses of ZnO NPs for degradation of methylene blue and methyl orange dyes.

Dye name and Conc. (M)	Weight of the catalyst (mg)	Time (min)	Degradation (%)
Methylene blue 10^{-4} (M)	**5**	180	96
	10	160	96.8
	15	125	97.2
	20	90	97.5
	25	50	98.3
Methyl orange 10^{-4} (M)	**5**	185	95.0
	10	162	95.8
	15	136	96.2
	20	105	96.5
	25	83	97.0
	30	60	97.3

2.3. Synthesis of zinc oxide nanoparticles

Required amount of precursor $Zn(NO_3)_3{\cdot}6H_2O$ was dissolved in de-ionized water to prepare 0.1 N 20 mL solutions after stirring for some time. Then 20 mL of *E. globulus* plant leaves extract was mixed with 20 mL precursor solution in equal ratio (1:1 v/v) drop by drop with the aid of peristaltic pump stirring at 600 rpm for 3 h till the formation of a brown colored precipitate and allowed to settle for 24 h. The solution was centrifuged at 6000 rpm for 15 min and finally washed 2–3 times with ethanol to remove impurities followed by drying at 80 °C in hot air oven for 24 h. Dried ZnO NPs powder was exposed to annealing in a muffle furnace at 400 °C for 2 h.

2.4. Characterization

The formed ZnO NPs powder was characterized by using powder X-ray Diffractometer (PXRD) (SMART Bruker D8 Advance X-ray Diffractometer) with Cu Kα radiation (λ = 1.5404 Å) after scanning at 2θ from 20° to 90° and at an accelerating voltage of 40 kV for determining crystallinity and size of crystallites/nanoparticles. The surface morphology and chemical composition i.e. purity were determined by using FE-SEM with Energy dispersive X-ray spectroscopy (EDX) (FE-SEM, Carl-Zeiss model ultra-microscope 55, Germany) at 30 kV electron beam energy. Transmission electron microscopic (TEM) studies (FEI-make electron microscope TECNAI G2 S-Twin) were carried out at an accelerating voltage of 200 kV. Electron diffraction patterns (EDP) and selected area electron diffraction (SAED) were recorded using Gatan CCD camera. Raman spectral analysis was performed by using Senterra R200-L apparatus (Bruker Optics) by passing laser light with a wavelength of 532 nm. Dynamic light scattering and Zeta potential studies were done using Horiba Scientific Nano particci (SZ-100) instrument to identify the particle size distribution and hence the stability of nanoparticles. Specific surface area, average pore diameter and pore volume were measured using Autosorb-1 instrument (Quanta Chrome Nova-1000 Instrument). The Brunauer-Emmett-Teller (BET) specific surface area of samples was measured by adsorption-desorption study of nitrogen molecules at 77 K. Barrett-Joyner-Halenda (BJH) method was used to measure the pore size distribution derived from desorption isotherms. UV-DRS (UV-Diffuse Reflectance mode) studies were conducted by using UV–Vis-NIR spectrophotometer (JASCO-V-670) to find out the band gap energy values at a wavelength range from 200 nm to 800 nm. To identify metal–oxygen bond interactions and functional moieties studies were performed by Attenuated Total Reflection-Fourier Transform Infrared spectrometer (ATR-FTIR) (ATR-FTIR, Jasco-4100) at wave number range from 4000 to 400 cm^{-1}. The chemical compounds present in *E. globulus* extract were identified by Gas chromatography–Mass spectroscopic (GC–MS) analysis using Clarus 680 electron ionization model (Perkin Elmer, India) and controlled by Turbo mass version 5.4.2 software. The GC–MS employed a fused silica column (packed with Elite-5MS (5% biphenyl 95% dimethyl polysiloxane, 30 m × 0.25 mm ID × 250 μm df) and the components were separated by using helium as inert carrier gas at a constant flow rate of 1 mL min^{-1} and scan time interval of 0.1 s with run time of 60 min. The spectra of the components were compared with the aid of NIST database (2008) library and identified.

2.5. Adsorption study

Batch tests for adsorption of MB and MO dyes by ZnO NPs as adsorbent were performed under normal room conditions in absence of UV light. Separate batch experiments were carried out for MB and MO in the absence of both ZnO NPs and UV light. In

Please cite this article in press as: S. Balaji Reddy, B.K. Mandal, Facile green synthesis of zinc oxide nanoparticles by *Eucalyptus globulus* and their photocatalytic and antioxidant activity, Advanced Powder Technology (2017), http://dx.doi.org/10.1016/j.apt.2016.11.026