COMPARATIVE STUDY ON THE PHOTOCATALYTIC EFFICIENCY OF ZNO-BASED NANOMATERIALS FOR WATER PURIFICATION

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ABSTRACT

The rapid increase in environmental pollution caused by industrial effluents and organic contaminants necessitates the development of efficient and sustainable remediation strategies. In this study, novel ZnO-based nanomaterials were synthesized and systematically characterized to explore their structural, morphological, optical, and surface properties. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier-transform infrared spectroscopy (FTIR) were employed to confirm the crystalline structure, particle size distribution, surface morphology, and chemical functionalities of the prepared nanomaterials. Optical properties were examined using UV–Vis diffuse reflectance spectroscopy (DRS) and photoluminescence (PL) analysis to evaluate the band gap and electron–hole recombination behavior. The photocatalytic activity of the synthesized ZnO nanomaterials was assessed under UV and visible light irradiation using model organic pollutants such as methylene blue and rhodamine B. The results demonstrated enhanced degradation efficiency, attributed to improved charge separation, high surface area, and synergistic effects of surface modifications and dopants.

Keywords: *ZnO-based nanomaterials, X-ray diffraction (XRD), crystalline structure, scanning electron microscopy (SEM).*

INTRODUCTION

On one hand, as a multifunctional material, ZnO possesses unique outstanding properties, such as a wide direct band gap; high electron mobility; piezoelectric, antibacterial, photocatalytic, and thermoelectric properties; as well as chemical and thermal stability and biocompatibility. On the other hand, ZnO nanomaterials can be obtained using easy and low-cost growth techniques including green synthesis methods, with easy morphological control altering seed layer composition and/or varying growth conditions. It should be emphasized that ZnO nanostructures can be doped to enhance different physical and chemical properties. These assets make nanostructured ZnO one of the most fascinating nanomaterials, leading to the development of many promising applications around the ZnO nanostructures, as presented in this Special Issue. Knowing that the properties are closely related to the nanostructures, the study of nanostructures' growth mechanism is important for the desired material properties and the targeted applications. In the case of the widely used classical two-step sol-gel hydrothermal method for ZnO nano array growth, the morphology of nano arrays, such as the number density of the nanorods array and the diameter of nanorods, is often tuned by changing the composition ratio of the seed solution.

LITERATURE REVIEW

Hynda Rezzaz-Yazid (2025) This study compares ZnO nanoparticles (NPs) synthesized via eco-friendly coprecipitation (ZnOE) using cactus juice and chemical coprecipitation (ZnOC). The optical band gap of ZnO nanoparticles, calculated from the diffuse reflectance, was observed to be 3.2 eV for ZnOC and 3.14 eV for ZnOE, respectively. SEM and EDX analyses were conducted for further investigation. Both ZnOE and ZnOC were applied to the photocatalytic degradation of Basic Yellow 28 textile dye (BY28) under solar and artificial UV light. ZnOE exhibited superior photocatalytic performance in removing BY28 compared to ZnOC under both irradiation sources. Under optimal conditions (1 g L^{-1} semiconductor, 10 mg/L BY28), ZnOE showed superior degradation rates: 100 % and 94.71 % under solar and UV light, respectively (rate constants: 0.0169 min^{-1} and 0.0127 min^{-1}). ZnOC achieved 73.68 % and 42.61 % degradation under solar and UV light (rate constants: 0.007 min^{-1} and 0.0037 min^{-1}). The treated BY28 solution demonstrated improved biodegradability and no phytotoxicity, indicating its environmental safety.

B. Gopalakrishnan (2023) In this study, an integral treatment consisted of UV/Fenton/ TiO_2 system in the batch systems was developed to perform degradation of synthetic Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX). Initially, the efficiency of photo Fenton catalytic degradation was compared with conventional treatment methods. Later, optimum levels of selected variables such as the initial concentration of BTEX, pH, temperature, reaction time, and initial dosage of TiO_2 were analyzed using one factor at a time method. Further, screening of variables and optimization were performed using Planckett-Burman design and central composite design, respectively. Finally, first-order kinetic model resulted in prediction of 19.43 kJ/mol of activation energy. Thus, process optimization and kinetic study using the developed photo Fenton catalytic system could be beneficial for real time waste containing BTEX pollutants.

Jamal Al-Fadhli (2022) In recent years, the oil market has witnessed high volatility due to unstable demand and supply. Considering the price volatility and stricter environmental regulations, there is a possibility of a decline in the demand for transportation fuels, which will force refiners to explore alternate ways to improve the yield of high-value products, to keep their margins high. The emerging virgin crude-to-chemicals (CTC) technology can provide an opportunity for integrating operational refineries with chemicals. The integration of refining with the production of high value-petrochemicals can lead to a framework that will add value to both sectors (upstream and downstream). Integration has been proven to be environmentally driven by utilizing various refinery waste and by-products. The importance of thermal and catalytic processes in the integrated refinery is high, particularly the process of integrated gasification combined cycle (IGCC) that generates electricity and by-product as a feedstock for chemicals.

H. Cengiz Yatmaz (2017) In this study, the degradation of high concentrated azo dye solutions was investigated by innovative hybrid process of hydrodynamic cavitation (HC) and photocatalysis in a pilot reactor. HC, photocatalytic, HC + UV and HC + photocatalytic processes were studied for decolorization of RR180 dye solutions. HC + photocatalysis together showed better mineralization at 5 bar of inlet pressure compared to stand-alone HC and photocatalysis. Synergetic coefficients were calculated for COD and TOC removal as 1.48 and 1.17, respectively. Different catalyst loading (0.5–1.5 g/L) was also investigated and 1 g/L of ZnO was found as an optimal loading amount. Increasing initial RR180 dye concentration resulted in decreasing degradation efficiency. Additionally, degradation of different azo dye solutions with two different chemical structures (reactive and direct dyes) was examined with optimum conditions. Tandem operating of hydrodynamic cavitation and photocatalytic processes was efficiently exposed for the treatment of recalcitrant textile dye effluents.

Parag R. Gogate (2016) The degradation of 4-chloro 2-aminophenol ($4C_2AP$), an acute toxic organic compound, has been studied using different approaches based on the hydrodynamic cavitation (HC) with orifice plate as cavitating device, photolysis (UV) and ozonation (O_3). The dependency of extent of degradation on operating parameters like operating pressure (2–5 bar), initial pH (3–8) and temperature (30–38°C) have been established initially to maximize the efficacy of hydrodynamic cavitation. Subsequently the degradation has been studied using combined treatment strategies as HC + UV, HC + O_3, UV + O_3 and HC + UV + O_3 at the established optimum parameters of operating temperature as 30 °C, initial pH of 6 and inlet pressure of 4 bar. The maximum extent of degradation as 96.85% and 73.6% reduction in TOC has been obtained using hydrodynamic cavitation in combination with UV photolysis and ozonation under the optimized operating conditions. The degradation products of $4C_2AP$ have been identified using GC–MS. The present work has clearly established the efficacy of combined treatment approach (HC + UV + O_3) for the removal of organic pollutant for the first time.

Photocatalysis

A large number of nano catalysed reactions are driven by thermal energy. As an alternative to this, light energy in the form of photons may also be used to activate the catalysts and drive the reaction to completion. Such nano catalytic materials which are activated on light (in the UV or visible regions) irradiation are termed as photo catalysts. A photo catalyst is thus a material that has the ability to absorb light which is responsible for the production of electron-hole pairs that facilitate the reactant molecules to undergo chemical transformations. At the end of each reaction cycle the original chemical composition of the catalytic material is restored. Nano photo catalysts find wider applications in the field of environmental remediation for example, the removal of toxic organic and inorganic contaminants from industrial wastewater, energy conversion and organic transformation reactions.

Environmental photocatalysis

Semiconductor photocatalysis finds extensive application in the field of environmental remediation. The electron-hole pair production that occurs when a semiconductor material is irradiated with light of a suitable wavelength is responsible for the production of highly reactive free radicals in solution such hydroxyl radicals (•OH), superoxide radical anions O_2-. These free radicals are powerful oxidizing agents. They can initiate a series of chemical reactions resulting in the oxidation of a wide spectrum of organic pollutants present in the solution breaking them down to smaller, less toxic compounds.

Synthesis of nanomaterials

A large number of synthetic methods are available for the development of nanomaterials with specific size, shape, structure and dimensionality. They are generally classified into two categories, viz., Top-Down and Bottom-Up approaches.

Top-Down Approach

This approach involves preparation of nanoparticles by the mechanical breaking down of larger bulk materials into nanoparticles. The force used to miniaturize the bulk materials can be controlled in order to obtain nanoparticles of desired structure and dimension. However, this process is generally slow and expensive. Various synthetic methods come under this category such as lithography (photo ion beam, electron beam and X-ray), etching, grinding, attrition or ball milling, etc. Some of the commonly employed top-down synthetic methods are discussed below in detail.

Lithography

Lithography is a commonly used top-down techniques in the synthesis of nanostructures with specific patterns. In this technique, desired patterns are deposited, etched or written onto a surface in the nanoscale dimensions. Based on the required minimum size of the nanostructures, light (optical or photolithography), electrons (e- beam lithography), ions (i-beam lithography) or X-rays (X-ray lithography) may be employed for patterning. Lithography has been used in the synthesis of several nanomaterials for example highly symmetrical ZnO nanowires, arrays of TiO_2 nanoparticles, surface cluster arrays of silver nanoparticles, well-defined silicon nanostructures, sub-10 nm graphene nano ribbons.

Ball milling or attrition

This top-down method is based on the principle of attrition. The precursor material in the bulk form is taken in a rotating stainless-steel mill chamber and is subjected to high energy collision with silicon carbide balls. Due to the mechanical force, the bulk materials get crushed and undergo size reduction, resulting in the formation of nano powders of uniform size. Examples of nanomaterials synthesized by ball milling include ZnO, TiO_2, nitrogen doped TiO_2, SnO_2/TiO_2 composite photocatalyst, WO_3/TiO_2 composite photo catalyst.

Sol-Gel method

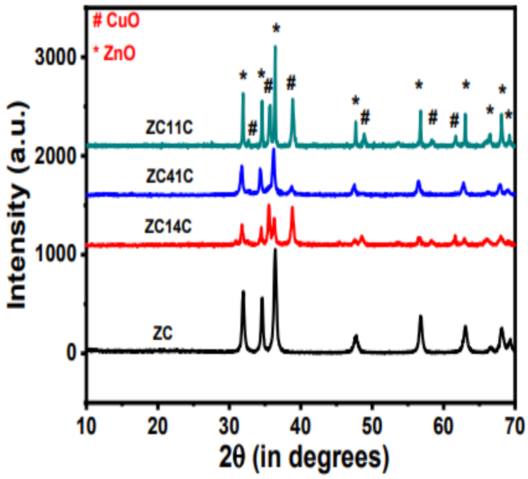
The sol-gel method is generally employed to synthesize nanostructured metal oxides and is a liquid phase synthesis method. Here, the precursors (metal alkoxides) are dissolved in a suitable solvent and are first transformed to a sol and subsequently they form a networked structure called gel. The hydrolysis of the alkoxides is responsible for the formation of the sol which on polycondensation yield metal-oxide-metal or metal-hydroxide-metal bonds. On aging, further condensation occurs within the gel and the dried gel is then calcinated at elevated temperatures, resulting in metal oxide nanoparticles. The sol-gel method has been employed widely in the synthesis of various nanoparticles such as mesoporous TiO_2, ZnO quantum dots, SnO_2, Nickel Ferrite nanoparticles

RESEARCH METHODOLOGY

Enhanced characteristics across multiple domains, particularly in terms of photocatalytic degradation efficiency. Moreover, the composition of the ZnO/CuO composite plays a crucial role in determining its efficiency, and researchers continue to explore and optimize different compositions to further improve the performance of the ZnO/CuO composite for practical applications. The synthesized nanocomposites are characterized by XRD, SEM, EDX, FTIR, UV-Visible absorbance and PL spectroscopy. The photocatalytic activities of the synthesized materials are investigated for the degradation of MG dye under UV-light illumination. The effect of various operational parameters (catalyst load; initial dye concentration; pH of the dye solution) is investigated for obtaining an optimum photodegradation efficiency. The effect of various scavengers for MG dye degradation under optimized conditions are investigated to identify the major reactive species responsible for photodegradation process. The photo stability of the photo catalyst is studied by performing the reusability test under the optimized condition. The analytical grade, zinc nitrate tetrahydrate ($ZnNO_3.4H2O$) and copper chloride dihydrate ($CuCl_2.2H_2O$) were procured from Merck and used without further purification. Sodium Hydroxide (NaOH) procured from Merck were used as precipitating agent for the preparation of pure ZnO and ZnO/CuO composites.

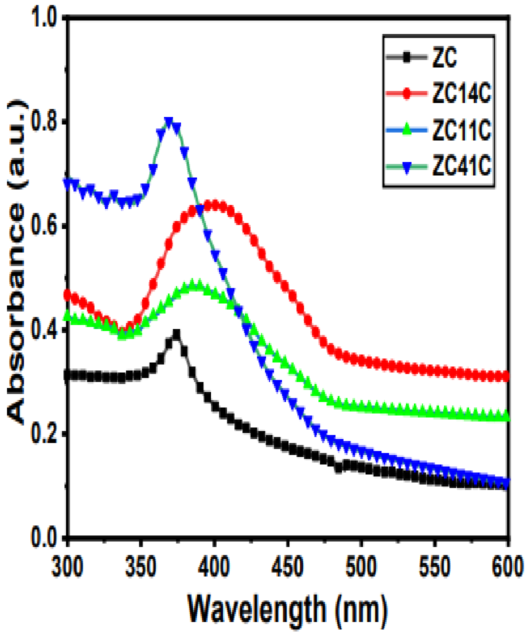
RESULTS AND DISCUSSIONS

The study on the photocatalytic activity of the synthesized samples was carried out undergoing the same procedures as described in section 2.5



Graph 1: XRD pattern of ZnO and ZnO/CuO composites

In a typical process, the catalyst loading, initial dye concentration and initial pH of the MG dye solution were 0.2g/L, 10ppm and neutral MG dye solution, respectively. Graph 1. shows the XRD pattern of pure ZnO and ZnO/CuO composite with different ratio (4:1, 1:1 and 1:4). Major diffraction peaks indicated by * correspond to the hexagonal wurtzite structure of ZnO (ICSD reference code: 01-079-0205) and those indicated by # correspond to monoclinic structure of CuO (ICSD reference code: 03- 065-2309). The intensity of the peak corresponding to the CuO phase increases when the concentration of CuO increases.

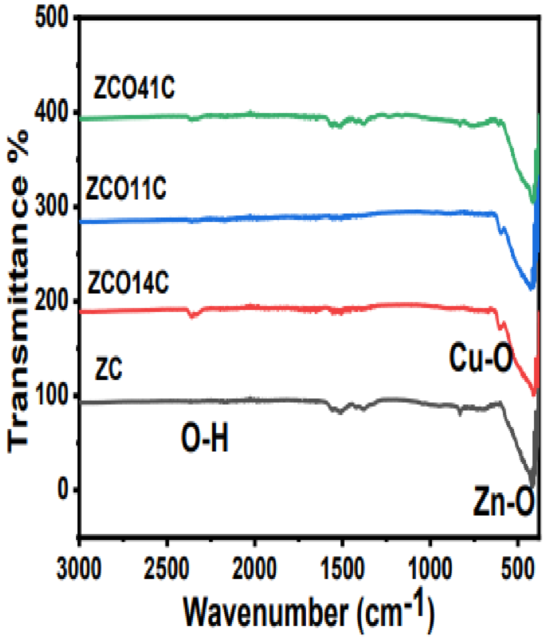


Graph 2: UV-Visible absorbance spectra of ZnO/CuO (4:1, 1:1 and 1:4) composites

As seen from the absorbance spectra of ZnO/CuO with ratios 1:1 and 1:4 composite, it is observed that when the amount of CuO increases, the absorption peak is shifted towards the visible region. This can be attributed to the narrow band gap of CuO which has a potential to red shift the absorption spectrum. This result suggests that visible light source can be effectively used for irradiation for the study of photocatalytic activity of these two compositions.

Fourier Transform Infra-Red spectroscopy

FTIR spectroscopy technique is mainly used for confirmation of the presence of functional groups in the sample. FTIR spectra of pure ZnO and ZnO/CuO composites are shown in Graph 3. The spectra are reported in the wavenumber range 400 $-3000cm^{-1}$. The peak at ~$416cm^{-1}$ is attributed to Zn − O and with the incorporation of CuO, the peak of Zn − O is slightly shifted. The peak at ~$596cm^{-1}$ is attributed to Cu − O bond which confirmed the formation of ZnO/CuO composites.



Graph 3: FTIR spectra of ZnO and ZnO/CuO composites

The peak at ~$2362cm^{-1}$ might be attributed to CO_2 adsorbed on the sample during sample preparation for FTIR analysis process. The absence of other peaks revealed the purity of the samples synthesized.

CONCLUSIONS

In this study, novel ZnO-based nanomaterials were successfully synthesized and systematically characterized to understand their structural, morphological, and optical properties in relation to photocatalytic performance. The results confirmed that controlled modification of ZnO, through surface engineering and suitable dopants, enhanced light absorption, reduced electron–hole recombination, and improved surface reactivity. Photocatalytic evaluation using organic dye pollutants demonstrated significant degradation efficiency under UV and visible light irradiation, following pseudo-first-order kinetics. Furthermore, the stability and recyclability tests established the robustness of the prepared nanomaterials, highlighting their potential for repeated use in wastewater treatment. Overall, the findings indicate that ZnO-based nanomaterials are promising, cost-effective, and eco-friendly photocatalysts for environmental remediation. Their ability to achieve efficient degradation of organic contaminants makes them highly suitable for applications in wastewater treatment and pollution control. Future research may focus on optimizing synthesis parameters, exploring heterojunctions with other semiconductors, and extending the evaluation to real industrial effluents to further enhance their practical applicability.

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