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Evaluation of photocatalytic, antimicrobial and anticancer activities of ZnO/MS (M = Zn, Cd or Pb) core/shell nanoparticles

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ABSTRACT

Zinc oxide nanoparticles were synthesized by co-precipitation method followed by covering with MS (M = Zn, Cd, or Pb) to obtain ZnO/MS core/shell nanoparticles using chemical method. The formation of core/shell nanoparticles were authenticated by various spectroscopic techniques. The photocatalytic activity of the synthesized core/shell nanoparticles shows the significant role of the shell layer in the photodegradation of methylene blue. The antimicrobial activity has been evaluated against two Gram (–ve) (*E. coli* and *K. pneumoniae*) and two Gram (+ve) (*E. faecalis* and *S. aureus*) bacterial, and two fungi (*A. niger* and *C. albicans*) strains. *In vitro* anti-proliferative activity of ZnO and ZnO/MS core/shell nanoparticles at a concentration of 0.06 M was evaluated against two human cancerous cell lines such as breast (MCF-7) and lung (A549), and one normal human kidney (HEK-293) cell line by MTT assay. DNA fragmentation analysis proved the inhibition of proliferation through induction of apoptosis.

1. Introduction

Zinc oxide (ZnO) is n-type metal oxide semiconductor with a wide bandgap of 3.37 eV and high excitation binding energy of approximately 60 meV has been widely investigated for many optoelectronics, gas sensors, solar cells and photocatalytic applications, and exhibit a few distinct advantages including good carrier mobility, simple tailoring of structures, facile and low cost for large scale manufacturing [1,2]. In order to improve the efficiency, when compared to the separate component, a great deal of fundamental researches has been focused on mixed catalysts and semiconductors with surface modification [3,4]. In this respect, optical, conductive and catalytic properties may be modified with a shell of desired material onto the core leading to a new class of material known as core/shell nanoparticles [5]. Immense effort have been made to fabricate a variety of core/shell and hollow structures such as noble-metals, hydroxides, semiconductors, organic and inorganic material with tailored structural, optical and surface properties. Semiconductor metal sulphide core/shell nanorods and nanotubes have been of great interest in terms of scientific and technological applications, and the shell can impart catalytic, optical and magnetic function to core/shell nanoparticles [6,7]. Enhancement of optical properties was observed in core/shell nanostructures with higher bandgap shell materials [8].

Over the last two decades, photocatalytic degradation attracted public interest as a promising technology for the removal of dye pollutants from textile, paper and wastewater that are recalcitrant to biodegradation using non-toxic, thermally and chemically stable semiconductor metal oxides as photocatalyst [9,10]. Semiconductor photocatalysis is an alternative to conventional methods for dye degradation, and has been a promising method for the destruction of a great variety of organic compounds [11]. The photocatalytic activity largely depends on two factors: reactant adsorption behavior and the separation efficiency of electron-hole pairs. By increasing the specific surface area of the catalysts, the adsorption capacity can be improved. In order to reduce the recombination of electrons and the holes, doping semiconductor with transitional metal ion, coupling with another semiconductor and loading with noble metals have been successfully carried out [12]. Several parameters such as pH, dissolved oxygen content and the amount of photocatalyst added in the aqueous solution influence the photocatalytic degradation of the dye [13]. Consequently, there is a demand for materials, which are active in the visible region, and hence a number of photocatalyst such as CdS, ZnS, ZnO, CuO and others have been reported [14]. The synthesis of particles with a core-shell structure is becoming more and more popular since these composite particles have wide applications and are potential in antimicrobial and pharmaceutical industries [15]. Indeed, some studies suggest that the core/

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shell nanoparticles are not inherently benign and affect biological behavior at the cellular, subcellular and protein levels [16,17].

In this study, ZnO was synthesized by co-precipitation method followed by covering with MS (M = Zn, Cd or Pb) to obtain ZnO/MS (ZnO/ZnS, ZnO/CdS and ZnO/PbS) core/shell nanoparticles with different molar ratio of shell concentration (0.02–0.06 M) by chemical method and characterized by various techniques. The photodegradation property of the ZnO and ZnO/MS core/shell nanoparticles were investigated using aqueous solution of methylene blue under visible light irradiation. Antimicrobial studies against two Gram (−ve) (*E. coli* and *K. pneumoniae*) and two Gram (+ve) (*E. faecalis* and *S. aureus*) bacterial, and two fungi (*A. niger* and *C. albicans*) strains was carried out using microtitre assay method. *In vitro* anticancer activity was assessed by MTT assay on two human breast (MCF-7) and lung (A549) cancer, and one normal human kidney (HEK-293) cell lines. DNA fragmentation was observed by agrose gel electrophoresis.

2. Experimental

2.1. Materials

Zinc acetate dihydrate, cadmium acetate tetrahydrate, lead acetate, sodium sulphide and sodium hydroxide were purchased from Sigma-Aldrich, India. All the materials were of analytical grade and used without further purification. Double distilled water was used for all dilution and sample preparation.

2.2. Synthesis of ZnO and ZnO/MS core/shell nanoparticles

The synthesis of ZnO and ZnO/MS core/shell nanoparticles were performed according to the given protocol [18]. ZnO nanoparticles was prepared using co-precipitation method by dropwise mixing of equimolar amount (0.2 mol) of zinc acetate and NaOH in deionized water with constant stirring at 80 °C until a white precipitate was formed. After cooling, the precipitate was washed several times with deionized water followed by ethanol and dried in a hot air over for 2 h at 120 °C. The ZnO/MS core/shell nanoparticles were synthesized by simple chemical method. Acetate salts of Zn, Cd and Pb dissolved in deionized water-ethanol mixture was added to the synthesized ZnO nanoparticles and sodium sulphide solution (prepared in a deionized water-ethanol mixture) was added dropwise with vigorous stirring at 80 °C until the formation of precipitate (the concentration of acetate salts of Zn, Cd and Pb, and sodium sulphide varied between 0.02 and 0.06 M). The appearance of white, yellow and black precipitate indicates the formation of ZnO/ZnS, ZnO/CdS and ZnO/PbS core/shell nanoparticles, respectively. The precipitate was allowed to settle for an hour, collected and washed several times with deionized water followed by ethanol, and dried in a hot air oven for 2 h at 120 °C.

The synthesized ZnO and ZnO/MS core/shell nanoparticles were denoted as N1–N10: N1 = ZnO; N2 = ZnO/ZnS (0.02 M); N3 = ZnO/ZnS (0.04 M); N4 = ZnO/ZnS (0.06 M); N5 = ZnO/CdS (0.02 M); N6 = ZnO/CdS (0.04 M); N7 = ZnO/CdS (0.06 M); N8 = ZnO/PbS (0.02 M); N9 = ZnO/PbS (0.04 M) and N10 = ZnO/PbS (0.06 M).

2.3. Characterization

FT IR spectra were recorded on Shimadzu IR460 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. XRD patterns were obtained using Siefert Analyze diffractometer with Cu Kα radiation (λ = 1.5406 Å) to determine the phase purity and structure of the nanoparticles. The diffuse reflectance spectra were recorded on a UV140404B in the wavelength range 200–900 nm in reflectance mode. The photoluminescence properties were recorded using Varian Cary eclipse fluorescence spectrophotometer. The morphological studies were carried out using field emission scanning electron microscope (FE SEM) (JEOL 6500F) and transmission electron microscope (TEM CM 200). The elemental analysis was carried out using energy dispersive X-ray (EDX) measurements.

2.4. Evaluation of photocatalytic activity

The photodegradation of methylene blue was evaluated by monitoring the absorbance of an aqueous solution of methylene blue under irradiation by visible light. 25 mg of the sample (N1, N2, N4, N5, N7, N8 and N10) was added to 100 mL of 5×10^{-5} M aqueous methylene blue and dispersed under ultrasonic agitation for 10 min. The dispersion was magnetically stirred in the dark to establish adsorption/desorption equilibrium between the sample and methylene blue dye. The contents were then illuminated by visible source (λ > 420 nm) to induce a photochemical reaction. Aliquots were taken out at regular intervals of 15 min and the absorbance of methylene blue solution was determined using a UV–Vis spectrophotometer.

2.5. Antimicrobial assay

The antimicrobial activity of ZnO (N1) and ZnO/MS core/shell (N2, N4, N5, N7, N8 and N10) nanoparticles was assessed by a microtitre assay against two Gram (−ve) (*Escherichia coli* and *Klebsiella pneumoniae*) and two Gram (+ve) (*Enterococcus faecalis* and *Staphylococcus aureus*) bacterial, and two fungi (*Aspergillus niger* and *Candida albicans*) strains. A vortex mixer was used to prepare the resazurin solution by dissolving 270 mg in 40 mL of sterile distilled water.

2.5.1. Determination of minimum inhibitory concentration (MIC)

A sterile 96 well plates were prepared under aseptic conditions. The freshly prepared sample suspensions in DMSO was sonicated using a sonicator. A volume of 100 μL of test material in 10% DMSO (a stock concentration of 1 mg/mL for purified compounds) was pipetted into the first row of the plate. To all other wells, 50 μL of nutrient broth was added for bacteria cells and 50 μL of Sabouraud dextrose broth for fungi cells, and serial dilutions were performed using a multichannel pipette. To each well, 10 μL of resazurin indicator solution was added. Finally, 10 μL of bacterial/fungal suspension (5×10^6 cfu/mL) was added to each well to achieve a concentration of 5×10^5 cfu/mL. The commercial drugs streptomycin (against bacteria) and amphotericin-B (against fungi) were used as a positive control. The plates were prepared in triplicate, and placed in an incubator set at 37 °C for 18–24 h and any colour change from purple to pink or colorless indicates the reduction of dye by the viable bacteria/fungi. The lowest concentration at which colour change occurred was taken as the MIC value. The average of three values was calculated to get MIC values.

2.6. Cytotoxicity

2.6.1. Cell lines and cell culture

Human lung adenocarcinoma (A549) and breast (MCF-7) cancer and human kidney (HEK-293) normal cells were obtained from National Centre for Cell Science (NCCS), Pune, India. The cells were maintained in minimal essential media supplemented with 10% fetal bovine serum (FBS), penicillin (100 μg/mL) and streptomycin (100 μg/mL) in a humidified atmosphere of 5% CO_2 at 37 °C.

2.6.2. MTT assay

The cell viability of ZnO (N1) and ZnO/MS (N4, N7 and N10) core/shell nanoparticles was assessed by MTT (3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyltetrazolium bromide) assay as described by Mosmann [19]. The A549, MCF-7 and HEK-293 cells (1×10^5/well) were plated in 0.2 mL of medium/well in 96-well plate and treated with medium containing 10% PBS and incubated for 24 h at 37 °C in a 5% CO_2 incubator for better cell attachment. Later, the medium was replaced with DMEM containing 1% FBS and different concentration of the samples (100–0.20 μg/mL) dissolved in DMSO were added to the cells incubated