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MICROWAVE ASSISTED SYNTHESIS, CHARACTERIZATION AND PHOTO-CATALYTIC STUDY OF Cu/ZnO NANOCOMPOSITE

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ABSTRACT

In recent years, nano-sized transition metal oxides gained interest due to their exceptional physical, chemical, magnetic, and electronic properties. Scientist figured out that, the properties of the nano metal oxides are tunable by adding impurities. Due to variable properties, they find application in gas sensors, batteries, wastewater treatment, and catalysis. In this work, copper doped zinc oxide nano-composites were prepared by irradiating with microwave radiation - a green method. The obtained material is characterized by diffuse reflectance spectroscopy (DRS-UV), X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), energy dispersive X-ray analysis (EDX), and scanning electron microscopy (SEM). Photocatalytic properties were studied using dye degradation of methylene blue under Sunlight and catalyst show promising remedy for wastewater treatment.

Keywords: Copper Oxide, Zinc Oxide, Photocatalyst, Effluent Treatment, Dye Degradation, Semiconductor.

INTRODUCTION

Synthetic dyes are one of the constituents of the industrial effluents, which are carcinogenic in nature and pose a major environmental threat.[1]Different methods such as biodegradation, coagulation, advanced oxidation processes (AOPs), photocatalytic technology and the membrane process have been adopted to remove organic dyes from the environment.[2-8] Among which photocatalytic technology is found to be an effective method in removing organic dye from the environment.[2]Photocatalytic technology employs a semiconductor material as photocatalyst. These semiconductor materials are activated by photons and lead to degrading the organic dye pollutants completely into carbon dioxide, water and minerals by the advanced oxidation process.[9,10] The production of superoxide and hydroxyl radicals are responsible for the oxidative degradation of organic dye.[11,12]

In the recent development of nanotechnology, involves the production of efficient materials with photocatalytic ability to degrade organic dyes in the presence of light. Semiconducting metal oxide nanocomposites are widely used in this field. Among the various material used as a photocatalyst, titanium dioxide (TiO_2)as a photocatalyst has gained attention mainly due to its availability, photoreactivity, and photostability.[13,14] Zinc oxide (ZnO) nanostructures, on the other hand, are considered as an alternative for TiO_2,though both the semiconductors have similar band gap and antibacterial property.[15,16]ZnO nanostructures could be more suitable for photocatalytic applications due to its high catalytic activity, availability, and non-toxicity. These semiconducting metal oxides have a wide band gap, hence they show photocatalyic activity mainly in UV region. It is found that, the band gap of the metal oxide is tunable by doping with different elements.[17-24]The copper doped ZnO nanocomposites (Cu/ZnO) are found to be an efficient photocatalyst to deal with the degradation of dyes under irradiation of ultraviolet (UV) or visible light.

There are various methods to synthesize Cu/ZnO nanocomposites. They are namely precipitation and co-precipitation method, sol-gel processing method, hydrothermal method, solvo thermal method, pyrolysis method, and microwave irradiation method.[24,25] In the above-mentioned method, Microwave (MW) irradiation method assists in the enhancement of the production of nanocomposites with improved photocatalytic efficiency of Cu doped ZnO. Microwave irradiation assisted the synthesis of Cu/ZnO nanocomposites has quicker reaction time, requiring only a simple reaction medium, and controlling over the morphology of particles.[26]

In this article, we describe the synthesis of Cu/ZnO nanocomposites by using microwave-assisted method and systematic study on the effect of doping of copper in zinc oxide. The consequent photocatalytic ability of synthesized Cu/ZnO nanocomposites in the presence of sunlight is demonstrated towards the degradation of methylene blue dye.

EXPERIMENTAL

All the chemicals used such as Zinc sulphate ($ZnSO_4.7H_2O$), copper sulphate ($CuSO_4.5H_2O$), sodium hydroxide (NaOH), and L-ascorbic acid ($C_6H_8O_6$) were bought from Loba Chemie, India is analytical grade reagents without any further purification. Double distilled water is used for the preparation of all solutions.

The prepared sample was characterized by diffuse reflectance spectroscopy(DRS-UV) using JASCO V - 660 UV-Visible spectrometer in the wavelength range 200 – 800 nm, Infrared (IR) spectroscopy using JASCO FTIR 4100 spectrometer by KBr pellet method and X-Ray diffraction (XRD) using Bruker D8 Advanced Powder XRD diffractometer with Ni-filtered Cu Kα radiation. The surface morphology and elemental composition studies are carried out by using scanning electron microscopy (SU6600, Hitachi, Japan).

Preparation of Zinc oxide Nanoparticles

Solution of zinc (II) sulphate (0.1 M, 250 mL) and sodium hydroxide (0.2 M, 250 mL) were prepared with double distilled water separately. Zinc sulphate solution was taken in a 1000 mL beaker, which is placed over a magnetic stirrer. Sodium hydroxide solution was added drop wise into the beaker containing zinc sulphate solution and stirred for 2 hours. A precipitate was formed, which indicates the formation of zinc hydroxide ($Zn(OH)_2$). The precipitate could be filtered and then dried at 120 ^oC for 2 hours in a hot air oven. The dried precipitated was irradiated with microwave for 15 minutes resulting in the formation of zinc oxide nanoparticles.

Preparation of Copper/ZincOxide Nanocomposites

Attempts were made to synthesize copper/zinc oxide nanocomposites in different ratios i.e., Zn and Cu in the ratio of 1:0.004, 1:0.008, and 1:0.012 were prepared. Solution of zinc (II) sulphate (250 mL, 0.1 M) and sodium hydroxide (250 mL, 0.2 M) were prepared with double distilled water. Zinc sulphatesolution was taken in a 1000 mL beaker and heated to 80 ^oC. To the above hot solution, freshly prepared mixture of copper sulphate solution and ascorbic acid solution were added with continuous stirring using a magnetic stirrer. To this, sodium hydroxide solution was added drop wise and stirred for 2 hours. The precipitate was filtered and then dried at 120 ^oC for 2 hours in a hot air oven. The dried precipitated was irradiated with microwave for 15 minutes resulting in the formation of copper/zinc oxide nanocomposites.

Photocatalytic Study

The photocatalytic property of each sample was studied by the degradation of methylene blue dye under sunlight. The photocatalytic studies were carried out between 11 am to 3 pm of a day (intensity above 10000 Lux) and the intensity was measured using an HTC instrument LX-101A Light Meter LUX meter. The dosages of the prepared catalyst for photodegradation studies were kept 0.5 g/L. To establish the adsorption-desorption equilibrium between the catalytic surface and the dye, the system was stirred for 2 h under dark, before irradiation. The experiments were carried out with 500 mL of methylene blue of 10 ppm concentration undert he constant stirring condition with simultaneous exposure to sunlight. The degradation process was observed by measuring the absorbance using a spectrocolorimeter at 660 nm wavelength. The time for the complete de-colourization is noted.

RESULTS AND DISCUSSION

Optical Study

DRS-UV spectra of ZnO nanoparticles and Cu/ZnO composites (1:0.012) are shown in Fig.-1a and 1b. Both the spectrum shows a characteristic peak of ZnO at 360 nm.[18,27] The incorporation of copper into zinc oxide is indicated by a shoulder peak at 450 nm in Fig.-1b.

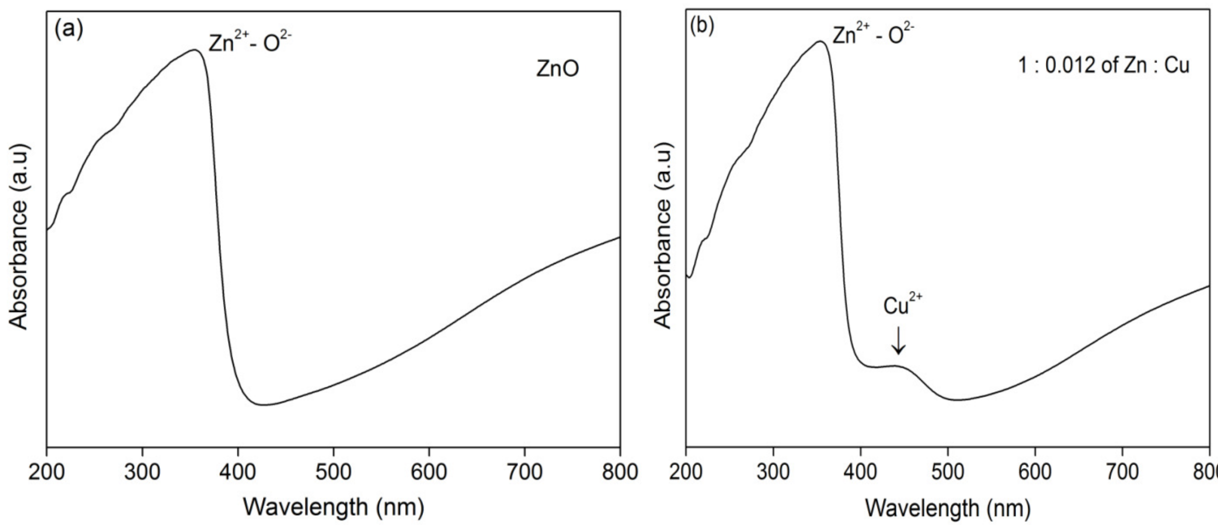

Fig.-1: DRS-UV Spectrum of (a) ZnO Nanoparticles (b) Cu/ZnO Nanocomposite

Fourier Transforms Infrared (FT IR) Spectroscopy Study

Figure-2 shows the FT IR spectrum of Cu/ZnO nanocomposite. The bands at 460 cm^{-1} and 552 $cm^{-1}$are characteristic peaks of Zn-O stretching vibrations.[27]Anotherband at 619 cm^{-1} is assigned to the interaction between copper and oxide ion indicating the formation of Cu/ZnO nanocomposite.

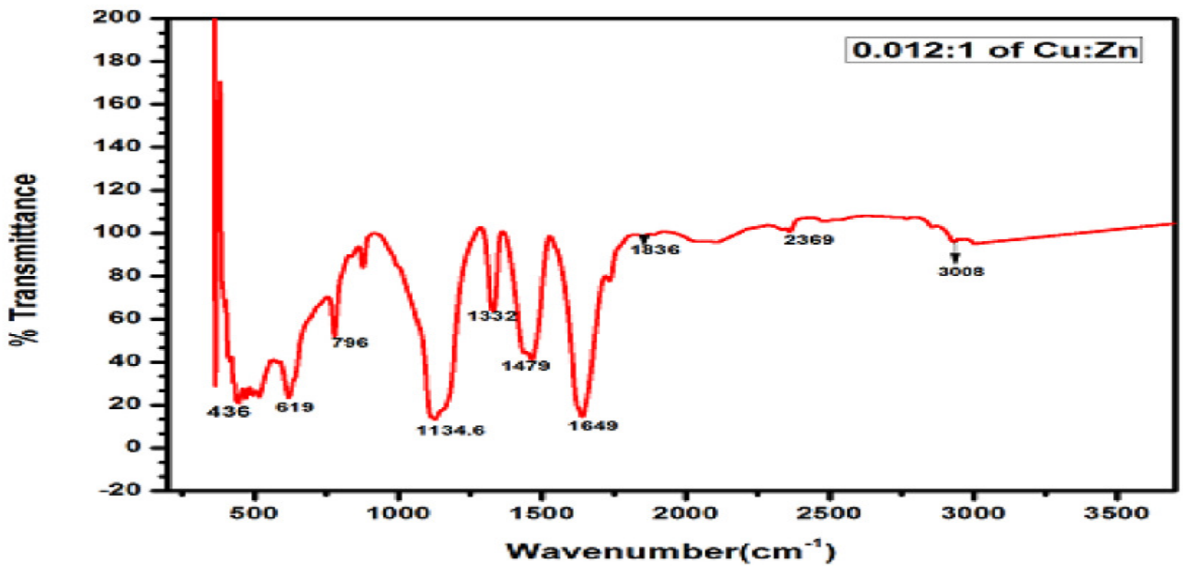

Fig.-2: FT IR Spectrum of Cu/ZnO Nanocomposite

X-Ray Diffraction Analysis

Figure-3 displays the XRD pattern of Cu/ZnO nanocomposite. The XRD pattern exhibits a hexagonal crystal structure without any other crystalline phases. The 2θpeaks at 31.72°, 34.46°, 36.35°, 47.43°, 56.51°, 62.79°, 66.44°, 68.01°, and 69.07° were assigned to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) reflection planes of hexagonal ZnO respectively.[16,18] This XRD is in accordance with the JCPDS No. 45-0937.The additional peaks at 22.66° and 23.66° could be attributed to the copper and indicating the formation of Cu /ZnO nanocomposites.

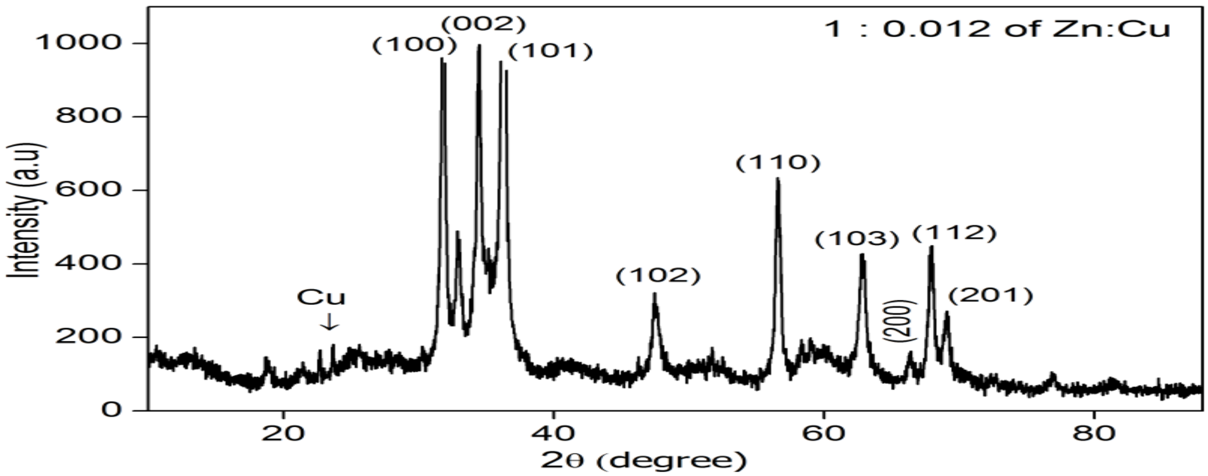

Fig.-3: XRD of Cu/ZnO Nanocomposite

Surface Morphology Study

The surface morphology of copper-doped zinc oxide nanocomposites was studied from scanning electron microscopy (SEM) images, as shown in Fig.-4 (a, b) It is inferred from Fig.-4 (a, b) that copper-doped zinc oxide having more dia. (around ~ 40 to 85nm). These pictures substantiate the formation of agglomerated nanocomposites showing flak like structure.

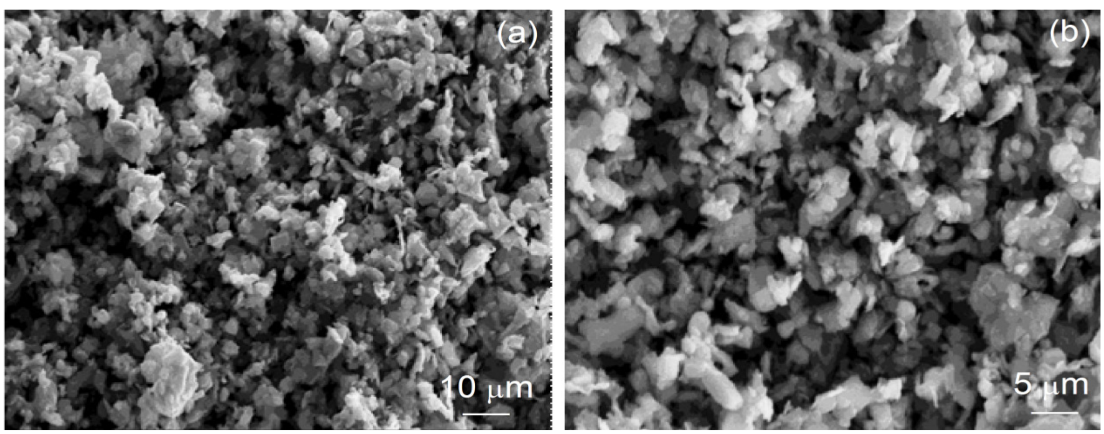

Fig.-4: SEM Images of Copper/Zinc Oxide Nanocomposite at Magnification of (a) 10 µm and (b) 5 µm

Energy Dispersive X-ray Analysis

The elemental composition of the prepared samples obtained from the EDX integrated together with the XRD confirms the presence of Zn, O and Cu as well as their composition. The elemental analysis of Cu/ZnO nanocomposite (ratio) is reflected in Table-1.

Table-1: Composition of Elemental Analysis of the Cu Doped ZnONanocomposites

Element	Weight Percentage	Atomic Percentage
O K	40.88	73.84
Cu K	2.81	1.28
Zn K	56.31	24.88
Total	100	100

Photocatalytic Studies

The photocatalytic property of zinc oxide nanoparticles and copper/zinc oxide nanocomposites (Zn: Cu ratio is 1:0.012) were studied by the degradation of methylene blue dye under sunlight.[28] It is observed that, pure zinc oxide nanoparticles failed to decolorise the dye solution under sunlight, whereas copper doped zinc oxide nanocomposites exhibited an excellent photocatalytic activity by decolorizing methylene blue dye solution under sunlight (Fig. 6a and 6b). The time taken for complete decolorization is 2h. The small hump observed in the DRS-UV spectrum (Fig.-1b) aids the copper-doped zinc oxide nanocomposites to show photocatalytic activity. The catalyst was filtered and similar experiments were repeated for five times. The prepared nanocomposite materials still exhibited similar activity, which shows promising to detoxify the effluents from the dye factory.

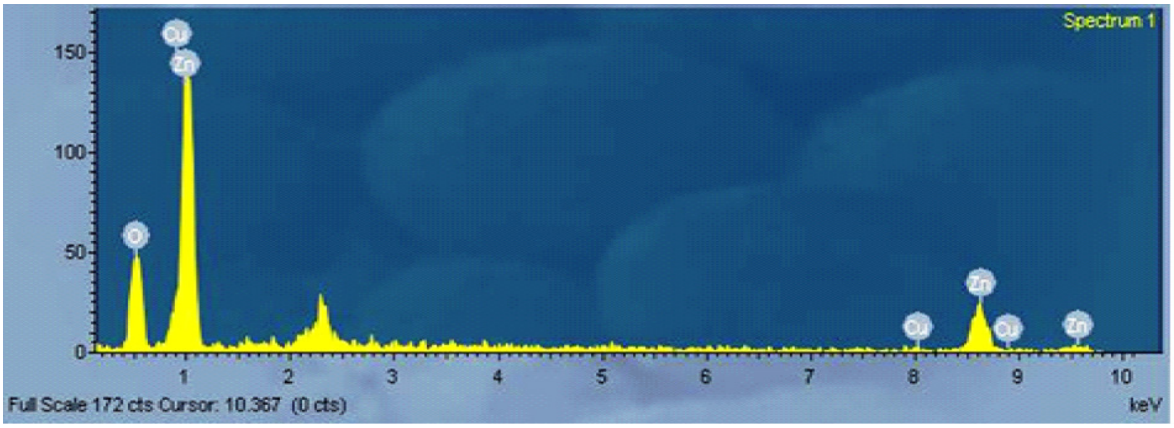

Fig.-5: EDX Spectra of the Cu/ZnONanocomposites

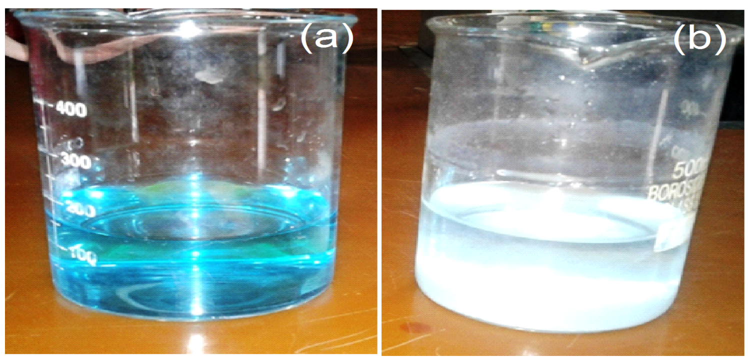

Fig.-6: Methylene Blue Dye(10 ppm) Solution Under Sunlight (a) Before and (b)After

CONCLUSION

Copper doped zinc oxide nanocomposites were synthesized in the varying composition of copper by microwave irradiation method. From the characterizations, it is evident that copper-doped zinc oxides are formed. The particles were found to be agglomerated with flak like structure in diameter around 40 ~ 80 nm. Photocatalytic studies were carried out for the pure zinc oxide nanoparticles and copper doped zinc oxide nanocomposites under sunlight. Copper doping has found to be enhancing the photocatalytic activity of ZnO. Copper doped zinc oxide nanocomposites exhibited excellent photocatalytic activity by decolourizing the methylene blue dye solution under sunlight. The reusability of the sample also showed promising results.

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