SYNTHESIS AND INVESTIGATION ON PHOTOCATALYTIC AND ANTIBACTERIAL ACTIVITIES OF DOUBLY DOPED ZnO AND SnO_2 PARTICLES

Synopsis of the thesis submitted to
MADURAI KAMARAJ UNIVERSITY, MADURAI
for the award of the degree of
DOCTOR OF PHILOSOPHY IN PHYSICS

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OCTOBER 2019

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SYNOPSIS

BRIEF DESCRIPTION

Development of economic and facile systems for the removal of pollutants in water is one of the greatest challenges in the field of materials research. In the modern period, the water pollution turns out to be the finest topic to discuss because of the depletion of underground water resources and the lack of managing waste water. In the recent decades water has been contaminating by the effluent pollutants from various industries. Mainly textile, leather and food industries discharge organic wastes which contaminate the water resources like rivers and ponds. These pollutants can be removed by several methods which include nanofiltration, adsorption, photocatalysis, biodegradation, electro coagulation, ozonization and chlorination. These processes have been employed to remove the water contamination problem but photocatalysis is one of the most gifted method for the treatment of water contamination. Photocatalysis is the science that uses a catalyst to speed up the chemical reaction in the presence of light. The photocatalytic activity depends on the ability of the catalyst to create electron-hole pairs. Photocatalytic reaction primarily depends on wavelength of light (photon) energy and the catalyst. In general, semiconducting metal oxide nanomaterials are used as a catalyst which belongs to the heterogenous type. Researchers are focusing more attention on the reactions that take place on the illuminating surface of semiconductor metal oxides.

The contaminated drinking water is the universal menance which produces water borne diseases. The disease causing bacteria known as pathogens present in water leads to severe problems. Antibiotics have been used in treating the bacterial infections because of their cost-effectiveness and powerful outcomes. But the metal oxide nanoparticles are being considered as an alternative to antibiotics. These NPs can effectively prevent the activity and growth of pathogens. Antibacterial agents (NPs) are very important in the textile industry, water disinfection, medicine and food packaging fields. Such improved antibacterial agents locally destroy the bacteria, without being toxic to the surroundings.

The photocatalyst and antibacterial agents found in literature are metal oxides such as TiO_2, ZnO, SnO_2 and CeO_2 which are more effective than metal sulfides and metal selenides.

Technology is creating a wealth of new micro and nanomaterials and manufacturing possibilities. Using nanotechnology, researchers and manufacturers can fabricate materials literally molecule-by-molecule. Nanotechnology is helping to considerably improve, even revolutionize, many technology and industry sectors such as medicine, transportation, energy, food safety and environmental science.

Nanoparticles are referred to as particles having atleast one dimension within the nanoscale (less than 100 nanometers). Nanomaterials exhibit extremely fascinating and strange properties which can be exploited for a wide variety of applications. Nanomaterials are exceptionally strong, hard, ductile at high temperatures and resistant to wear, erosion and corrosion.

When the size of the material is reduced to reach the micro and nanoscale regime, it will exhibit totally different properties. Nanomaterials exhibit peculiar and interesting chemical and physical properties mainly because of their larger surface to volume ratio.

The nanomaterials are classified into four main types.

- Carbon based materials
- Metal based materials
- Dendrimers
- Composites

Among these classifications, metal oxide nanomaterials play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites.

Nanostructures can be synthesized using physical and chemical methods. In both of these methods, two different approaches viz. top-down approach and bottom-up approach can be adopted. Top-down approach refers to a subtractive process in which a bulk starting material is divided into smaller ones having nanoscale. Bottom-up approach refers to an additive process that starts with precursor atoms or molecules which combine to form nanosized structure.

Doping is one of the proven techniques to obtain the nanostructured materials with tunable properties. In other words, one can desirably modify several of the properties by doping with appropriate type of dopants (cationic or anionic) or more than one dopant simultaneously. There are several methods used by researchers to prepare doubly doped nanoparticles such as co-precipitation, sol-gel, hydro thermal, combustion and wet chemical method. Of them, wet chemical route is preferred for our work as it offers several advantages like simplicity, low cost, low hazardousness, easy doping and low processing temperature.

The synthesized nanoparticles can be subjected to various characterization techniques such as XRD, FTIR, UV, Photoluminescence, SEM with EDAX, antibacterial and photocatalytic studies in order to study the material's feature. From XRD studies, the particle size and other structural properties were studied. Fourier Transform Infrared Spectroscopy (FTIR) identifies the chemical bonds in a molecule and detects the various functional groups. PL measurements were carried out to understand the surface defects and emission properties. SEM studies were carried out to analyze the morphology and size of the prepared samples. The EDAX profiles confirm the presence of the expected elements in the samples and also exhibit that they are in the respective proportions as they were in the precursor solution. The antibacterial studies were carried out by measuring the zone of inhibition around the samples by employing either the disc diffusion method or well diffusion method. The photocatalytic activity of the synthesized nanoparticles were evaluated from the degradation of the particular dye solutions under visible and near UV irradiation.

1. OBJECTIVES

The main objective of this study is to synthesize doubly doped nanoparticles using soft chemical route and characterize the synthesized sample using XRD, FTIR, PL, SEM, antibacterial and photocatalytic studies.

This work includes

(i) Synthesis and characterization of undoped, Mg or Co doped ZnO microparticles and their combinations are given here under.

ZnO
ZnO:Mg
ZnO:Co
ZnO:Mg:Co

(ii) Synthesis and characterization of pristine and (Mg+Co) doped SnO_2 nanoparticles are given here under.

SnO_2
SnO_2:Mg:Co

(iii) Synthesis and characterization of pure and (F+Mg) doped ZnO nanoparticles and their combination with different wt. % are given below.

ZnO
ZnO:F
ZnO:F:Mg (3 at. %)
ZnO:F:Mg (6 at. %)
ZnO:F:Mg (9 at. %)
ZnO:F:Mg (12 at. %)

(iv) Synthesis and characterization of pure and (F+Mg) doped SnO_2 nanoparticles and their combination with different wt. % are given below.

SnO_2
SnO_2:F
SnO_2:F:Mg (3 at. %)
SnO_2:F:Mg (6 at. %)
SnO_2:F:Mg (9 at.%)
SnO_2:F:Mg (12 at.%)

2. DESCRIPTION OF THE RESEARCH WORK

2.1 Synthesis and characterization of undoped and (Mg/Co) doped ZnO microparticles

The focus of this work is to realize ZnO microparticles with simultaneously enhanced antibacterial and magnetic properties through double cationic (Mg+Co) doping. Undoped and magnesium (Mg) + cobalt (Co) doped ZnO microparticles were synthesized using a cost-effective simple soft chemical route. Their surface morphological, magnetic, antibacterial, photocatalytic and structural properties were investigated. Antibacterial studies of the prepared samples were carried out against gram-positive and gram-negative bacteria. From the antibacterial studies, it is found that the double cationic doped ZnO microparticles exhibit superior antibacterial efficiency compared with undoped and single cationic doped ZnO microparticles. The FESEM images show that the undoped and single cationic (Mg/Co) doped ZnO particles have hexagonal block structures of micro scale dimensions whereas the double cationic doping causes the formation of hexagonal plate structures having near nano scale thickness (~150 nm), thereby increasing the effective reactive surface area. This increase in surface area leads to enhanced photocatalytic degradation of methylene blue (MB) dye molecule. The magnetization curves show that the coexistence of Mg^{2+} and Co^{2+} ions in the ZnO lattice causes a pronounced increase in the ferromagnetic behavior, already present in the undoped and single cationic doped ZnO material. The XRD, FTIR and PL results support the discussion on the antibacterial and magnetic results. The EDAX profiles and the compositional mapping images confirm the presence of expected proportions of the constituent elements and their uniform distribution in the final product. Structural studies show that the products exhibit hexagonal wurtzite structure of ZnO without any secondary phases.

2.2 Synthesis and characterization of undoped and (Mg+Co) doped SnO_2 nanoparticles

In this study, the photocatalytic activity of pristine and (Mg+Co) doped tin oxide (SnO_2) nanopowders have been investigated towards the degradation of aqueous solutions of methylene blue (MB) and malachite green (MG). In addition, the antibacterial activities of the synthesized samples were evaluated against gram-positive *S. Aureus* bacteria and gram-negative *P.Aeruginosa* bacteria by the well diffusion method. The SnO_2:Mg:Co nanopowders exhibit superior photocatalytic activity when compared with pristine SnO_2. The degradation process follows a pseudo first order kinetics. The rate constant of SnO_2:Mg:Co nanopowder is 1.2 times greater than that of pristine SnO_2 nanopowder for the degradation of MB dye while for MG dye, it is 1.5 times. Moreover, antibacterial activity of SnO_2:Mg:Co nanopowder showed better antibacterial properties compared to pristine SnO_2. The above mentioned samples were synthesized using a simple and low-cost soft chemical process.

2.3 Synthesis and characterization of pure and (F+Mg) doped ZnO nano-particles

This study focuses the effect of Mg doping level (0–12 at. % in steps of 3 at. %) on the photocatalytic efficacy of ZnO:F:Mg nanopowder synthesised using a simple cost-effective chemical method. The structural, surface morphological, photoluminescence studies were carried out for all the samples. The photocatalytic dye degradation study under visible light against the two different dyes viz methylene blue (MB) and malachite green (MG) revealed that ZnO:F:Mg nanopowder doped with 12 at. % of Mg shows superior photocatalytic activity compared to other doped and undoped samples for both the dyes examined. The degradation efficiency of undoped ZnO is found to be 65 % and 74% for MB and MG, respectively, whereas the F+ Mg co-doped ZnO nanopowder (10+12 at. %) exhibits enhanced photocatalytic activity against both the dyes and the degradation efficiency values for MB and MG are 88 % and 97%, respectively. The reasons for this enhancement are addressed appropriately with the evidences obtained from photoluminescence and X-ray diffraction studies.

2.4 Synthesis and characterization of pure and (F+Mg) doped SnO_2 nano-particles

In this work, the nanocrystalline SnO_2:F:Mg powder samples with different concentration levels of Mg (3, 6, 9 and 12 at. %) keeping the F doping level constant as 10 at. % were synthesized using a simple and cost effective soft chemical route. The influence of dopant concentration on prepared samples is investigated by different analytical techniques including X-ray diffraction (XRD), Fourier Transform Analysis (FTIR), photoluminescence (PL), Scanning Electron Microscope (SEM), antibacterial and photocatalytic studies. The XRD studies revealed that the Mg doping significantly increases the crystallinity of the doped samples. From the antibacterial and photocatalytic studies, it is observed that the efficiency of doped SnO_2 (12 at. %) are found to be increased due to (i) the presence of hydroxyl radicals and (ii) reduction in the shape and size of the particles. The presence of hydroxyl radical is evidenced by FTIR and PL studies. From the SEM images, the 12 at. % doped Mg sample shows linear flake like structures which will lead to enhance the photocatalytic and antibacterial efficiency.

III. LIST OF PAPERS PUBLISHED

1. N. Mala, K. Ravichandran, S. Pandiarajan, N. Srinivasan, B. Ravikumar, K. Catherine Siriya Pushpa, K. Swaminathan, T. Arun. *Ceramics International*. **42** (2016) 7336.

2. N. Mala, K. Ravichandran, S. Pandiarajan, N. Srinivasan, B. Ravikumar and K.Nithiyadevi, *Materials Technology. Advanced Performance Materials.* **32** (2017) 686.

3. G. Muruganandam, N. Mala, S. Pandiarajan, N. Srinivasan, R. Ramya, E. Sindhuja, K. Ravichandran, *Journal of Materials Science: Materials in Electronics*. **28** (2017) 1.

IV. CONCLUSIONS

a) ZnO, ZnO:Mg, ZnO:Co and ZnO:Mg:Co microparticles were synthesized using a facile soft chemical route. The Mg^{2+} and Co^{2+} single-doped ZnO powders exhibit enhanced antibacterial activity when compared with undoped ZnO whereas Mg^{2+}+Co^{2+} double cationic doping results in further enhancement of this property. With Mg^{2+} single doping, the ferromagnetic component exists only over a short range of lower magnetic fields whereas in the case of Co^{2+} single doping, it extends over a relatively wider range. But with double cationic doping, the ferromagnetic behavior is improved remarkably with the ferromagnetic component extending into the higher magnetic fields upto 12500 Oe. The double doping causes a drastic reduction in the grain size along the Z direction resulting in hexagonal plates thereby increasing the effective reactive surface area to interact with bacteria. This increase in surface area along with the penetration ability of the grains leads to an enhancement in the antibacterial efficiency and photocatalytic activity. The enhancements in the antibacterial and magnetic behaviors make the Mg^{2+}+Co^{2+} double-doped ZnO powder, a potential candidate for targeted drug delivery systems.

b) Pristine and (Mg+Co) doped SnO_2 nanoparticles have been successfully synthesized by wet chemical route. The doped samples showed better photocatalytic activity for MG and MB dye degradation compared to the pristine SnO_2 sample. The enhanced antibacterial property for the doped nanoparticles may be due to the increase in surface area. The presence of hydroxyl ions (confirmed by FTIR and PL studies) is mainly responsible for the enhanced photocatalytic and antibacterial activities. The degradation rate constant of MB dye for undoped SnO_2 is 0.0401 min^{-1}. It increases 1.2 times for Mg+Co doped SnO_2. Similarly in the case of MG dye the rate constant increases 1.5 times due to doping. From the excellent photocatalytic and antibacterial properties of the doped samples, it is predicted that the (Mg+Co) doped

SnO_2 nanoparticles can be used as an efficient material for purification of dye contamination in water.

c) Among the undoped, F doped and (F+Mg) doped ZnO nanoparticles, Mg doped ZnO nanopowders show better photocatalytic activity compared to the others. Of the Mg doped ZnO samples, the one with the highest Mg doping (12 at. %) exhibits the highest dye degradation efficiency. The reason for this enhanced photocatalytic efficacy may be due to the smaller crystallite size, higher defect states and increased number of oxygen vacancies present in that case. The degradation efficiency of undoped ZnO is found to be 65 % and 74 % for MB and MG respectively whereas the F+Mg co-doped ZnO nanopowder exhibits enhanced photocatalytic activity against both the dyes and the degradation efficiency values for MB and MG are 88 % and 97 % respectively. The structural studies confirm the hexagonal wurzite structure of ZnO in all the prepared samples. F and Mg incorporation does not alter the structure of ZnO. The photoluminescence study confirms the presence of larger number of singly ionized oxygen vacancies in the co-doped samples which can generate more number of hydroxyl radicals mainly responsible for the photocatalytic activity of the material.

d) Pure, F doped and (F+Mg) doped SnO_2 powder samples with different concentration levels of Mg were synthesized using a simple soft chemical route. From the results obtained in this study, it is found that simultaneous addition of a cationic (Mg+) and an anionic (F^-) dopant into SnO_2 can result in the modification of surface morphology and certain antibacterial and photocatalytic dye degradation activities. The (F +Mg) doped SnO_2 with 12 at. % of Mg doping shows different morphology and smaller size particles with high reactive surface area which make it a good candidate for antibacterial activity. Similarly, the same with 12 at. % doping of Mg exhibits 90% of dye degradation in 75 min making it a good photocatalyst.

The results obtained from all the four parts of the study show that by employing simple soft chemical route procedure incorporating suitable dopants, one can prepare micro and nanomaterials suitable for photocatalytic and antibacterial applications.