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ZnO nanostructure fabrication in different solvents transforms physio-chemical, biological and photodegradable properties

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ABSTRACT

Zinc oxide (ZnO) nanostructures are synthesized in various organic solvents (acetone, chloroform, ethyl acetate, ethanol and methanol) and water via coprecipitation process using zinc acetate as precursor. The resultant ZnO nanoparticles, nano rods and nano sheets are characterized by UV–vis spectrophotometric analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transmission infrared spectroscopy (FTIR), and energy dispersive X-ray spectroscopy (EDX). The variable size and geometry of nanoparticles depend upon medium used for synthesis. The synthesized ZnO nanostructures exhibit minor to moderate antioxidative (DPPH based free radical scavenging activity, total antioxidative potential and total reducing power) response. Mild to moderate antibacterial and antifungal activities, excellent antileishmanial potential (IC50 up to 3.76), and good cytotoxic perspective (LD50 up to 49.4) is also observed by the synthesized ZnO NPs. The nanoparticles also exhibit moderate α-amylase inhibition response. Furthermore the nanostructures are evaluated for methylene blue photodegradation response within 60 min time period. It is found that organic solvent alters shape, size and other physio-chemical properties of ZnO that ultimately modulate the biological, chemical, and environmental properties.

1. Introduction

ZnO nanoparticles (NPs) has already been synthesized through different routes that resulted in variable properties such as size, shape other physiochemical characters. Most of the applications involving photonic and electronic are because of wide band gap energy of 3.37 eV at room temperature [1]. Some of the other applications include UV photodetection, transparent electronics, humidity sensor, gas and chemical sensor, micro lasers, memory arrays, coatings, catalysts, and biomedical applications [2–6]. However the capability and capacity of ZnO NPs for these applications also depends upon size and shape [7]. A number of reports disseminate to control physiological properties of nanoparticles [8,9].

Coprecipitation method is adoptive mostly for synthesis of metallic nanoparticles because it is simple, reproducible and cheap, though the size and shape may vary depending upon modification of procedure. Although, coprecipitation methodology is based on three lattices; i) formation of mixed crystal, ii) occlusion, and iii) surface adsorption by the precipitate after it has been formed. The pure nanoparticles are based on third principle where crystal grows after nucleation. The idea for the synthesis of ZnO nanostructures is based on a two-step self-assembly process including nucleation and secondary crystal growth. In the template-free process, well-defined ZnO nanowires have been synthesized in ammonia solutions or ethanol solutions of NaOH at moderate temperatures via the two-step self-assembly process. However, most wet chemical methods have failed to produce rods with diameters <100 nm ([10–12]. Particle size, shape, solubility, crystallinity and other characteristics depend upon medium in which crystals are fabricated. Researchers have tried to synthesize ZnO nanoparticles via coprecipitation methods using different solvent system. Some are elaborated in Table 1.

The synthesis, characterization and application of various ZnO nanostructures including the rods/wires, belts/ribbons, rings, tetrapods, combs, sheets and complex structures [12,22–27] were presently the subject of intense research. Most of the synthetic procedures involve high temperature, long reaction time and toxic template. In the present work, the coprecipitation process is employed to synthesize ZnO nanoparticles. Effect of different organic solvents, i.e., methanol, ethanol, chloroform, ethyl acetate and acetone in comparison with water on size shape and other properties are investigated. Furthermore the results obtained from this study also offer some insights onto the role of

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Table 1
Effect of different solvents on synthesis of ZnO nanoparticles from different zinc precursors and procedures.

Solvent	Precursor	Method	Avg diameter	Avg length	Shape	Reference
Alcohols	Zn(CH3COO)2	Solvothermal synthesis	81–107	184–455	Hexagonal	Ayudhya et al. [13]
Glycols			42–69	55–139	Oval	
n-Alkanes			48–67		Cylinders	
Aromatic compounds			43–78		Cylinders	
Water with different amount of precursors	Zn (CH3COO)2	Hydrothermal	100–300		Varying	Li et al. [14]
1-Butyl-3-methylimidazolium chloride	Zn(CH3COO)2	Microwave-heating route	80–200 nm	200–400 nm	Multipod, flower-like and shuttle-like	Wang et al. [15]
1-Butyl-3-methylimidazolium tetrafluoroborate						
Methanol	ZnCl2	Solvothermal growth	9		NPs	Hu et al. [16]
Ethanol			100	3 μm	Nanowires	
1-Propanol			40	200	Nanorods	
1-Butanol			50	300	Nanorods	
1-Pentanol			150	1 μm	Nanorods	
Acetone			8		NPs	
Isopropanol			40	500	Nanorods	
1-Hexanol			20	1 μm	Nanoneedles	
Methanol	Zn(CH3COO)2	Coprecipitation	4.5–7	5–100	NPs, nanorods	Seow et al. [17]
Ethanol methanol	Zn(CH3COO)2	Electrochemical	16		NPs	Stypuła et al. [18]
Ethanol or deionized water	$ZnNO_3 \cdot 6H_2O$	Solvothermal growth	20–60		NPs	Khoza et al. [19]
Acetone			45–100	37–94	Rods, NPs	
Water	Zn(CH3COO)2	Coprecipitation	20		NPs	Hussin et al. [20]
Acidic water	Zn(CH3COO)2	Coprecipitation	11–20		NPs	Purwaningsih et al. [21]

morphological parameters in the biological, pharmaceutical and photocatalytic properties of synthesized ZnO nanoparticles.

2. Experimental

2.1. Synthesis of zinc oxide nanoparticles

The ZnO nanoparticles are synthesized through coprecipitation method as described by Shankar et al. [28] with slight modifications. Briefly, an aliquot of 1 mM $Zn(CH_3COO)_2 \cdot 2H_2O$ was drop wise mixed with 2 M NaOH with consistent stirring at room temperature for 2 h. The white precipitate appeared were collected by centrifugation and thoroughly washed with distilled water to remove impurities followed by overnight drying at 60 °C. The ZnO particles were fabricated in different solvent systems such as acetone, chloroform, ethyl acetate, ethanol and methanol instead of water as a solvent

2.2. Characterization

Images of ZnO NPs were taken by SEM operating at of 20 keV voltage. The FTIR spectra were recorded in the wave number frequency ranged from 4000 to 600 cm^{-1} with a speed of 16 scans per spectrum using bench-top Spectrum™ 65. XRD measurements were determined using Bruker D8 Advance brand *-2* configuration (generator-detector) X-ray tube copper S = 1.54°A and LYNXEYE PDS detector.

2.3. Antioxidative activities of ZnO NPs

For antioxidative analysis, ZnO NPs were suspended in DMSO at 20 mg/mL and the mixture was sonicated for 15 min before use.

2.3.1. DPPH free radical scavenging

Standard 2,2-diphenyl 1-picryl-hydrazyl (DPPH) method was used for free radical scavenging potential of samples [29]. For ZnO NPs; solution of 10 μL in DMSO (final concentration 200 μg/mL) was combined with DPPH solution of 190 μL (in methanol). After the incubation for 15 min in dark at 37 °C, absorbance was measured at 517 nm using spectrophotometer.

2.3.2. Total antioxidant capacity (TAC) assay

TAC was determined by phosphor-molybdenum method [30]. The reagent solution of 1 mL (4 mM ammonium molybdate, 28 mM sodium phosphate and 0.6 M sulfuric acid) was added with 0.1 mL of ZnO NPs. The mixture was incubated at 95 °C for 90 min and then cooled to room temperature. Sample TAC was expressed as ascorbic acid equivalent and the absorbance was measured at 695 nm.

2.3.3. Total reducing power (TRP) assay

Samples were mixed with 200 μL phosphate buffer (0.2 mol, pH 6.6) and 250 μL potassium ferricyanide [$K_3Fe(CN)_6$] (1%). The mixture was then incubated at 50 °C for 20 min and then 10% trichloro-acetic acid (200 μL) was added. At room temperature, the mixture was centrifuged at 3000 rpm for 10 min. The upper layer of solution (150 μL) was then mixed with $FeCl_3$ (50 μL, 0.1%). Finally, the absorbance was measured at 630 nm on spectrophotometer. The enhanced absorbance of the reaction mixture showed better reducing power. Blank was prepared by adding 400 μL of DMSO to the above-mentioned reaction mixture instead of the sample. The reducing power of samples was expressed as ascorbic acid (vitamin C) equivalent [30].

2.4. α-Amylase inhibition assay

α-Amylase inhibition assay was performed using a method previously reported with slight modification [31]. The activity was performed in 96 well microplate, and to each well included in the test, 15 μL phosphate buffer, 25 μL α-amylase enzyme, 10 μL of sample (20 mg/mL) and 40 μL starch was added in subsequent steps. Incubation was done at 50 °C for 30 min, followed by the addition of 20 μL of 1 M HCl and finally 90 μL iodine solutions. Suitable wells were assigned for blank, positive and negative control. Blank contained buffer solution, starch and dH_2O, while negative and positive control wells contained the respective dH_2O and acarbose instead of test sample. Results were noted