Operational and Ocular Activity Studies of Metal di-oxide Nanoparticles

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Abstract

In this study, pure and Co-doped tin oxide (SnO_2) nanoparticles were synthesized by sol–gel method, and the effect of Co-doping on the Operational, Ocular, photocatalytic, and "antimicrobial" activities was studied. The prepared samples were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy, UV–visible diffuse reflectance spectroscopy, and N_2 adsorption/desorption analysis. The XRD patterns of all the samples are identified as tetragonal rutile-type SnO_2 phase which is further confirmed by TEM analysis. The Ocular spectra showed redshift in the absorption edge of doped samples, which enhances their absorption toward the visible light region. The photocatalytic activity of all the samples was assessed by monitoring the degradation of methylene blue solution under daylight illumination, and it was found that the photocatalytic activity significantly increases with the increase in dopant concentration, which is due to the effective charge separation of photo generated electron–hole pairs. The "antimicrobial" studies investigated against standard bacterial and fungal strains showed enhanced "antimicrobial" activity in doped samples, which can be attributed to the production of reactive oxygen species and large surface area of the nanoparticles.

Introduction

Cerium is a rare earth element of the lanthanide series which is found in abundant amounts in the Earth's crust. It exists in dual oxidation states—Ce^{+3} and Ce^{+4}. Cerium dioxide (CeO_2) has attracted significant attention due to diverse Operational, Ocular, magnetic, and "antimicrobial" properties in a wide range of applications in different fields. The swapping of the oxidation state from +3 to +4 state and vice versa is due to quick gain or release of oxygen through oxidation and reduction reactions due to which it can store and transport oxygen. These distinctive properties of CeO_2 make it a prominent material for various magnetic, catalytic, and industrial applications. CeO_2 becomes a reactive element because of its interchangeable states, which makes it relevant for catalytic purpose. CeO_2 is also well acknowledged for its other applications in spintronic devices, optoelectronics, gas sensors, cosmetic products, water splitting, solar cell devices, solid oxide fuel cells, and many more. Due to a wide bandgap, CeO_2 has been considered as a prominent candidate, among which defects, disorders, and nonstoichiometry are recognized as the key features for its magnetism. The involvement of transition metals (TM) and rare earth (RE) elements in host material has increased professionals' interest in it. The addition of TM/RE elements, such as Fe, Cu, Ni, Cr, Mn, Co, Gd, Sm, Eu, Nd and Pr as a dopant, has been reported as a significant change in the Operational parameters, increasing the creation of Ce^{+3} states and oxygen vacancies in CeO_2. In recent years, it has been found that the nano-sized materials are making remarkable contributions to the medical industry in the form of imaging, combating bacterial pathogens, drug delivery, etc.. In addition, the nanoscale "antimicrobial" agents have a long-lasted effect on the living systems as compared to conventional molecular "antimicrobial" agents. It is remarkable that, as the size of the material is reduced to nanoscale, their surface to volume ratio increases. This high surface-to-volume ratio increases the chemical reactivity of the particles and enables them to perform as efficient catalysts and antibacterial agents. This attribute of nanoparticles has been utilized in the treatment of various infectious microorganisms such as *Escherichia coli*, *Candida albicans*, etc., which form biofilms on the affected surfaces. These bacterial biofilms are developed when the bacteria inhabit the biomedical surfaces, resulting in microbial infections. The cure for such infections can be found in the nanoparticles of metal oxides such as TiO_2, ZnO, MgO, CeO_2, etc., exhibiting antibacterial properties]. Since the last few decades, researchers have been working on developing biocompatible and non-toxic nanomaterials which can be seen as a possible cure for various bacterial infections. From the above-mentioned metal oxides, CeO_2 is one such material that has proven its effectiveness in various processes

such as photocatalytic activity, water treatment and as an antibacterial material. The dual oxidation states of CeO_2 (Ce^{3+}/Ce^{4+}) associates with excellent redox properties. The interchangeable oxidation states change the valence of Ce at the surface of the particle and expedite the chemical reaction with the surrounding environment such as the membrane of the bacterial cell. Thereby, the biologically active CeO_2 nanoparticles can be developed to treat bacterial infections. The nanoparticles utilize various effective mechanisms to degrade bacteria as compared to conventional antibiotics. The treatment followed by CeO_2 nanoparticles-based antibiotics is a mechanism involving the development of the oxidative stress as addressed by Isabela, et. al. The pH value of the nanoparticles is kept low in order to preserve their acidic nature because the acidic nature of CeO_2 favours the adsorption of the nanoparticles on the cell membrane of the bacteria. During adhesion, the valence state of Ce changes and develops oxidative stress on the cell membrane. This mechanism works well in Gram-negative bacteria such as *E. coli*. However, Alpaslan et al. have shown that CeO_2 nanoparticles are more effective at higher pH values to kill bacteria.

Experimental

$Ce_{1-x}Fe_xO_{2-\delta}$, ($0 \leq x \leq 20$) NPs were prepared using a co-precipitation technique. This method requires a chemical reaction between the precursors, followed by stirring. The iron nitrate nonahydrate and cerium nitrate hexahydrate were taken as precursors. The stoichiometric amount of the salts was mixed in 50 mL de-ionized water to attain a solution of 0.04 M. The thus-obtained solution was kept stirring at room temperature. After half an hour of stirring, the ammonia solution was decanted dropwise whilst stirring the solution, until the pH level became 9. The colour of the solution changed with dopant concentration. The stirring continued for 3 h at room temperature at 5000 rpm. The stirring provided homogeneous mixing to the solution. Then, the mixture was centrifuged at 5000× *g* rpm to collect the precipitates. Finally, the precipitates were washed three times with de-ionized water and two times with ethanol and then dried at 80 °C for 12 h. The dried precipitates were collected in a pastel mortar and ground to make fine powder, which was kept in the furnace for annealing at 500 °C for 5 h.

Literature Review

Despite the apparent wide range of strains, against which nanoparticles exert the “antimicrobial” activity, their effectiveness against particular strains can be significantly different. As a rule, gram-negative bacteria are less sensitive to ZnO nanoparticles than gram-positive bacteria. Somewhat higher resistance of gram-negative bacteria can be explained by the peculiarities of their cell wall structure. In contrast to gram-positive bacteria, the cell wall of gram-negative bacteria includes the additional outer membrane containing lipopolysaccharides (LPS) . It is shown that LPS can improve the barrier properties of the outer membrane and, therefore, increase bacterial resistance, in particular, to antibiotics. Epidemiologically significant microorganisms deserve a special attention, for example, Mycobacterium tuberculosis, against which ZnO nanoparticles exert the bacteriostatic effect but not bactericidal.

On the contrary, several microorganisms (for instance, Campylobacter jejuni) have an increased sensitivity to ZnO nanoparticles, which make them a convenient model for studying molecular 126 mechanisms of the “antimicrobial” effect of nanoparticles. ZnO nanoparticles (ZnONPs) disturb the processes of bacterial DNA amplification, reduce expression of a wide range of genes of C. jejuni that are responsible for virulence, significantly alter expression of genes of oxidative and general stress . An important feature of ZnO nanoparticles used in one of the studies is the antibacterial activity against resistant bacterial strains, for example, carbapenem-resistant Acinetobacter baumannii (RS-307 and RS-6694) . The dependence of effectiveness on a bacterial growth phase was shown for ZnO nanoparticles. In particular, ZnO nanoparticles are effective against gram- negative and gram-positive bacteria at the exponential growth phase; however, the antibacterial properties of nanoparticles are significantly decreased at the lag and stationary phases. A range of bactericidal concentrations of ZnO nanoparticles is usually significantly less than a range of 4 . At present, an active search for methods to increase the “antimicrobial” action of nanoparticles is carried out. Below we present the literature search. Nanoparticles are classified by the method for synthesis, size, structure, form, absence

or presence of the envelope or nucleus. The objects, on which nanoparticles influenced, are classified by types, biological effect of nanoparticles, concentration of nanoparticles, duration of exposure, temperature and environment.

Samples Characterizations

The effect of Fe doping in host CeO_2 was studied using various characterization techniques, the XRD patterns were scanned using Philips X-pert X-ray diffractometer with radiation of wavelength ~1.5418 Å (Cu *Kα*). The particle size was calculated using Scherrer's equation. Morphological measurements were performed using FETEM (JEM 2100F) transmission electron microscope. To record the UV–visible Ocular spectra, S-4100 (SINCO Instrument Co., Seoul, Korea) photo spectrometer was used in the wavelength range of 200–800 nm at room temperature. The dielectric properties have conveyed out using Alpha-A High-Performance Frequency Analyser at room temperature in the frequency range from 1.0 Hz to 10 MHz.

Growth Kinetic Analysis and Biofilm Formation in A 96-Well Microplate

Initially, effects of interaction pattern at NPs-bacteria interface were studied by following growth kinetics of *S. aureus* in absence and presence NPs concentrations in the range between 20–50 µg/mL. Test organisms were prepared in LB broth, taking loop full of bacteria from the specified slant culture and were cultured overnight at 37 °C and 180 rpm agitation. The stock solutions were prepared by dispersing NPs in sterilized LB and were sonicated for 10 min followed by UV radiation sterilization before use. The reaction mixtures without NPs were taken as controls. Briefly, 20 µL of bacterial cultures were added to the different reaction mixtures prepared in a 96-well plate, and the reaction volumes were adjusted by LB broth with NPs. Upon addition of the NP, data collection for growth kinetic studies were immediately performed by measuring Ocular density (O.D.) at 620 nm using a plate reader (Thermo scientific Multiskan EX, REF 51118170, China) at regular time intervals. The biofilm inhibition assay was performed according to Dwivedi et al., 2014. The microtiter plates were incubated under stationary conditions at 37 °C for 3 days. At an interval of every 28 h for 3 days, the medium was discarded from each well. The wells were then treated with a 0.1% aqueous solution of crystal violet (1 mL). The solution was washed with water, and the remaining stain was solubilized with 2 mL of 95% ethanol. Biofilm inhibition was quantified by measuring the OD570 into quartz cuvette for analysis. The assays were performed in triplicate manner.

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