Morphological influence of ZnO nanostructures and Cu loading for the photodegradation of methyl parathion

A

Thesis submitted

In partial fulfillment of the requirements for the degree of

MASTERS OF SCIENCE

in

CHEMISTRY

Submitted By

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UNDER THE SUPERVISION OF

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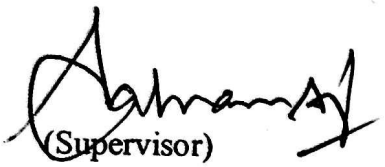
THAPAR UNIVERSITY, PATIALA-147004

July, 2017

Certificate

This is to certify that the thesis entitled **"Morphological influence of ZnO nanostructures and Cu loading for the photodegradation of methyl parathion"** being submitted by **Ms. Satinder Kaur** in partial fulfillment of the requirements for the award of degree of Master of Science in Chemistry to the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out by her under my supervision. The contents of this thesis have not been submitted for the award of any other degree or diploma.



(Supervisor)

Dr. Satnam Singh

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Candidate's Declaration

I hereby declare that the work being presented in the thesis entitled **"Morphological influence of ZnO nanostructures and Cu loading for the photodegradation of methyl parathion"** in partial fulfillment of the requirements for the award of degree of Master of Science in Chemistry, and being submitted to School of Chemistry & Biochemistry, Thapar University, Patiala, is my own work during the period of January to July 2017, under the supervision of Dr. Satnam Singh. I have not submitted the contents embodied in this thesis for the award of any other degree.

Date: 14/07/2017

Place: Patiala

(Satinder Kaur)

This is to certify the above statement made by Ms. Satinder Kaur is correct and true to the best of my knowledge.

(Supervisor)

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Satinder Kaur

Place: Patiala

Satinder Kaur

List of content

List of abbreviations

˚C	Degree Celsius
%	Percent
G	Grams
Mg	Milligram
CB	Conduction band
VB	Valance band
μ	Micro
Nm	Nanometer
SEM	Scanning electron microscope
NP	Nanoparticles
NR	Nanorods like structure
NS	Nanospheres like structure
NF	Nanoflowers like structure
Ppm	Particles per million

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Abstract

Pesticides accumulation in ecosystem becomes a major concern that causes many health problems. Zinc oxide is a promising photocatalyst for the degradation of pesticides and dyes because of its high stability, low cost and low toxicity. Different shapes of ZnO nanoparticles were prepared and loaded with Cu^{2+} ions. These materials were characterized by XRD, SEM, EDS and diffuse spectroscopy. The photocatalytic degradation of methyl parathion, an organophosphorus pesticide is investigated by different shapes of ZnO and by Cu loaded ZnO nanoparticles. ZnO nanorods gave better catalytic activity than other shapes because of it elongated morphology and with Cu loading its activity is further enhanced. Moreover, among different shapes of the nanocomposites, nanorods exhibited the highest catalytic activity for the photooxidation for methyl parathion (98%) into CO_2 and H_2O.

Introduction

The chemical species which increases or decreases the rate of reaction by association or dissociation of chemical bonds of reactants is known as catalyst.[1] In chemical industry, roughly 90% of the products made by the use of catalytic processes. The term "catalysis" was first discovered by chemist Elizabeth Fulhame which was later used by Berzelius in 1835 to identify a new species capable of promoting the chemical reaction by "catalytic contact", the catalyst was seen as a specie that was added to reaction mixture to increase the rate of the reaction without being produced or consumed.[2] From many centuries, catalystic technology has been used like in production of wine by enzyme as catalysts and making of soaps by inorganic catalyst. In 1875, platinum catalyst used for the production of H_2SO_4 on large scale. Various materials like clays, silica and many metal oxides like TiO_2, ZnO, CdS, WO_3, SnO_2, ZnS, CdTe, etc. all have been used as catalyst in nanoscale from many years. But the correct explanation of marvelous catalytic behavior of nanoparticles (NP) still has not been fully understood, may be a reasonable explanation of marvelous catalytic activity is large surface area of NP which directly increase reaction rate. Different morphologies formed are based on the properties of any materials at its nanoscale size which also effect catalytic activity of a material.[3-7] According to thermodynamic, chemical entity which enhance the rate the of attainment of equilibrium but itself remain unchanged is called the catalyst and such reactions are known as catalytic reaction. A catalyst provides different mechanisms which include an alternative transition state which lower the activation energy of reaction than uncatalyzed reactions.

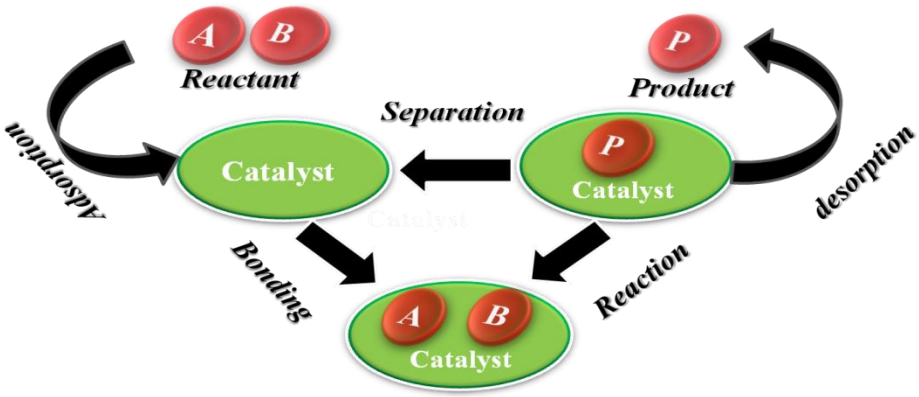
Catalysis plays an essential role in chemical reactions and it is heart of numerous chemical protocols, from academic research to industrial level.[8] Catalysis has great importance because it affects our daily life. Main sectors of the world economy like energy production, polymer production, chemicals production, pollution control and food industry, involve catalytic processes. In pharmaceutical industries for drug production which save lives and cure many health problems, many a time catalysts are used for fast and better yield. Catalysis contribute the method by which chemical transformations take place that enabling the commercially sufficient formation of desired materials. By the use of catalysts we get more sustainable, green and cost-effective methods.[9]

There are two types of catalytic reactions: Heterogeneous and Homogeneous .When phase of catalyst and reactant used in reaction is same, such reactions are known as homogeneous catalytic reactions. Generally, in these reactions all the reactants/catalysts are either in liquid phase or gas phase. For most industrial processes, homogeneous catalyst used in liquid phase for most industrial processes.[10]

When reactant and catalyst used in reaction are in different phase then such reaction is known as heterogeneous catalytic reaction. It is believed that the whole outer surface of catalysts does not take part in catalytic reaction. Only certain sites on the surface take part in reaction which is known as active sites on the catalysts. Adsorbed reactant atoms or molecules interact with these sites. Catalytic activities depend upon number of active sites present on catalytic surface which is expressed in term as turnover frequency. Turnover frequency means the number of molecules reacting per active site per second at condition of the reaction.

In a heterogeneous catalytic reaction, reactant to product goes through the following steps:

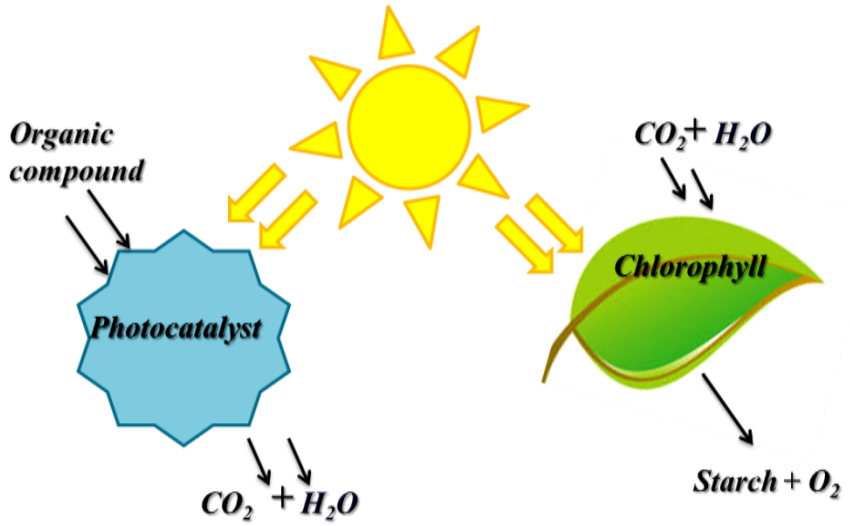
1. Transfer of reactant (R) from bulk fluid to catalytic surface
2. Reactant (R) diffusion to internal catalytic surface
3. Reactant (R) adsorbed on catalytic surface
4. Reactant (R) react on the catalytic surface to produce product
5. Product (P) desorbed from the surface of catalyst.



Scheme 1: Schematic representation of reaction process over the catalyst surface

Photocatalysis

The word "photocatalysis" came from Greek origin and composes of two words, the prefix "photo" means light and the word "catalysis" means is change the speed of the reaction.. Chlorophyll is one of natural occurring photocatalyst. The difference between chlorophyll to man-made photocatalyst is that chlorophyll absorbs sunlight to convert water and CO_2 to O_2 and glucose, but photocatalyst creates holes and electrons which break the large organic molecules to CO_2 and water in the presence of light and water as shown in scheme.2. Heterogeneous photocatalysis includes several reactions such as dehydrogenation, mild/total oxidation and transfer of hydrogen, removal of gaseous pollutant, water detoxification, deuterium-alkane isotopic exchange and degradation of organic pollutants. Heterogeneous photocatalysis is a technique, which is valuable for environmental and energy purposes. Heterogenous catalysts have many advantages because they are cheap, non-toxic, reusable and easy to separate from reaction mixture. Some common semiconductors used as photocatalysts are: TiO_2, ZnO, CdS, WO_3, SnO_2, ZnS, CdTe, α-Fe_2O_3, $AgNbO_3$ and $SrTiO_3$.[11]



Scheme 2: Photocatalysis process (Photosynthesis v/s Semiconductor)

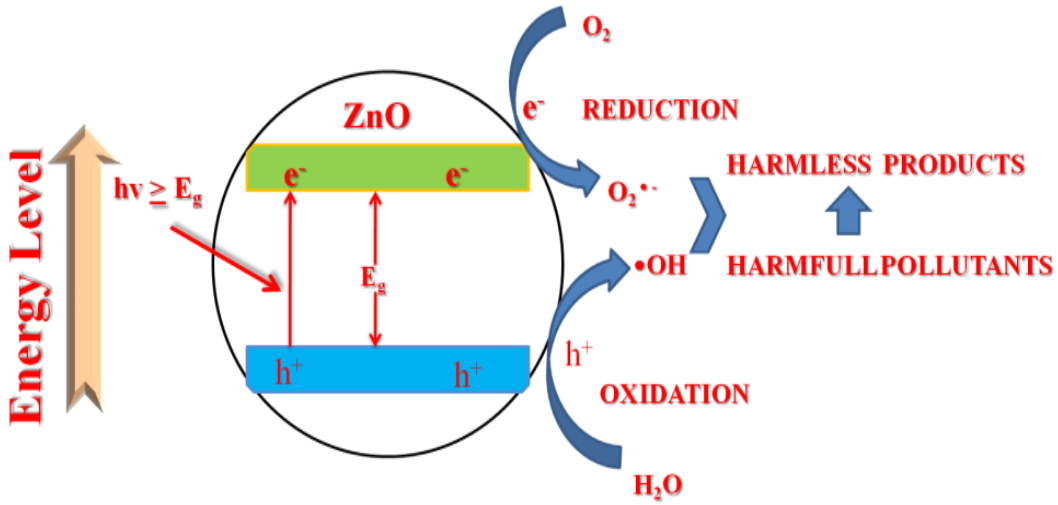
ZnO as Photocatalyst

Wurtzite phase of ZnO is mostly used as a photocatalysts. ZnO is believed to be more efficient then TiO_2 due to its high quantum yield in many cases.[12,13] Nanostructures of ZnO semiconductor have large bandgap E_g = 3.37 eV, therefore they suffers from intrinsic limitation

which is responsible for only 4% absorption of the UV light of solar energy.[14] ZnO is a II-V oxide semiconductor having excitation binding energy about 60 meV and bandgap of 3.37 eV.[15] ZnO NP (nanoparticles) are widely used for electronic and optoelectronic applications which includes LEDs, field-emission devices, solar cells, ultra-violet laser diodes, photocatalysts, spintronic and also for piezoelectronic devices because of its good piezoelectric properties, optoelectronic properties, biocompatibility, thermal stability and environmentally friendly nature.[16,17] There are many reports that describes progress in expansion and applications of various ZnO nanostructures. Rock-salt and zinc-blends are different structures of ZnO, but wurtzite structure being thermodynamically more stable.[16]

Mechanism of working of ZnO as a Photocatalyst

In photocatalytic processes, ZnO absorb radiations with energy *(hv)* greater than or equal to its original bandgap energy. Absorption of photons results in the excitation and electron transfer to the conduction band (CB) from valence band (VB) which leads the formation of holes in the valance band. These h^+ and e^- recombines and emits energy which resulting in low quantum yield of photocatalytic reactions. This recombination rate of holes and electrons depends on various parameter like shape, size and bandgap.[17, 18] These holes and electrons at the catalytic surface of ZnO results in oxidation and reduction reactions to form superoxide anion radicals ($O_2^{-\bullet}$) and hydroxyl radicals ($^\bullet$OH), respectively. These $^\bullet$OH radicals react with harmful pollutants to give harmless products as shown in Scheme.3.



Scheme 3: Photocatalysis at the surface of ZnO

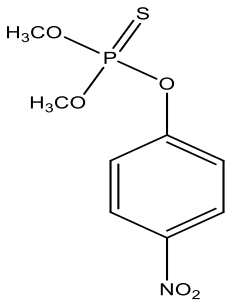
Modification strategies for better photocatalytic activity

Most of the widely used photocatalysts have wide energy gap, thus their activation energy is very high (UV irradiations), which make its use difficult on large scale and is less economical. Therefore, in these days, research is focused on photocatalysis by visible light as there is only 4% of UV irradiation in sunlight whereas nearly 45% of sunlight consist of visible light.[14] On the way to make photocatalyst solar light active, plasma coupling, nonmetal and metal loading, self-loading of crystal and band matching with semiconductors have been described in literature.[19, 20, 21] ZnO photocatalysts gives a poor activity under solar radiation. Metals and non-metals loading is widely applied to expand the range of wavelengths absorbed by ZnO by altering electronic band structure without decreasing photocatalytic activity in visible-light spectrum. Usually this is done by narrowing bandgap of ZnO, which happens through doping ZnO that may be result of i) introducing new localized energy level between the bandgap of ZnO, ii) lowering the conduction band and iii) the elevation of the valence band maximum.[22] Doping of transition metal (TM) in ZnO crystal lattice is quite popular strategy for making ZnO active in visible-light.[23] Change in the environment of Zn in ZnO crystal structure and electronic band structure arise many crystal defects like oxygen vacancies by additions of TM cations. Oxygen vacancies are good electron traps that can increase efficiency of photo-generated electron-hole separation.[24] Due to the difference in stoichiometry and the existence of intrinsic defects like zinc interstitials (Zn_i), oxygen vacancies (V_O), and zinc vacancy (V_{Zn}), ZnO is intrinsically n-type semiconductor. Doping of metals in ZnO controls its structure and therefore magnetic, electrical and optical properties, which leads to the number of changes like transparency, bandgap, magneto-optical properties, ferromagnetism and piezoelectric properties.[16, 17, 25] Copper (Cu) is a cheap element and its size is nearly same as Zn, hence copper cation can easily penetrate the substitutional sites of ZnO crystal lattice and modify absorption/emission spectrum of Zinc Oxide in solar light.[26]

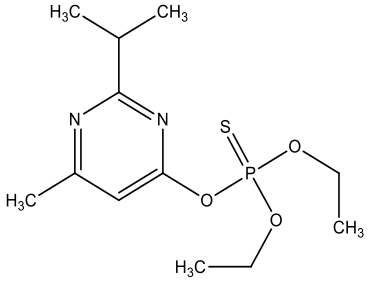
Pesticides

Pesticides are organic species which were used to increase the production of crops by killing unwanted pests. Pesticides, insecticides can easily diffuse into ground-water/ surface water which become a big problem in present days. The pesticides have longer half life time,

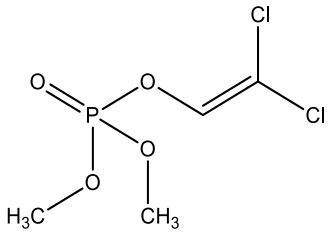
they don't degrade easily as they accumulate in eco-system and cause many health problems. The use of organophosphorus pesticides is increasing day by day and methyl parathion, dichlorvos, diazinon and fenthion are member of this family. They cause many health problems like abdominal pain, cough, skin irritation and decrease in size of red blood cells. It is reported that methyl parathion gets completely oxidized by Fenton system in UV light to produce sulphuric acid, oxalic acid and in other harmless products. Malwa region of Punjab, India is found to be highly contaminated by pesticides due to their overuse. Analysis of water and agriculture products from this region provides the proof for the presence of pesticides.



Methyl Parathion



Diazinon



Dichlorvos

Literature review

Synthesis, characterization and applications of nanomaterials have strongly promoted its broad use as catalysts. Nanomaterials have been the centre of scientific interest because of structures and high surface areas. These NP can be synthesized through various pathways and have various applications. Like ZnO can be obtained from metallurgical processes as well as from Chemical process. For metallurgical processes, ISO 9298 standard classifies ZnO in two types on the basis of processes they obtained: First is American process developed by Samuel Wetherill (also named as direct process) which includes reduction of zinc ore by heating coal then oxidation of Zn vapors. The particles obtained are usually of needle shaped and some are of spherical shape.[27] Second method is French method (indirect process) in which metallic zinc ore is vaporized at 910 ºC in furnace, Zn vapors react with oxygen present in air to give ZnO. The ZnO particles obtained have size from 0.1 to few micrometers. This method is carried out in vertical furnace and ZnO obtained by this method is purer than American process.[28] There are many laboratory methods for the synthesis of ZnO nanoparticles from precursors like $ZnCl_2$, NaCl, Na_2CO_3 etc. Weiqin *et al.* prepared ZnO NP by using Na_2CO_3 and $ZnCl_2$ with mechano-chemical method to get $ZnCO_3$ by 6 h milling which was further calcined at 400-800 ºC. Studies

showed that size of NP depends upon calcination temperature and the milling time for preparation of $ZnCO_3$. Size of NP was reduced by increasing milling time but increase in calcination temperature results in increase in the particle size.[29] Jiaguo *et al*. decolorized the rhodamine B aqueous solution by ZnO hollow sphere prepared from different molar ratio between 0-20 of $ZnCl_2$ and glucose by hydrothermal method at 180 ºC for 24 h then calcined at 500 ºC for 4 h in air. The results showed that the size, specific surface area, thickness of shells and activity of NP depends on the molar ratio of Zinc chloride and glucose. The sample with high ratio showed better catalytic activity then P25-TiO_2 probably because hollow spheres showed unique hierarchical nonporous structure thus well-organized transfer of reactant to active sites which increase photocatalytic activity of ZnO particles.[30]

Kansal *et al.* demonstrated photocatalytic degradation of lignin by using TiO_2 and ZnO in UV radiations at different pH (3 to 11) and different concentrations of oxidant (3.06×10^{-6} M to 15.3×10^{-6} M) and lignin (10–100 mg/L). Variations in amount of photocatalysts show no effect at all but rate of photodegradation was maximum at the pH 11 and for lower concentrations of lignin. Photodegradation rate increased in the presence of ZnO as it absorbs large portion of UV radiations than TiO_2.[12] Senthilnathan *et al.* degraded the commonly used pesticides like methyl parathion and diclorvuos with TiO_2. N-doped TiO_2 was used to degrade both the pesticides under UV and visible light. Nitrogen used for doping was immobilized obtained from different organic compound.[31] Birben *et al*. demonstrated the humic acid photocatalytic degradation by Ce doped ZnO nanoparticles. $Zn(NO_3)_2\cdot6H_2O$ water solution at pH 10-11 was used to synthesize ZnO by hydrothermal method at 175 ºC for 16 h and same procedure was repeated after adding 1% molar concentration of Ce.[32]

Sini *et al*. studied the superior activity of Co doped ZnO nanodiscs and nanorods using Zinc chloride, hexamethylenetetramine and cobalt chloride as starting materials. In this facial wet method ZnO NP in 1:1 ratio of HMTA and Zn^{2+} water solution were stirred and heated for 20 hours at 80 ºC and Co doped ZnO particle obtained by adding $CoCl_2.6H_2O$ in $ZnCl_2$ HMTA solution by same procedure. Photocatalytic activity of ZnO and Co doped ZnO studied by degrading methyl blue in sunlight.[33]

Ji *et al.* described a novel catalyst prepared by a modified polymerizable complex method. Water soluble tantalum obtained from tantalum oxide and potassium oxide, both were heated at 400 ºC in K: Ta =1:10. For Ta doped ZnO, Zinc nitrite mixed with citric acid in DI (deionized)

water and stirred for 1 h then citrio- tantalum in ethylene glycol added with zinc nitrite solution in the presence of nitric acid as a catalyst (1:100). Mixture was sonicated for 15-20 min and evaporated to 70 % of its original weight. $3.5x10^{-3}$ g/ml of HPC (hydroxypropyl cellulose) and $2.5x10^{-1}$ g/ml acetylacetone was added to the mixture as steric dispersant and stabilizer, then mixture was aged for 24 h at normal temperature in air after that baked at 140 °C for 12 h for poly-esterification at Ta^{2+} doping caused the number of change in ZnO lattice. 1mol % of Ta^{2+} loading in ZnO nanocrystals showed excellent photocatalytic activity than ZnO nanocrystals.[34]

Kanade *et al.* synthesized self-assembled aligned hexagonal prismatic Cu doped ZnO of average particle size in range of 40-85 nm. The Cu-Zn oxalates were prepared by using water or methanol or ethylene glycol as solvent. Zinc acetate, oxalic acid, $CuCl_2$ in any of these solvent and mixture was decomposed at 450 ºC in aerobic conditions. Nanoparticles produced hydrogen from water, H_2S and organic waste.[35] Vignesh *et al.* used zinc sulfate (0.1 M) and $NaHCO_3$ (0.2 M) to synthesize ZnO nanoparticles. The $NaHCO_3$ solution was drop wise added to zinc sulfate solution under continues stirring and then obtained precipitates washed and calcined at 350 ºC for 3 h. Zinc oxide with 10% of silver iodide gets suspension of ZnO, KI and $AgNO_3$ with ammonium hydroxide by vigorous stirring. The molar ratio of I^-/Ag^+ was 1:1. The photocatalytic decolorization of rosaniline hydrochloride dye (RA) was 1st order reactions and effect by factors like pH, catalyst concentration and concentration of RA. AgI sensitized ZnO showed best catalytic activity at pH 8 and concentration of catalyst 0.3 g/L.[36]

Mohammed *et al.* prepared ZnO nanoparticles by colloidal solution of $Zn(CH_3COO)_2.2H_2O$ and NaOH in ethanol then this colloidal solution was heated at 70 ºC for 30 min after this NaOH was added to mixture and hydrolyzed at 60 ºC for 2 h in commercial microwave. For 1 wt% of dopant manganese acetate mixed directly to zinc acetate during hydrolysis. Photocatalytic activity test by degradation of methylene blue. The high absorption of solar light proves the presence of defects in nanoparticles.[37] Shengwei *et al.* used zinc nitrite and PEG 2000 and urea solution in DI water in autoclaves and heated it at 180 ºC for 12 h. This procedure gave the hierarchical flower like carbon doped ZnO super structure. The production of OH radicals detected with the help of photoluminescence technique and its photocatalytic activity was studied by degradation of dye Rh B.[38]

Paul *et al.* discovered that ZnO at nanoscale have antimicrobial activity thus it can be used for food packaging. ZnO particles prepared by using $ZnCl_2$ and Na_2CO_3 as precursors, both of

them milled to get $ZnCO_3$ dust and then $ZnCO_3$ and NaCl were milled again at low temperature. These nanoparticles were used for food packaging because of their antimicrobial properties.[39]

Mehdi *et al*. prepared the Cu doped ZnO NP for the degradation of Organophosphorus insecticide named as diazinon. $CuCl_2$ was drop wise added to the $ZnCl_2$ under constant stirring then pH of solution was maintained by adding ammonia. After 3 h stirring white precipitates were obtained and dried. Degradation of diazinon follows the pseudo 1st order kinetics. Cu-doped ZnO NP gave better efficiency then ZnO NP under UV irradiations.[40]

Research gaps

The literature revealed that various dyes and other organic harmful compounds have been degraded using ZnO nanoparticles under UV light irradiation. However, there are some limitations for the use of ZnO as photocatalyst such as lack of visible light activity and slow degradation rate of intermediates which are sometimes more toxic than parent molecules. The improvement in photocatalytic activity of ZnO can be achieved by:

(i) Alteration in the size and shape of ZnO that can improve the electronic properties.

(ii) Metals loading of over different shapes of ZnO NPs can further give better catalytic activity.

Although, these modified ZnO NP exhibits higher photocatalytic activity than unmodified ZnO have been well considered for degradations of many environment pollutants like dyes and many other organic compounds. Yet it is rarely used of degradation for pesticides.

Objectives

(i) To prepare various nanostructures of ZnO.

(ii) To prepare Cu loaded ZnO composites by different methods.

(iii) To study comparative catalytic activity and physiochemical properties of prepared nanocomposites for the degradation of methyl parathion.

Materials and Methods

Chemicals and reagents

Zinc nitrite hexahydrate ($Zn(NO_3)_2.6H_2O$, 98%, Loba Chemie Ltd), Ammonia (NH_3 Merck Specialties Private Ltd), Zinc Chloride ($ZnCl_2$, 97%, Loba Chemie Ltd), Sodium hydroxide (NaOH, 96%, Avantor Performance Material Private Ltd), Isopropyl alcohol, Argon gas, Polyvinyl Pyrrolidinone (PVP, 90%, Spectro Chem. Ltd), $Zn(CH_3COO)_2.2H_2O$, Cupric nitrite ($Cu(NO_3)_2.3H_2O$, 99%, Loba Chemie Ltd).

Methods

Synthesis of ZnO Porous Spheres

Zinc nitrite hexahydrate, ammonia and starch were used for the preparation of porous ZnO as reported perivously[41]. Starch (2.5 g) was dissolved in 150 mL of boiled deionized water (DI) to obtain clear starch solution. $Zn(NO_3)_2.6H_2O$ (0.01 mol/L) was added to the clear starch solution followed by continuously stirring for 15 min at 80 ºC. The pH of solution was maintained between 8-9 by slow addition of ammonia to get a milky solution. This solution was stirred father for 30 min at 85 ºC. The resulted precipitates were centrifuged, washed with deionized water and ethanol, and dried at 50 ºC. The dried powder was calcined at 500 ºC in the presence of air to obtain ZnO spheres and ware used for the further application.

Synthesis of ZnO flower like structures

In a typical procedure,[42] 0.27 g of $ZnCl_2$ (2.0 mmol) and 0.27 g of NaOH (10.0 mmol) were dissolved in 30 mL of DI water and stirred for 5 min. The solution was transferred to Teflon lined stainless sealed autoclave and heated at 80 ℃ for 24 h, and the contents were cooled to the room temperature. The resulting white precipitates were separated by centrifuge, washed with distilled water and ethanol few times and dried at 60 ℃ for 12 h.

Synthesis of ZnO rod like structure

In typical procedure,[43] 1.68 g of PVP was dissolved in 80 ml of DI water and added 2.3 mmol of zinc acetate dihydrate along with stirring for 15 minutes followed by addition of 0.025 mol (1 g) of NaOH. The resultant solution was transferred to 100 mL of Teflon lined stainless steel autoclave. The autoclave was placed in furnace at 80 ºC for 48 h and then cooled to room

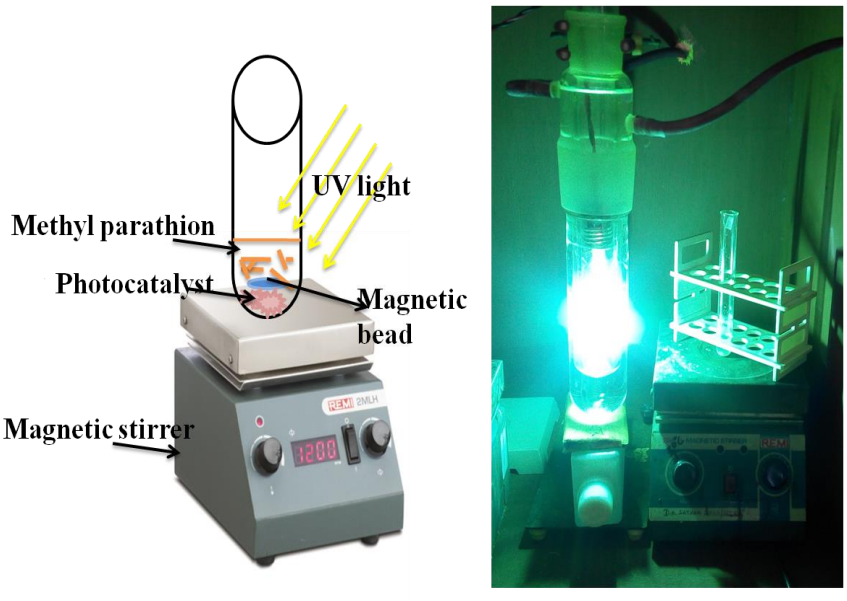
temperature. The resultant white precipitates were filtered and washed with DI water, with ethanol for few time and dried at 60 ºC in air.

Photodeposition of metal ions such as copper ZnO NP

Cupric nitrite (Cu^{2+}) solutions (1wt%) were prepared and 1.574 mL of it was added in respective test tubes containing 100 mg of ZnO NP. Isopropyl alcohol and distilled water (1:1 mixture) was added in test tube. High purity argon gas was purged all the time to maintain anoxic conditions during the preparation of metal deposited ZnO. After that the test tubes were sealed with paraffin film. The contents in test tube were irradiated for 6 to 7 h in UV photo reactor. The obtained material was separated by centrifugation and washed with DI water and ethanol and dried the precipitates at room temperature.

Catalytic Activity

Catalytic activity and stability of prepared ZnO NP and Cu loaded ZnO NP catalysts was evaluated for the degradation of Methyl parathion by adding 20 mg of the catalyst to a solution of substrate (5 ml, 500 ppm) under constant stirring in UV radiation. The analysis of the products was done on UV spectrometer after a fixed time interval.



Scheme and image of Photocatalytic activity

Catalyst characterization

Different characterization techniques like SEM, Powder XRD, Solid-state UV absorption Spectroscopy, Zeta potential etc.

Ultraviolet-Visible Spectrophotometer (UV-Vis spectrophotometer)

The measurement of the reduction of a beam of light after it passes through a sample was done by UV-Vis absorption spectroscopy. Absorption spectra give the information about size distribution and nanoparticles formation. The principle of this instrument is that when sample is exposed to light (having suitable energy for electronic transition within the molecule), required energy is absorbed and the transition of electron takes place from lower energy level to higher energy level. Analytic Jena, SPECORD 205 instrument was used in this research in order to examine the characteristic absorbance band of the synthesized NPs. Aqueous suspension of all samples was analyzed in a 3.5 ml quartz cuvette in the detection range of 190-1100 nm.

Zeta Potential Measurement

When the NPs are suspended in an aqueous medium, the adsorption or ionization of ions takes place on the NPs surface, which leads to the formation of an electrical double layer resulting in the development of net charge, called zeta potential (ζ). Therefore, zeta potential is an important tool for understanding the state of NP surface and also predicts the long-term stability of the NPs. The measurements were carried out by means of Brookhaven Zeta Plus at 25 ^{o}C using a cuvette comprising a palladium electrode mounted on a machine support immersed in ≈ 2-2.5 mL of NCs solution.

Scanning Electron Microscope (SEM)

The external morphology (shape and size) of the samples were analyzed by scanning electron microscopy. Morphology, topography, crystallographic and composition information about the sample surface can be investigated from SEM images. A beam of electrons is focused on a selected area of a sample at the time of SEM analysis and therefore an exchange of energy from the electron beam to the sample surface takes place. The electron gun produces electron at the top, referred to as primary electrons and these electrons are then analyzed, amplified and translated into images. JSM-7600F (0.1 to 30 kV) instrument was used for SEM images analysis,

where samples were placed on a specimen stub with conducting tape and then coated with a thin layer of gold to reduce sample charging.

Powder X-Ray Diffraction (P-XRD)

This technique is primarily used for identification of phase, composition and crystal system of the materials; it can also give information on unit cell dimensions. For the identification of crystal system, phase, composition and crystallinity of the materials this technique was used. PAN alytica X' pert PRO X-ray diffractometer with Cu Kα (λ = 1.54 Å) radiation was used for XRD pattern analysis. A smooth plain surface paper was used to press the powder samples into a sample holder. The XRD study was done from Sophisticated Analysis Instrumentation Laboratory (SAI Lab), Thapar University, Patiala, India.

GC Chromatograph (GC)

This study was used to evaluate CO_2 released during the degradation of pesticides. It is done by injecting 1 mL of gaseous mixture from the test tube (tightly sealed) into GC (NUCON-5765) equipped thermal conductivity detector and Porapak-Q column having flow of nitrogen gas as carrier gas.

Results and Discussion

Solid- state UV-visible absorption

The solid-state UV-visible absorption spectra of ZnO nanoparticles (nanorods, nanoflowers and Nanospheres) as shown in Fig.1, showed strong absorption edges near about 397 nm, 390 nm and 400 nm respectively. The difference in absorption edges is mainly due to variation in the morphologies. Upon loading of Cu ions over ZnO, the absorption band edge shifted towards the higher wavelength i.e. red shift. This red shift could be attributed to strong interactions between the surface of ZnO and Cu.[44]

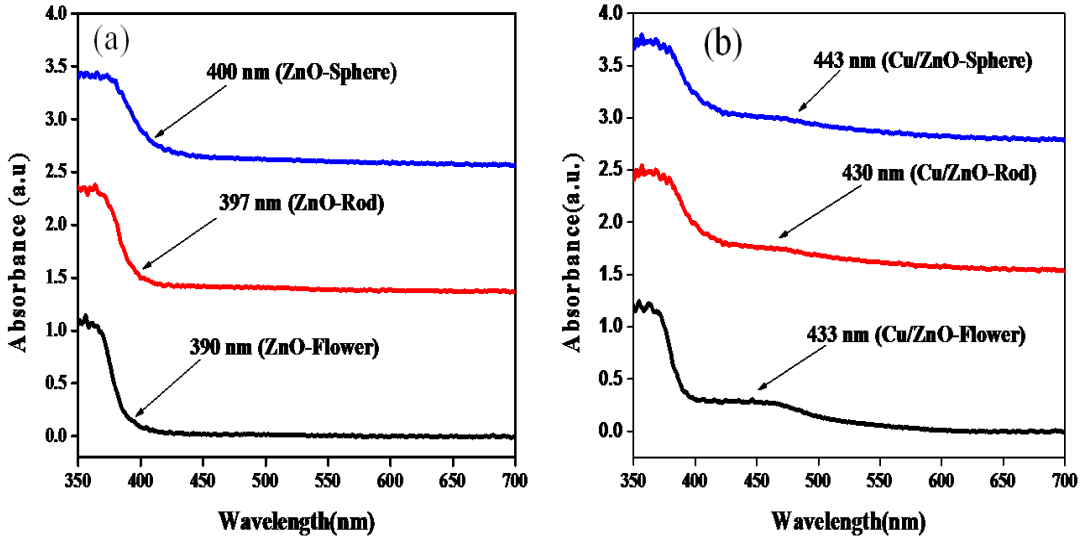


Fig.1 Solid state UV-Vis absorbance spectra of ZnO and Cu loaded ZnO nanoparticles

Zeta Potential

It is an indicator for the stability of colloidal suspension and electrostatic repulsion between similar and adjacent charge revealed by its magnitude. The surface charge of ZnO NP is +1.6 eV and Cu loaded ZnO NP is -0.313 eV.

X-Ray Diffraction

The phase and purity of as-prepared ZnO catalysts were analysed by X-Ray diffraction spectra (Fig.2). The narrow and sharp peaks in XRD show the crystalline nature of as prepared sample. The main diffraction peaks were found at 2 theta positions 31.98°, 34.33°, 36.48°, 47.57°, 56°, 62.9°, 66.1°, 68.28°, 72.81° and 76.97° with their corresponding planes (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) respectively. XRD peaks confirms the hexagonal crystal system with lattice parameters a = 3.251 Å, b = 3.025 Å and c = 5.201 Å. An

increase in the intensity in XRD peaks was observed after Cu loading. It is noted that the no peak of copper oxide was found in XRD spectra and also that there was no influence of Cu-ions loading towards the phase and structure of ZnO crystal system. The crystallite size of ZnO nanoparticles was found to be 37.23 nm (nanospheres), 40.027 nm (nanorods) and 35.46 nm (nanoflowers). The Cu-loaded ZnO nanoparticles showed crystallite size 36.7 nm (spheres), 31.173 nm (nanorods) and 33.84 nm (nanoflowers). The crystallite size was reduced after Cu ions loading due to the formation of Zn-O-Cu complex at the surface, which hinders the growth of grains.[44] The diffraction peaks were indexed with the standard JCPDS card 00-001-0664 for ZnO nanoparticles and JCPDS card 01-079-2205 for Cu loaded ZnO nanocomposites

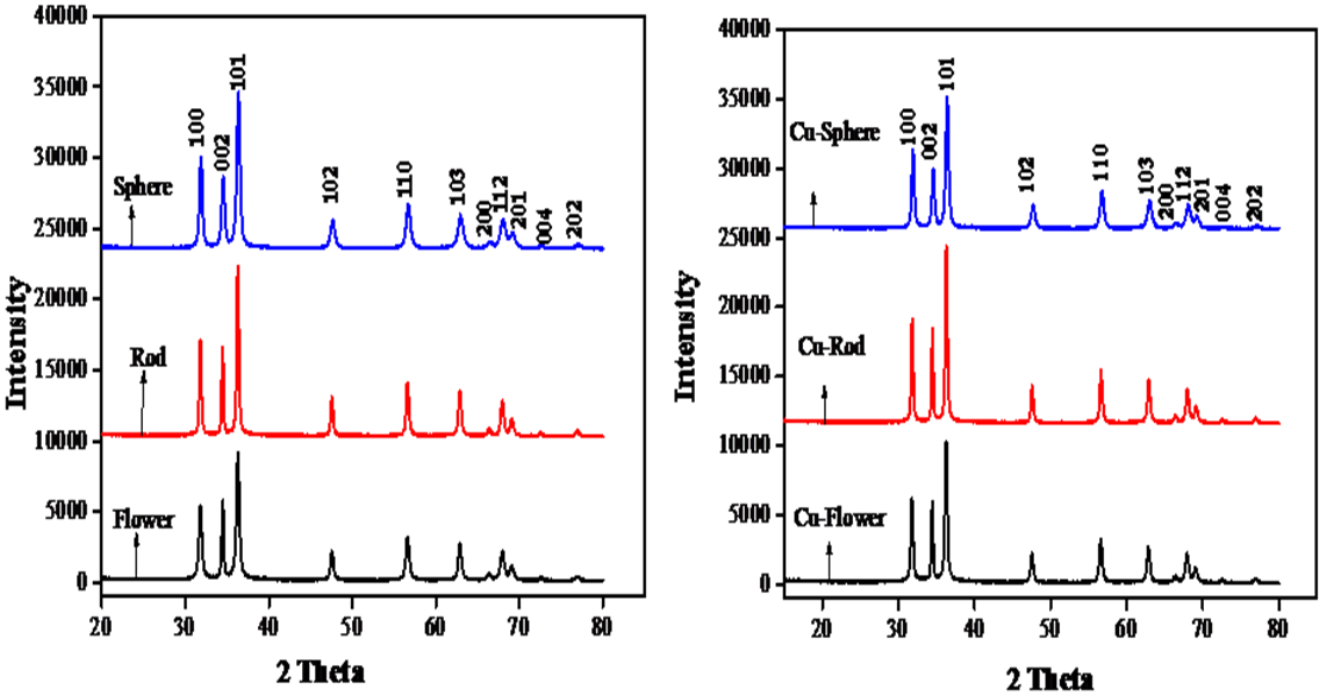


Fig. 2 X-ray diffraction pattern of ZnO nanoparticles and Cu loaded ZnO nanoparticles.

SEM and EDS

The various morphologies of ZnO NP have been studied by SEM images. The formation of NF (nanoflowers like structures), NR (nanorods like structures) and NS (nanospheres like structures) of ZnO, confirmed by SEM images are shown in Fig.3 (a and b), Fig.3 (c and d) and Fig.4 (e and f) respectively. The percentage and composition of loaded metal ions over as-synthesized various shapes of ZnO and Cu loaded ZnO nanorods was further confirmed by EDS analysis in Fig.4. and Fig.5. respectively

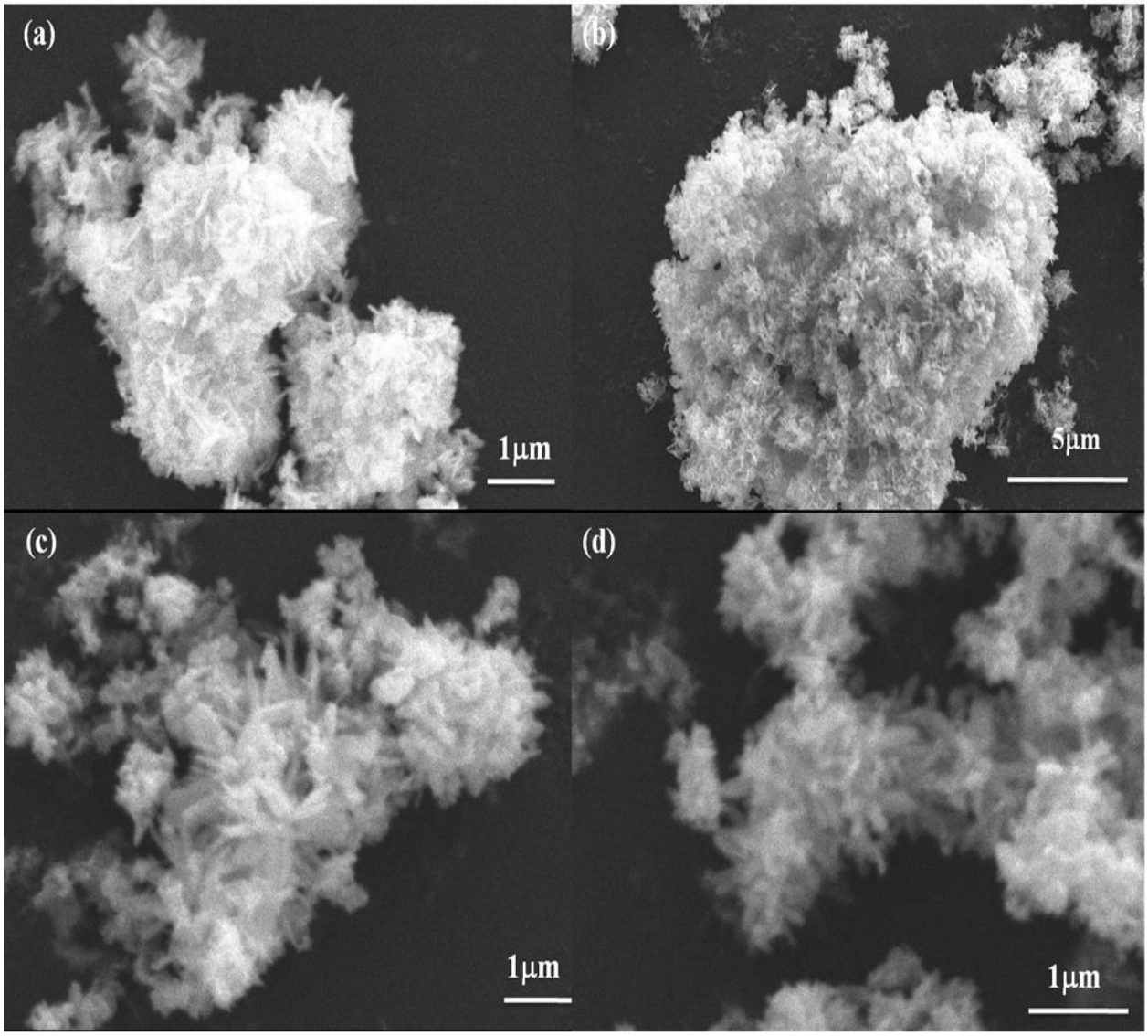


Fig.3. SEM images of ZnO (a and b) Nanoflower like, (c and d) Nanorods like.

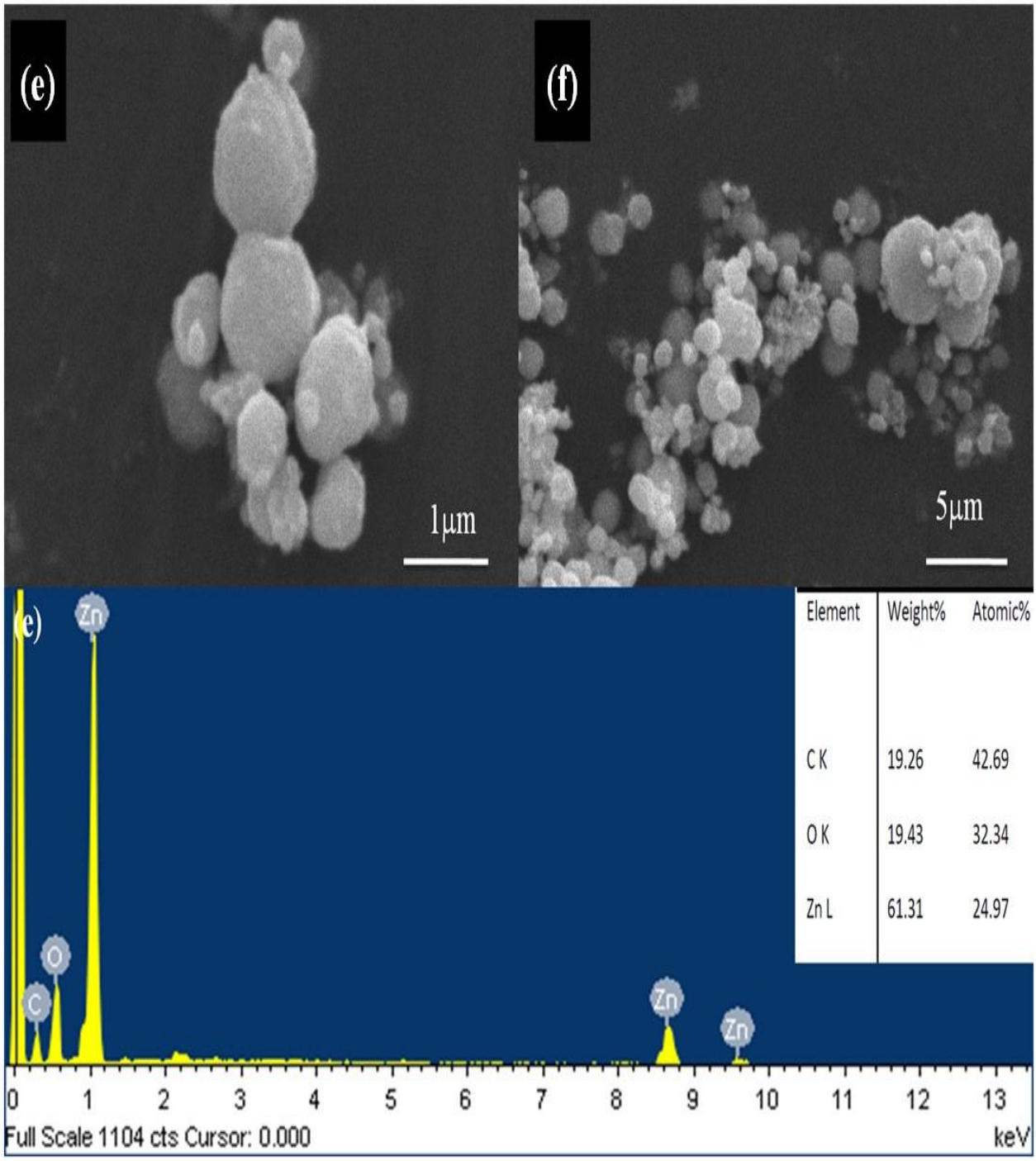


Fig.4. SEM images of (e and f) Nanospheres and EDS spectra

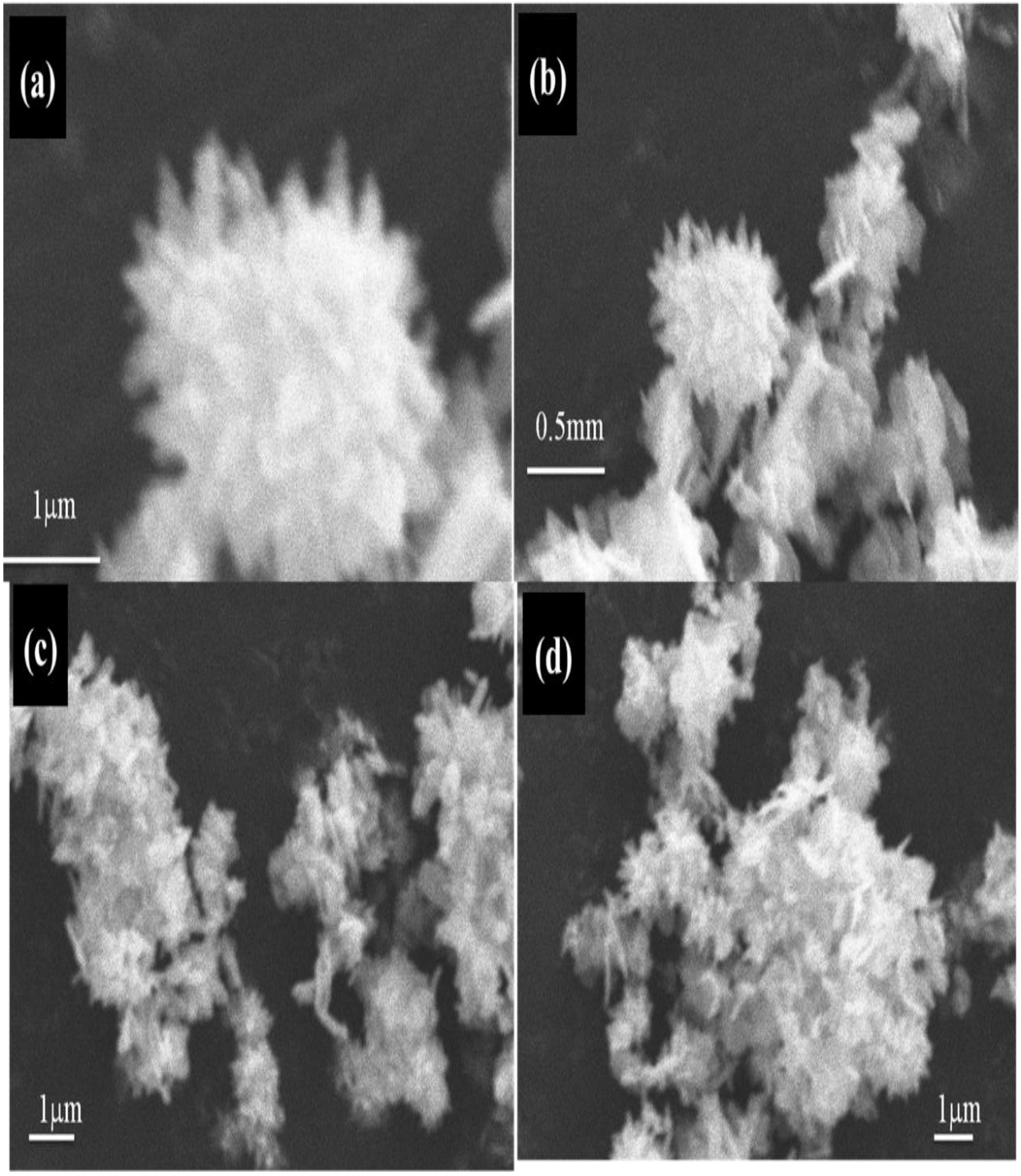


Figure.5. SEM images of Cu-ZnO (a and b) Nanoflower like, (c and d) Nanorods like.

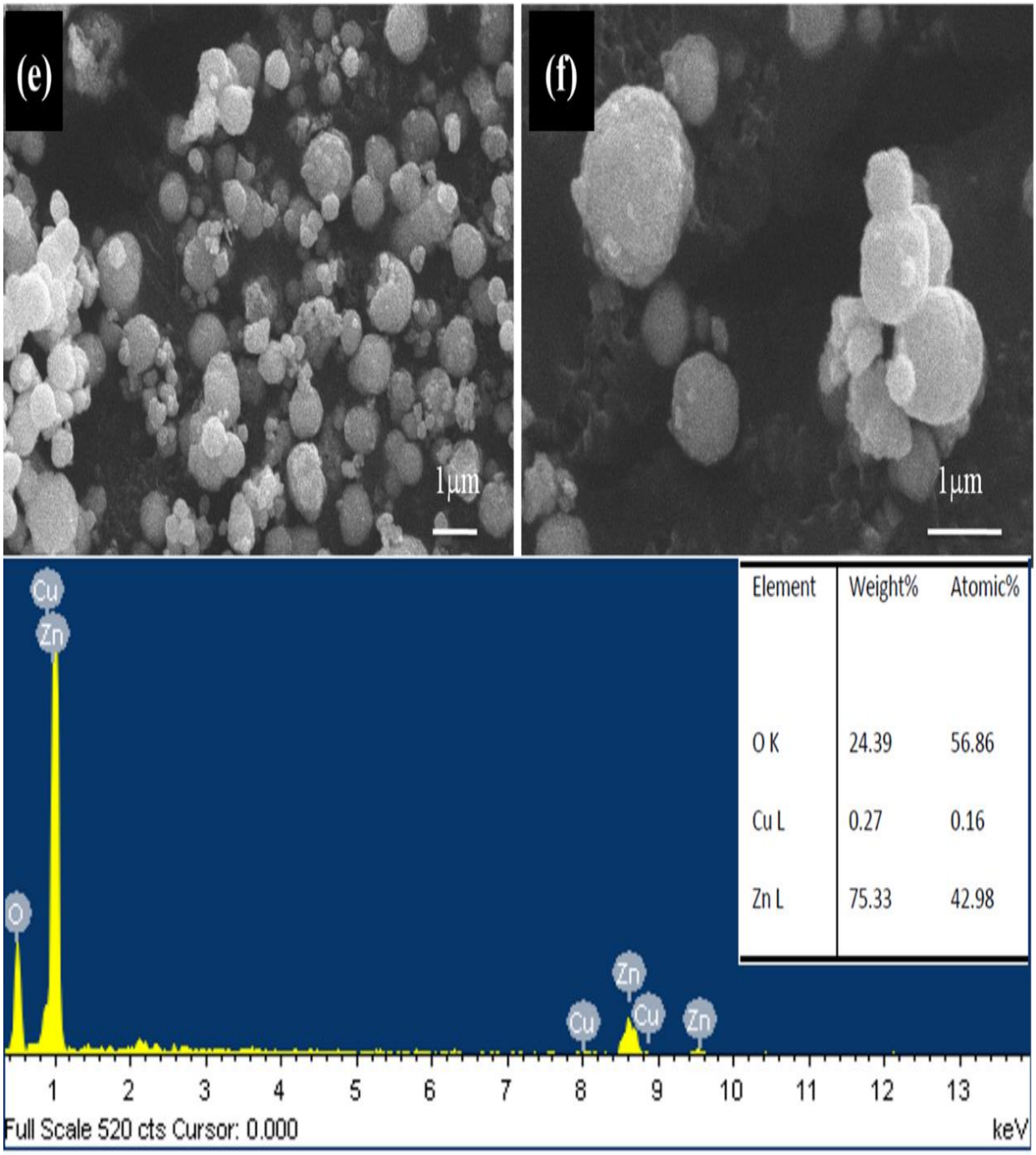


Fig.6. SEM image of (e and f) nanospheres like and EDS spectra

Photocatalytic activity

The catalytic performance of as-prepared nanocomposites of ZnO and copper loaded ZnO were evaluated for the degradation of methyl parathion pesticide. UV absorbance spectra of degradation of methyl parathion with ZnO NF, ZnO NR and ZnO NS are shown in Fig..7. The conversion and selectivity of obtained products were found to be greatly influenced by the synthetic method that indirectly control the size and with the loading of metal ion. ZnO NR took 3 h for catalytic degradation with 98% conversion while ZnO NF and ZnO NS took nearly 4 h and 6 h respectively for the degradation of pesticide (Fig.7). ZnO NR, ZnO NF and ZnO NS degraded 98%, 91%, and 65% of methyl parathion respectively under 3 h UV-light irradiation. ZnO NR showed more catalytic activity than ZnO NF and ZnO NS.

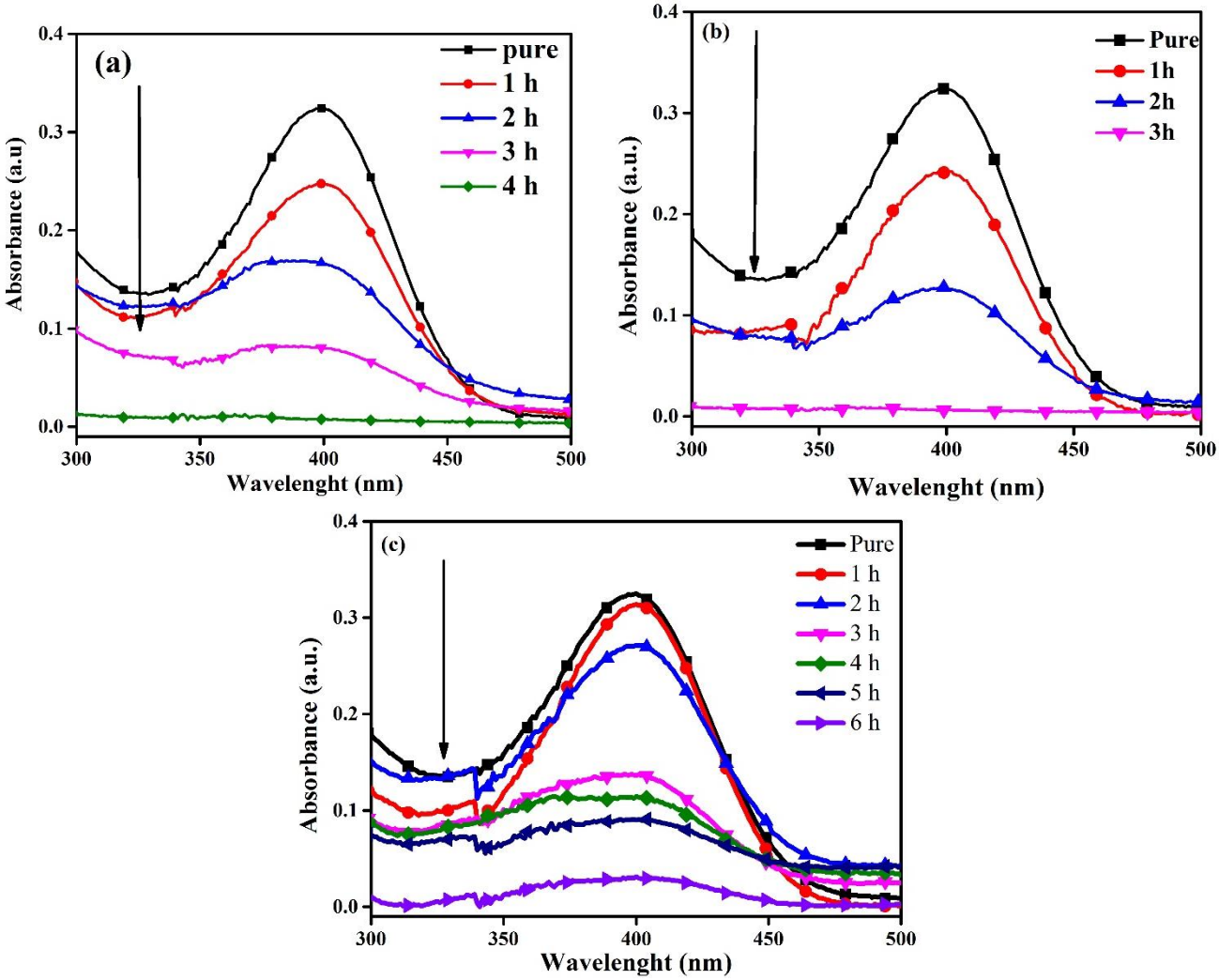


Fig.7. UV absorbance spectra of degradation of methyl parathion with (a) ZnO NF (b) ZnO NR (c) ZnO NS.

This may because NR morphology offers smaller crystallite size which may provide more active sites for photocatalytic reaction and 1D ZnO NR has better charge transport through a one-dimensional direction, which decreases the rate of charge recombination and promotes the photocatalytic efficiency.[45]

After metal loading recombination rate of photogenerated charge carriers at the surface of ZnO decrease. Solid UV absorbance shows the red shift in spectra with loading of Cu ion. Loading of Cu ion decrease the rate of recombination of charges which provide better activity.[45, 46] As shown in Fig.8. Cu loaded ZnO NR took 80 mins for 99% degradation of methyl parathion and Cu loaded NS took 120 mins and ZnO NS took nearly 280 mins for the degradation.

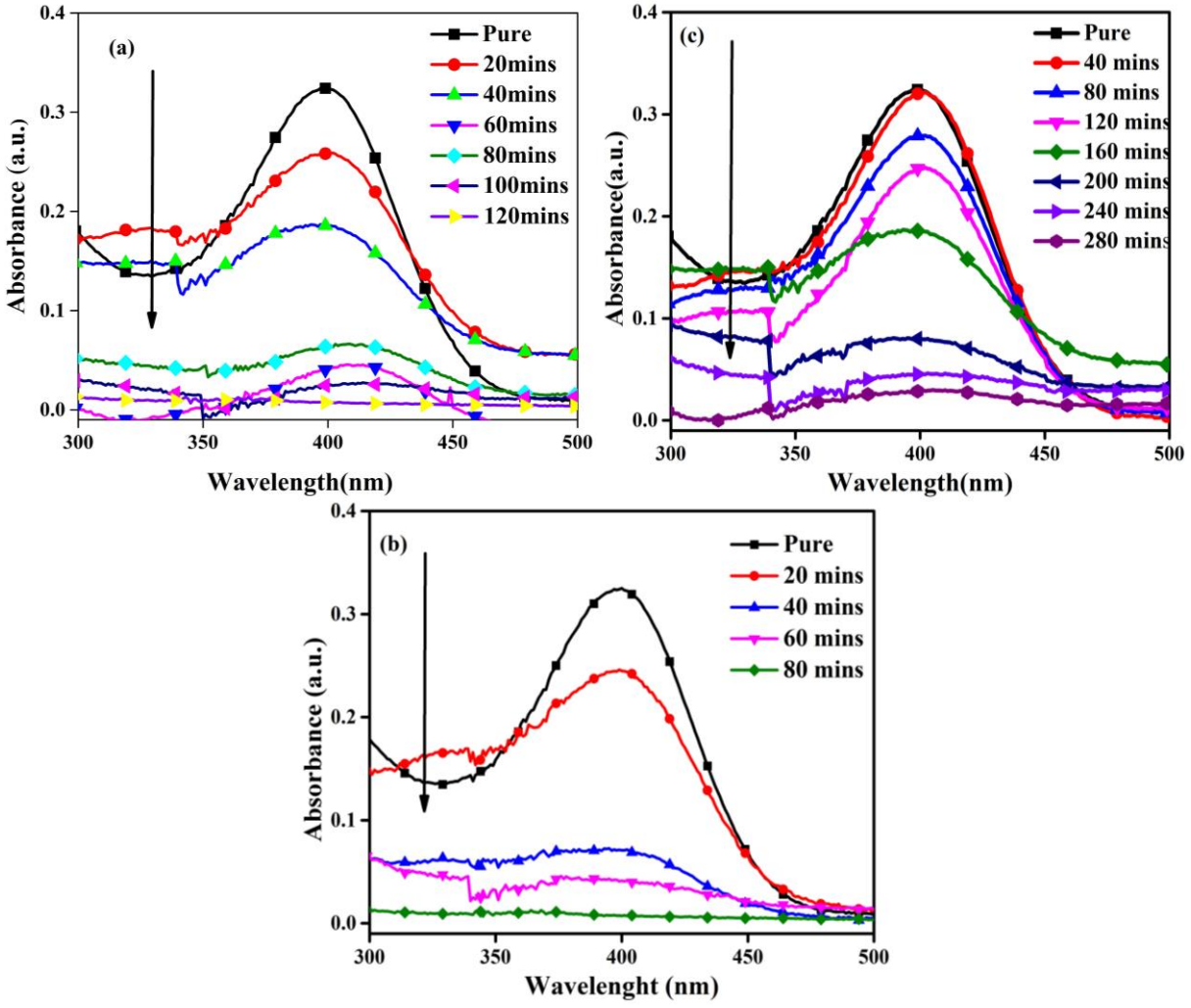


Fig.8. UV absorbance spectra of degradation of methyl parathion with (a) Cu-ZnO NF, (b) Cu-ZnO NR, (c) Cu-ZnO Ns.

The ZnO NR, ZnO NF and ZnO NS degrade 98%, 91% and 65% of pesticide in 3 h respectively whereas the Cu-ZnO NR, Cu-ZnO NF and Cu-ZnO NS degraded 99%, 86% and 14% of pesticide as shown in Fig.9. in 80 min respectively. The photodegradation efficiency of different nanocomposites calculated by following equation:

$$\eta\% = \left(1 - \frac{C}{C_0}\right) * 100$$

Where C=Final concentration, C_0=Initial concentration

Time versus Concentration graph shows that the reaction of Time versus Concentration graph shows that the reaction follows pseudo 1st order kinetics [40] shown in Fig.10

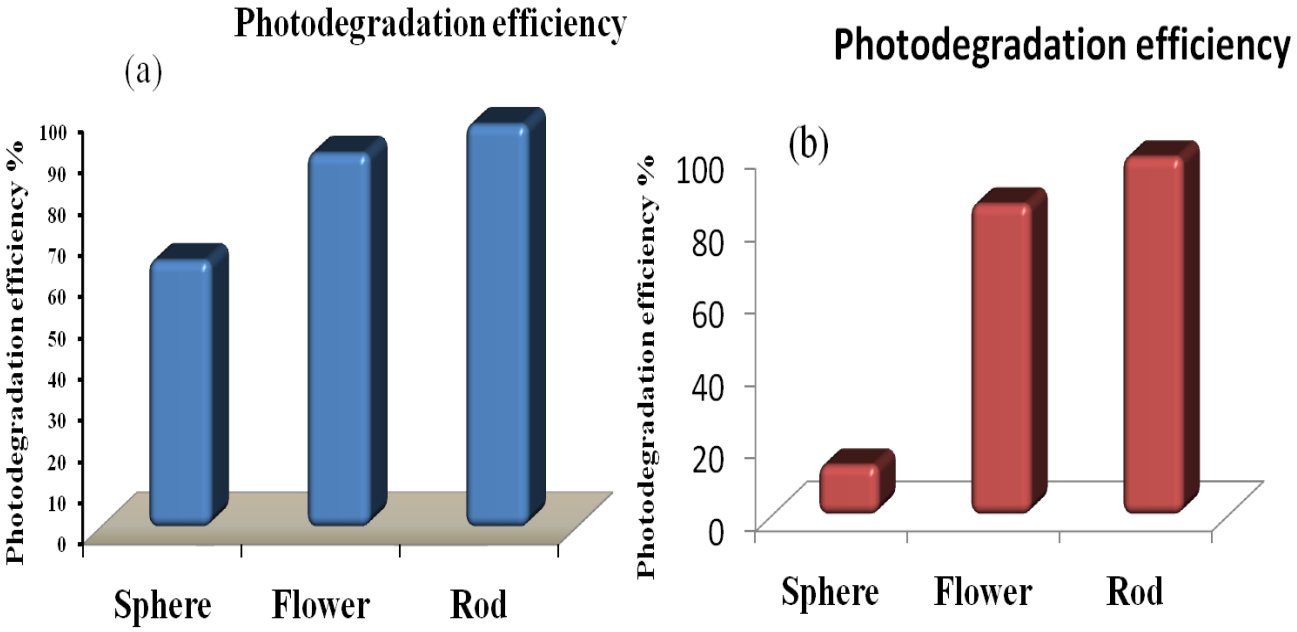


Fig.9. Photodegradation efficiency η% with (a) ZnO NP in 4h

(b) Cu loaded ZnO NP in 80 min

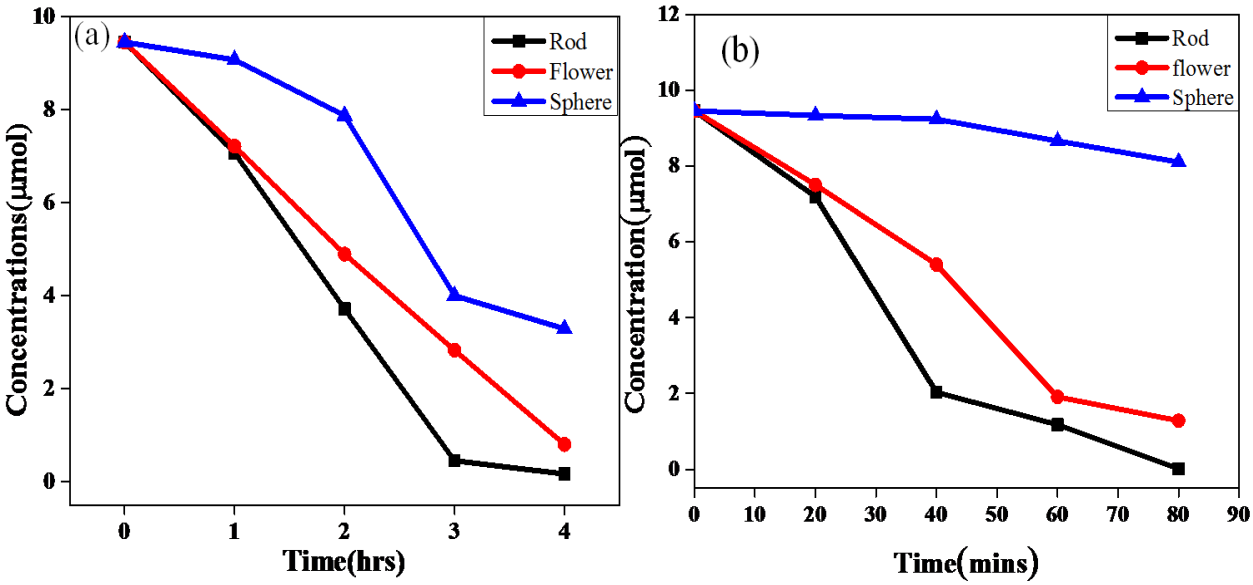


Fig.10. Time versus concentration graph of photodegradation (a) ZnO NP in 4 h

(b) Cu loaded ZnO in 80min.

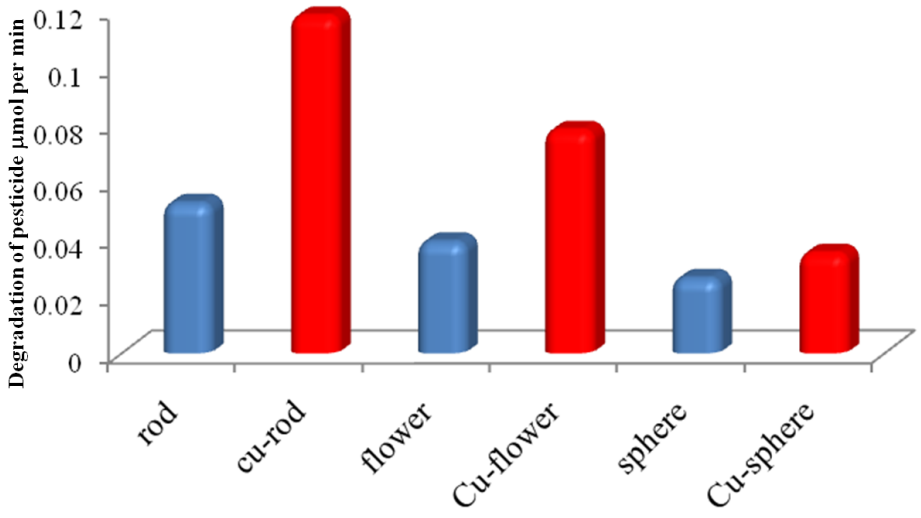


Fig.11. Comparative photodegradation of methyl parathion with different

ZnO and Cu loaded ZnO NP

With the Cu loading the rate of degradation of methyl parathion increase because the rate of recombination of electrons/holes decrease.

Quantitative measurement of produced CO_2 by GC

The GC was used for the quantification of produced CO_2 during photodegradation of the pesticide. It was carried out by injecting 1 mL of gaseous mixture from the test tube (tightly sealed) into GC (NUCON-13A) equipped with thermal conductivity detector (TCD) and Porapak-Q column with nitrogen as a carrier gas. The oven temperature was set at 50 ºC, injector and detector temperatures were set at 80 ºC and 90 ºC respectively. The quantification of CO_2 was done with standard 180 ppm as compared to retention time. The pesticide photooxidized to give smaller fragments that further degrade into smaller fragments like CO_2 and water. More photoactive catalyst produces more CO_2 which means comparatively more oxidation of the pesticide. The Cu loaded ZnO NR produced maximum amount of CO_2, showing it to be better photocatalytic active.

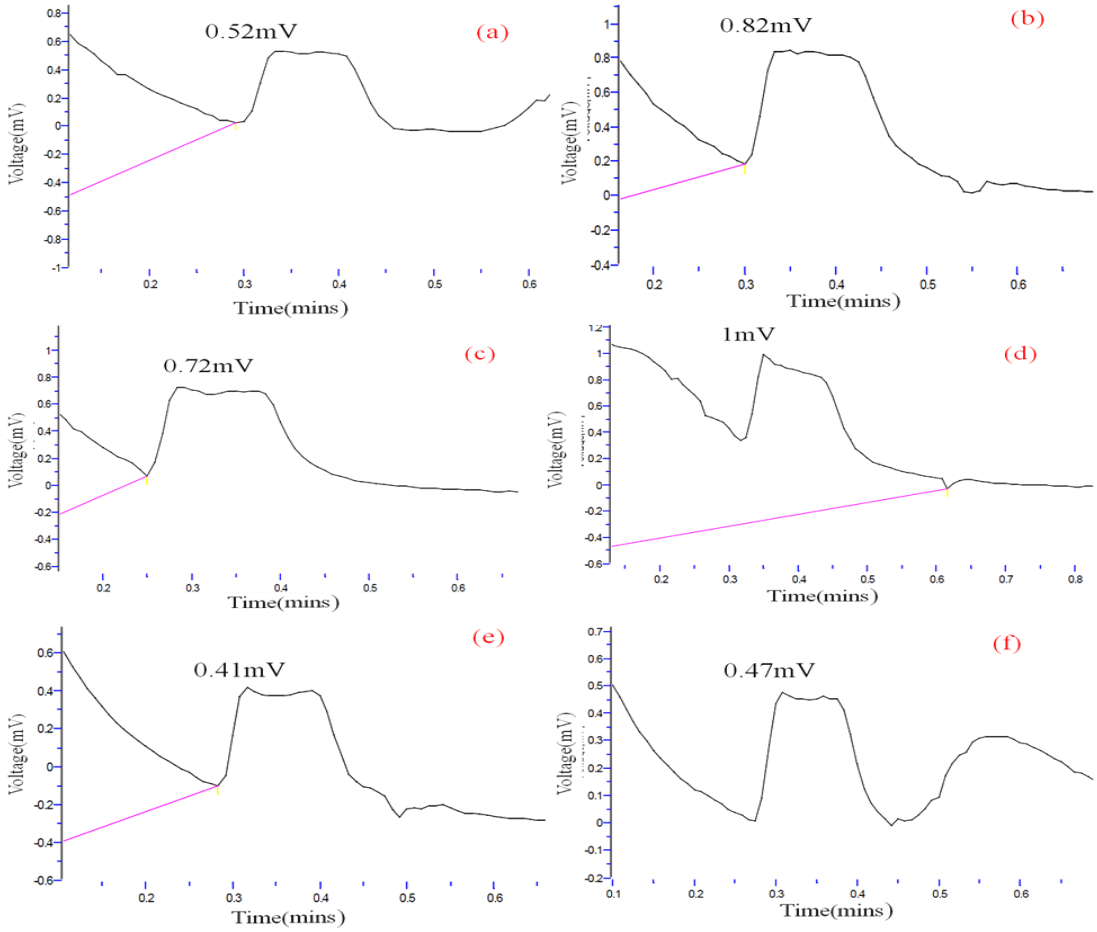


Fig.12.Quantification by GC graph using (a) ZnO NF, (b) Cu-ZnO NF, (c) ZnO NR, (d) Cu-ZnO NR, (e) ZnO NS.(f) Cu-ZnO NR as catalysts

The extent of photodegradation of pesticide was found by means of the amount of released CO_2 during the process. More the amount of released CO_2 means pesticide degrades properly into CO_2 and water. Lesser amount of produced CO_2 means other intermediate species were present during degradation which are not completely converted into CO_2. The CO_2 produced during the reaction by different morphologies of ZnO shown in Fig.12.

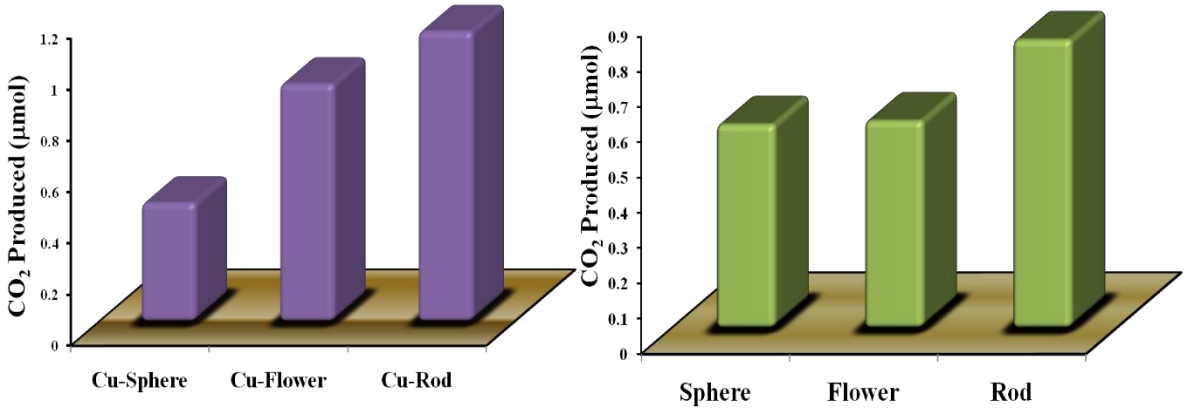


Fig.13. Amount of CO_2 produced by (a) ZnO NP, (b) Cu loaded ZnO NP

Reaction Mechanism

In photocatalytic processes, ZnO absorb radiations energy (hv) greater than or equal to its original bandgap energy. Absorption of photon results into electronic excitation and transfer of electrons to the conduction band (CB) from the valence band (VB) which forms holes in the valance band (migration of e^-/h^+ pairs). These holes and electrons at the catalytic surface of ZnO that results in oxidation and reductions reactions to form superoxide anion radicals ($O_2^{\bullet-}$) and hydroxyl radicals (•OH), respectively. The •OH radicals react with methyl parathion and finally oxidize it into carbon dioxide. With the Cu loaded ZnO, the electrons form the conduction band of ZnO to conduction band to Cu metal thus the recombination of charge is decreased, therefore it gives better activity than bare ZnO. The photocatalytic reaction may be formations of reactive radical species through the following reactions.[46]

$$ZnO + hv \rightarrow ZnO\ (h^+_{VB} + e^-_{CB}) \quad (a)$$

$$H_2O + h^+_{VB} \rightarrow {}^{\bullet}OH + H^+ \quad (b)$$

$$O_2 + e^-_{CB} \rightarrow O_2^- \quad (c)$$

$$O_2^- + H^+ \rightarrow HO_2^- \quad (d)$$

$HO_2^- + H^+ \rightarrow H_2O_2$ (e)

$H_2O_2 + hv \rightarrow 2^{\bullet}OH$ (f)

$^{\bullet}OH$ or $O_2^{\bullet-}$ + Methyl Parathion $\rightarrow$ Intermediates $\rightarrow CO_2 + H_2O$ (g)

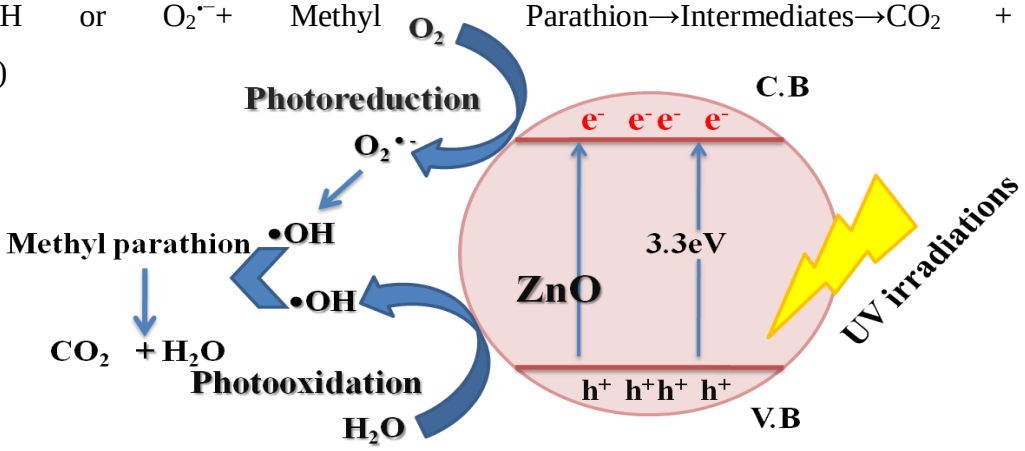


Fig.14. Photodegradation of methyl parathion with ZnO NP

Cu loading on ZnO lead to formation more holes, V_o and surface defects which increase the photocatalytic activity of the catalyst and the formation $^{\bullet}OH$ radical for the photodegradation as per following reactions:

$Cu^+ \quad H_2O_2 \rightarrow Cu^{2+} + OH^- + {}^{\bullet}OH$

$Cu^{2+} + e^-_{CB} \rightarrow Cu^+$

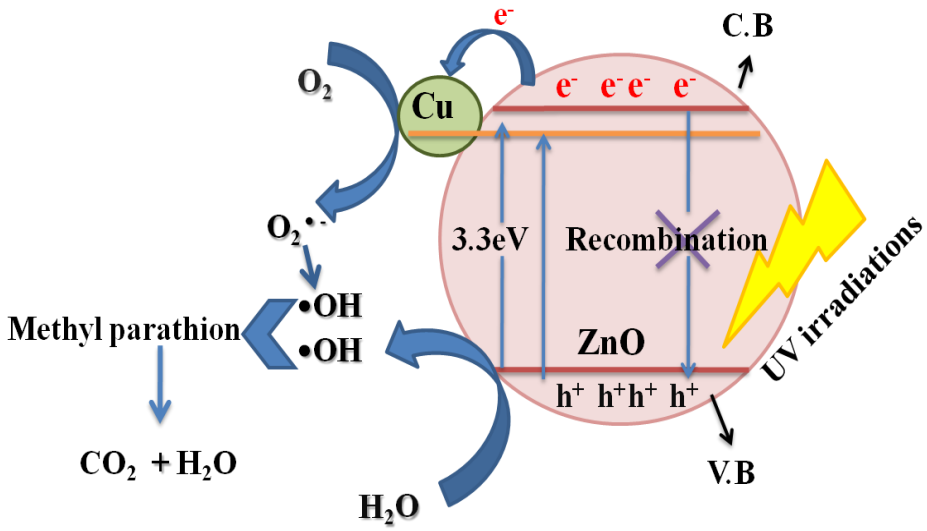


Fig.15. Photodegradation of methyl parathion with Cu loaded ZnO NP

Conclusion

In summary, various shape and size of ZnO nanoparticles have been synthesized and successfully applied for the photodegradation of methyl parathion. It was found that among the as synthesized various shapes, ZnO nanorods exhibited higher photodegradation efficiency. Furthermore, various morphologies of ZnO were decorated with Cu metal. As prepared ZnO nanorods showed almost complete conversion (~ 98%) of methyl parathion to CO_2 and water molecules in 3 h under UV light irradiation. However, Cu loading over ZnO increases the photodegradation efficiency (~99%1) in 80 min. This increase in the conversion efficiency and rate of photodegradation could be attributed to the less rate of recombination due to Cu loading, narrow bandgap and anisotropic morphology.

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SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

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2	doria.fi Internet Source	%1
3	He, Yiming, Jun Cai, Lihong Zhang, Xiaoxing Wang, Hongjun Lin, Botao Teng, Leihong Zhao, Weizheng Weng, Huilin Wan, and Maohong Fan. "Comparing Two New Composite Photocatalysts, t-LaVO4/g-C3N4 and m-LaVO4/g-C3N4, for Their Structures and Performances", Industrial & Engineering Chemistry Research, 2014. Publication	<%1
4	Vignesh, K.. "Photocatalytic activity of AgI sensitized ZnO nanoparticles under visible light irradiation", Powder Technology, 201207 Publication	<%1