

Preparation, Properties and Applications of Chemically Synthesized Semiconducting Nanostructures

ABSTRACT

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Gaurav Hitkari

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Under the Supervision of

Prof. Gajanan Pandey

DEPARTMENT OF APPLIED CHEMISTRY
SCHOOL FOR PHYSICAL SCIENCES
BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
VIDYA VIHAR, RAE BARELI ROAD, LUCKNOW-226 025

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Abstract

Nanotechnology and nanoscience is a newly advanced prospective area to import welfares to various fields of investigation and application in the world of sciences. The significance means of prefix “nano” is one billionth. The scaling of nanometer is equivalent to a billionth of a meter scale, or 10^{-9} part of a meter which implies that these structures are extremely small (e.g: there is an inch equal to 25,400,000 nanometers or a single sheet of newspaper is nearly 100,000 nanometers thick or ten thousand times lesser compare to the width of a human hair).

Nanostructures are any shape and size of the intermediate structure at a microscopic or molecular level which may have one or more dimensions in the range of 100 nm or less. Nanostructures have various commercial and scientific application in areas like drug delivery, analytical chemistry, bio-encapsulation, electronics, magnetics, optical and mechanical devices.

In the modern area of nanotechnology, there are numerous kind of nanostructures such as zero-dimensional (0-D) e.g. quantum dot, fullerene, one dimensional nanostructure (1-D) e.g. nanotubes, nanorods/wires/tubes, two dimensional (2-D) e.g. graphene and three dimensional (3-D) e.g. graphite has fascinated the terrific attention due to their high aspect ratio and fascinating properties. There is various type of method are employed for the fabrication of different type of nanostructure and nanocomposite materials. Among the synthetic process, the chemical method is the most common approach for the synthesis of nanoparticles and composite materials due to high-purity, high functioning, low cost and easy availability.

The commercial use of synthetic dyestuffs in various industries like paper, textile, plastic leather, printing, and food industries. Among the numerous dyestuffs,

most are synthetic organic dyes of an azo compound such as congo red (CR), methyl orange (MO), and methylene blue (MB) which comprise chromophore (-N=N-) in their molecular composition. Water contamination with these azo dye is one of the major consequences which continuously causing increasing threats to terrestrial as well as aquatic life.

Over the past two decades, a great deal of research efforts has been made towards the development of nanostructures/nanoparticles for the practical applications in the removal of organic dye-stuff from the waste-water to continuous environmental monitoring.

The whole research work is divided into seven chapters. First chapter comprises the general introduction of nanomaterial's and nanostructures containing preparation methods including physical, chemical and biological methods. The exhaustive literature review on the topic and the objective of the present work have been discussed. This chapter also containing the general characteristics and applications of nanostructure/nanoparticles and the effect of it shape, size and orientations.

In the second chapter the various instrumentation technique is discussed for identification of prepared nanoparticles and nanostructured materials.

In the third chapter, zinc oxide (ZnO) and ZnO-ZnS nanocomposite materials have been prepared by simple chemical co-precipitation method. The X-ray diffraction analysis revealed the formation of ZnO and ZnO-ZnS crystalline materials. FESEM and HRTEM analyses indicated the formation of flake-like ZnO and sheet-like ZnO-ZnS structures. Energy dispersive X-ray (EDS) study further established the formation of ZnO and ZnO-ZnS materials. In the FTIR spectrum the presence of Zn-O symmetric stretching vibration at 442 cm^{-1} and 809 cm^{-1} , due to weak vibration of

ZnO, while the other peak at 687 cm^{-1} due to Zn-S symmetric bending vibration proved the formation of ZnO-ZnS composite material. Optical absorption spectrum showed that the band gap energy decreased for ZnO-ZnS composite compared to the pure ZnO NPs. The photoluminescence spectral analysis shows that the broad emissions spectrum caused due to several different bands, owing to the presence of zinc vacancies, oxygen vacancies, and surface defects. The photocatalytic performance of these samples was tested for degradation of a dye methylene blue under UV light exposure. ZnS-ZnO composite shows the higher dye degradation efficiency (93 %) than that of pure ZnO (55 %).

In the fourth chapter, ZnO, and ZnO/CuO nanocomposites have synthesized by simple chemical co-precipitation method through calcination at $400\text{ }^{\circ}\text{C}$ for 4hrs. Prepared nanocomposite samples were appraised by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM), Brunauer-Emmett Teller analysis (BET), and UV-visible spectroscopy. From the XRD analysis, it's proved that the forming of crystalline nanocomposites material while magnified SEM images showed that single hexagonal structural of pure ZnO and agglomeration of grain like structure of ZnO/CuO composite by calcination on $400\text{ }^{\circ}\text{C}$. HRTEM investigation proves that hexagonal structure of pure ZnO is obtained by aggregation of the knife-like structure. BET analysis accepted that the mesoporous nature of nanocomposites. UV-Visible spectra have been also discussed the optical behaviour of the materials. The photocatalytic operation of the fabricated materials, ZnO and ZnO/CuO composite was well-established for the photo-degradation of Congo red (CR) organic waste in aqueous phase under irradiation of visible light. The ZnO/CuO composite shown better photocatalytic activity for decolourization of CR dye.

In the fifth chapter, ZnO/ γ -Fe₂O₃ nanocomposites are prepared by the simple co-precipitation method. The prepared composites materials were characterized by X-ray diffraction (XRD), high resolution scanning electron microscope (HRSEM), energy dispersive X-ray spectroscopy (EDX), Brunauer Emmett Teller analysis (BET), and UV-visible spectroscopy. XRD confirmed the formation of hexagonal wurtzite nature of ZnO and cubic structure of γ -Fe₃O₄ in the composite materials, while SEM images showed spherical and rod-like structure. BET analysis confirmed the mesoporous behavior of nanocomposites. UV-Visible spectroscopy has been applied to the measurement of band gap and photo-oxidation behavior of organic dye methyl blue and rhodamine B (Rh B). Experimental data suggested that ZnO/ γ -Fe₂O₃ nanoparticles catalyst possessed the highest catalytic activity towards Rh-B degradation in aqueous solution as comparison to the methylene blue at the tested concentration level of 1×10^{-5} M.

In the sixth chapter, achieve effective, economic, and easily synthesizable photocatalyst like as ZnO, ZnO/ZnS and ZnO/ZnS/ α -Fe₂O₃ nanocomposites have been prepared by a simple chemical synthetic route in the aqueous medium for the degradation of dye methyl orange (MeO). Phase, crystallinity, surface structure and surface behavior of the synthesized materials have been determined by X-ray diffraction (XRD) and Brunauer Emmett Teller analysis (BET) technique. XRD revealed that ZnO, ZnO/ZnS and ZnO/ZnS/ α -Fe₂O₃ are good crystalline and in nano-region. From the XRD patterned the percentage composition of photocatalyst have also been determined. From the BET analysis, the prepared materials show mesoporous behavior containing type IV curves along with H4 hysteresis. The ZnO/ZnS/ α -Fe₂O₃ composite sample shows more surface area as comparison to the other materials. From the UV-visible spectra, the band gap energy of the materials has

been determined. Photoluminescence spectra (PL) have been used to determine the emission behavior and explanation of the surface defect present on the surface of the composites materials. In PL spectra the intensity of UV peak of ZnO/ZnS is lowered than ZnO while in case of ZnO/ZnS/ α -Fe₂O₃, the intensity become further decreased. The visible emission spectra of ZnO/ZnS is increases as comparison to ZnO NPs where ZnO/ZnS/ α -Fe₂O₃ is further increases from ZnO/ZnS. The lowering of the intensity of UV emission peak and increases of the intensity of visible emission is the resultant of decrease of recombination of electrons and holes which indicates the enhanced the rate of photocatalytic reaction. The as-synthesized composite materials have been used for the photocatalyst for degradation of dye MeO. The photo-degradation data revealed that the ZnO/ZnS/ α -Fe₂O₃ is the best photocatalyst material among these materials for the degradation of dye MeO. In the present work, ZnO, ZnO/ZnS and ZnO/ZnS/ α -Fe₂O₃ nanocomposites have been synthesized via simple chemical co-precipitation followed by calcination at 600 °C for 1/2 h. Nanocomposite powders were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), particle size distribution, Brunauer Emmett Teller analysis (BET), photoluminescence and UV-visible spectroscopy. XRD confirmed the formation of crystalline nanocomposites while SEM images shown sheet-like ZnO and ZnO/ZnS and needle-like acicular ZnO/ZnS/ α -Fe₂O₃ nanocomposite. BET analysis confirmed the mesoporous behavior of nanocomposites. Optical properties and band gap energy of as-synthesized materials were determined using UV-Visible spectral analysis. Photoluminescence spectra have been used to determine emission properties and photo-oxidation behavior of as-synthesized materials for degradation of methyl orange. ZnO/ZnS/ α -Fe₂O₃

nanocomposite exhibited the highest photocatalytic activity among the three samples for degradation of methyl orange (MeO).

In the last seventh chapter, summary and conclusion of all the work has been discussed.
