SOLAR ENERGY ASSISTED PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS BY VARIOUS TRANSITION METAL OXIDE NANOPARTICLES

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***Abstract*- ZnO, Fe_2O_3 and CuO nanoparticles have been successfully grown, without the use of additives like surfactants, capping agent or complexing agent etc. by hydrothermal reaction technique. The structural, morphological, of ZnO, Fe_2O_3 and CuO nanoparticles were studied using Scanning electron microscopy (SEM). The photocatalytic degradation properties of ZnO, Fe_2O_3 and CuO nanoparticles were further studied by using UV-Vis spectroscopy. The resulting morphology of the end product can be regulated by changing the concentration of precursor and the time and temperature of the reaction. SEM throws light on the morphology of the as synthesized nanoparticles. UV-Vis spectroscopy gives evidence that the as synthesized Fe_2O_3 nanoparticles have narrow absorption width in UV range and broad absorption width in visible range and thus can be useful for the photocatalytic reactions in visible light.The highest photo catalytic efficiency was observed for the particles of Fe_2O_3 as compared to CuO and ZnO nanoparticles.**

Key words: **Nanoparticles, UV-Vis spectroscopy, Scanning electron microscopy, Photocatalysis.**

INTRODUCTION:

Photocatalytic degradation of organic pollutants using solar energy could be highly cost-effective compared with the processes using artificial UV–Vis irradiation. However artificial radiation has its inbuilt drawback like it requires substantial electrical power input. Therefore, development of solar light harvesting photocatalytic materials is a focus of current research in this field.

ZnO, Fe_2O_3 and CuO are promising semiconductors with a large excitation binding energy, catalytic and electronic properties. (Band Gap ZnO-3.7 eV, Fe2O3 -2.3 eV, CuO - 3.14 eV) [1]. Due to these properties, ZnO, CuO, Fe_2O_3 are used in various applications such as room-temperature UV-lasers [2], ultraviolet light-emitting diodes [3], field-effect transistors [4], solar cells [5] and optoelectronics [6].

These are important materials in “green chemistry”, taking into account of its usefulness for photo catalytic degradation of hazardous organic dyes [7]. The photocatalytic activity of the nanoparticles is strongly dependent onthe morphologyof crystallites. Concomitantly, higher surface area of the catalyst facilitates the higher efficiency of the catalyst. Incidentally, both the properties are dependent on the process of preparation of catalyst. Among various applications of nanostructures, the photocatalytic degradation of hazardous organic dyes and chemicals are very important considering the present day problem of environment protection.

Various methods have been reported in the literature such as thermal evaporation [18], molecular beam epitaxy [8], vapor deposition [9] and metal-organic chemical vapor deposition [10] for the preparation of nanoparticles having suitable structure and morphology for catalytic application. Many of these methods consist of complex procedures, use of sophisticated and expensive instrumental systems, high temperature, low or high pressure and toxic source materials, higher energy inputs etc. On the other hand, the hydrothermal approach can allow the growth of nanoparticles form at much lower temperature (< 200^{o} C) without using any sophisticated instrumentation.

There are also different method like solvothermal [11], sol-gel [12], chemical bath deposition (CBD) [13], template-based self assembly processes [14]. Chemical methods normally use capping agent capable of stabilizing a particular crystal facets and also to tune the size and shape of nanostructures.

Among various applications of the mentioned nanostructures, the photocatalytic degradation of hazardous organic dyes and chemicals are very important considering the present day problem of environment protection. Rhodamine B is a commonly discharged material from papers, plastics, textiles and rubber industries and cause severe water pollution and hence effectively disturbs the ecosystems [15]. Therefore, it is important to develop an effective method to degrade the Rhodamine B in water. Photocatalytic degradation can become green technology for industrial down-flow water treatment. These nanomaterials have been proved to be effective photocatalysts for the said purpose in earlier studies [16, 17].

MATERIALS AND METHOD.

1.1Materials for Fe_2O_3

The precursor used for the preparation of Fe_2O_3 nanoparticles was Analytical grade Ferric Chloride ($FeCl_3$) and Tetramethyl ammonium hydroxide (TMAH).

1.2 Materials for CuO

The precursor used for the preparation of CuO nanoparticles was Analytical grade Copper Acetate {$Cu(CH_3COOH)$} and Tetramethyl ammonium hydroxide (TMAH).

1.3 Materials for ZnO

The precursor used for the preparation of ZnO nanoparticles was Analytical grade Zinc Sulphate ($ZnSO_4$) and Tetramethyl ammonium hydroxide (TMAH).

2.1 **Method of Preparation of nanoparticles**

The nanoparticles were synthesized by hydrothermal process. Initially the precursor of the particular nanoparticles were prepared of various concentration viz. 1M, 2M, 3M, 4M, 5M. 40 ml of precursor and 40 ml of TMAH were taken in the hydrothermal apparatus.The apparatus was kept in the oven and heated at 120^{o}C for 4 hrs.

3.1 **CHARACTERIZATION**

The Formation of nanoparticles was detected by UV Spectroscopy.

The as-synthesized products were investigated for their morphological, structural and optical properties. The morphologies were examined by Environmental scanning electron microscope which was taken in Savitribai Phule Pune University and National Chemical Laboratory respectively.

The surface characterization of the ZnO nanoparticles was also done by XPS analysis.

4.1 **PHOTODEGRADATION OF RHODAMINE B**

The photocatalytic activity of as-synthesized nanoparticles was evaluated by monitoring the photocatalytic decomposition of Rhodamine B. 0.2 PPM of Rhodamine B aqueous solution was used to study the catalytic activity of film. Before the sample was exposed to UV-Vis radiation by a 250 W Mercury lamp to study photocatalytic degradation, sample was immersed in 10 ml of 0.2 PPM Rhodamine B dye solution in Petri-dish and then kept in dark for 30 min to obtain adsorption equilibrium. The concentration of Rhodamine B in solution after reaction at various time intervals was calculated by measuring the UV-Vis absorption.

To estimate the photostability of catalyst, 3 cycles of photodegradation experiments were carried out. The decomposition of the Rhodamine B was observed by measuring the absorbance at regular time intervals after each cycle.

RESULTS AND DISCUSSION:

UV-Vis spectroscopy gives evidence that the as synthesized Fe_2O_3 nanoparticles have narrow absorption width in UV range and broad absorption width in visible range and thus can useful for the photocatalytic reactions in visible light.The highest photo catalytic efficiency was observed for the particles of Fe_2O_3 as compared to CuO and ZnO nanoparticles. The Spectrum obtained is as shown below in Fig A.

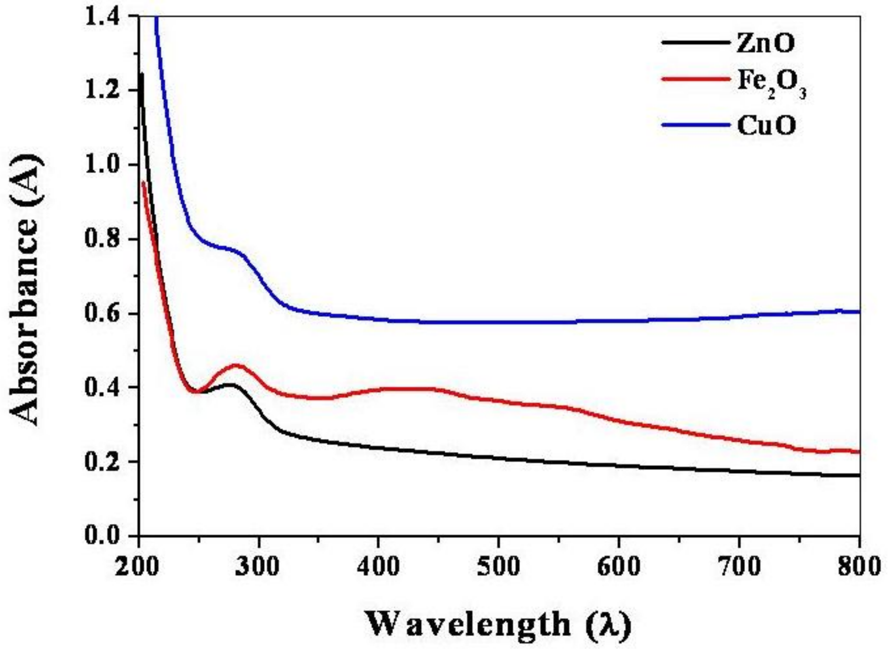


Fig A: -UV-Visible absorption spectra of the as grown nanoparticles

The evaluation of the structural morphology of as synthesized nanoparticles was studied by characterizing it by SEM. The results are shown in Fig B.

The SEM observations indicate that the products are composed of various morphologies porous and flowery for CuO Spherical homogenous well dispersed for Fe_2O_3 and porous spongy for ZnO.

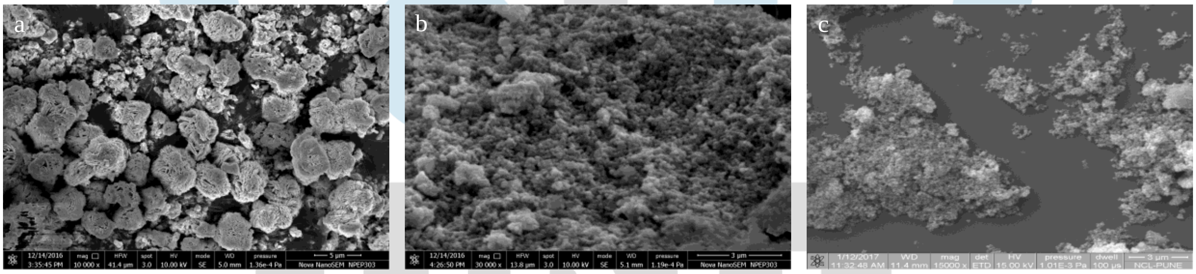
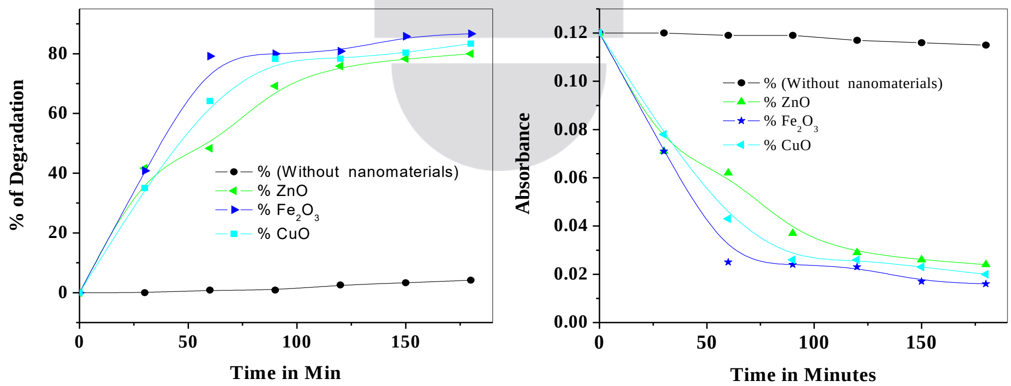


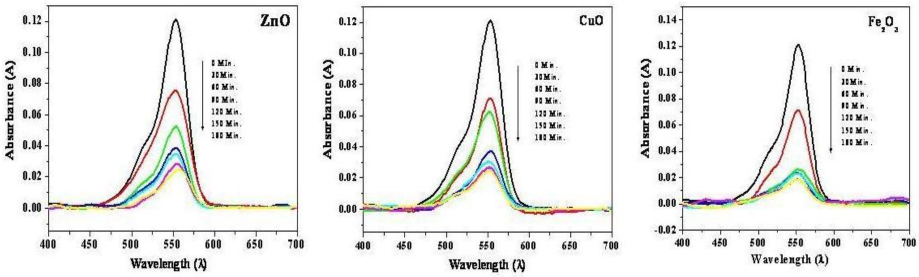
Fig B SEM images of a) CuO b) ZnO and c) Fe_2O_3 respectively

To demonstrate the potential application of the end product nanoparticles, photocatalytic decomposition of Rhodamine B, is studied as a function of time of reaction under UV exposure.

Fig. C (supporting information) shows a typical time-dependent UV-Vis spectrum of Rhodamine B dye in presence of nanoparticles. It clearly shows that with increasing the UV-irradiation time, the absorption intensity of Rhodamine B decreases confirming the degradation of Rhodamine B.



Typical plot of (a) % degradation versus irradiation time, (b) relative absorption (A/Ao) versus irradiation time



Typical time-dependent UV-Vis spectrum of Rhodamine B dye in presence of nanoparticles..

CONCLUSION:

In conclusion, we have successfully synthesized surfactant free well-crystalline nanoparticles of ZnO, CuO and Fe_2O_3 with different morphologies by using hydrothermal technique. The as-synthesized nanostructures are utilized as an efficient photo catalyst for the photo catalytic degradation of organic dyes which exhibits sufficiently high degradation ~ 80% within 180 min. Fe_2O_3 showed 80% catalytic efficiency ZnO 60% and CuO 70% thus Fe_2O_3 was found to be the best catalyst. Fe_2O_3 can be reused as it can be magnetically separated.

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