CuO-ZnO nanostructure for photocatalysis application using methylene blue(MB)

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Abstract
Implementing a hydrothermal method, ZnO modified copper oxide (CuO) photocatalysts were developed. The morphology, structure, composition and photocatalysts were examined using Scanning electron microscopy (SEM), X-ray diffraction (XRD), Energy dispersive X-ray (EDX), Fourier Transform Infrared Spectroscopy (FTIR) and UV-visible spectroscopy. The X-ray data confirmed the crystalline nature of CuO. The EDX and FTIR showed composition of samples as Cu, O and Zn.

Additionally, the effect of zinc oxide impurity on the photocatalytic activity of CuO nanocatalysts in the methylene blue (MB) process of degradation was investigated by UV-Visible spectroscopy. The degradation results indicated that ZnO doped CuO (CuO-ZnO) photocatalysts were more effective in degrading the MB because of their band gap.

Keywords: Nanostructure, Photo degradation, Methylene blue, Conduction band, Photocatalysis.

Introduction

Chemical, soil and air pollution levels have recently surpassed global limits, endangering entire ecosystems. There are numerous ways to address environmental pollution including legislation, policies, monitoring and more. Therefore, it is crucial to investigate effective solutions for these environmental issues if our society is to develop sustainably. Technically speaking, the scientific community concentrated on creating techniques for getting rid of the pollutants, including chemical oxidation, oxidation, biological, ultrafiltration, physical treatment, photocatalysis, adsorption and phytoremediation. In this case, photocatalysis is a useful method with a low working temperature, a reasonable cost and particularly the absence of secondary pollutants[2,3,20].

Organic dyes and pigments are considered to be the cause of water pollution in a number of industries, including the printing, paint, leather, textile and paper industries. In particular, approximately 20% of all water pollution from paints, food coloring, food and other items is caused by industrial textile dyes, which contain a variety of harmful organic compounds[8,23]. Transition-metal oxides are considered to be the most promising catalysts for effectively, rapidly and sustainably cleaning wastewater because they have the highest photocatalytic activity, the best solubility and the best stability. Recently, organic dyes have been broken down or oxidized into chemical compounds using nanostructured semiconducting materials as photocatalysts[12]. Most common P-type metal oxide semiconductors are made of CuO, NiO and SnO. CuO has been identified as a particularly promising material for use in a wide range of applications, such as field-effect transistors, sensor memory devices, solar energy, photocatalysts for the degradation of organic pollutants and lithium-ion batteries.[3,6,9,11,22].

CuO's effective hole transport and notable decrease in the localized character of the valence band maximum (VBM) make it a promising P-type oxide semiconductor[4]. Cu vacancies that are negatively charged cause P-type behavior. CuO materials can be used in transparent electronics and active matrix devices due to their excellent optical transparency, low processing temperature, good consistency, chemical and thermal stability and easy fabrication method. However, CuO's narrow band-gap energy, tiny surface area and poor conductivity result in low photocatalytic activity. CuO's surface area can be increased.

Doping and composite formation are two methods that can be used to increase the conductivity of CuO extrinsically and intrinsically respectively[5].The most beneficial doped sample appears to have been achieved by doping an appropriate metal cation in the CuO lattice, as this approach not only reduced the band-gap but also improved the electrical properties of the doped sample. The heterojunction is formed when p-type CuO and n-type ZnO are coupled together. High photocatalytic efficiency can be achieved using heterostructures of nano structured CuO-ZnO due to their large specific surface area and increased optical absorption[10,14,16,21].

In this work, we report the synthesis of CuO-ZnO hydrothermally. Catalyst for the quick breakdown of the food color or organic pollutant, the as-prepared CuO-ZnO was extensively studied.

Material and Methods

Materials: Copper 2,4-pentanedionate purity 98%, sodium hydroxide solution (NaOH) 98% purity, zinc nitrate hexahydrate purity 98% were purchased from Thermo Scientific Company.

Synthesis of pure CuO and CuO-ZnO nanostructure: Using a low temperature hydrothermal process, CuO

nanoparticles that were both pure and metal oxide (ZnO) doped, were produced. In order to make CuO, 70 milliliters of doubly de-ionized water were mixed vigorously for 30 minutes after dissolving 3g of copper 2,4-pentanedionate in it. The combination was gradually mixed with the required amount of sodium hydroxide solution (NaOH) until the pH of the mixture reached 8.5. To get a homogeneous solution, the mixture was stirred for three hours. After that, the generated solution was put in an autoclave made of stainless steel with a teflon lining and it was heated to 180°C for eight hours. After letting it cool, the dark brown precipitate was removed.

One gram of zinc nitrate hexahydrate was added to the solution above and the CuO-ZnO nanostructure was prepared in the same way.

Characterization of pure CuO and CuO-ZnO nanostructure: The crystal structure, microstructure, chemical composition, functional group and optical properties of the pure CuO and CuO-ZnO nanostructure films were studied by X-ray diffractometer (XRD), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Fourier transform Infrared Spectroscopy (FTIR) and UV-visible spectroscopy.

Photocatalysis of pure CuO and CuO-ZnO nanostructure: Pure CuO and CuO-ZnO nanostructures that were created were used as a catalyst to break down MB. A standard protocol involved combining 1.6 mL of 1 mM MB solution with 1 mL of 10 mM $NaBH_4$, adding DD water to the reaction mixture to make it up to 10 mL. Stir it for five minutes. The necessary amounts of the synthesized solution were introduced to a cuvette containing 3 milliliters of the reaction mixture. UV-visible spectra were taken at various periods of time.

Results and Discussion

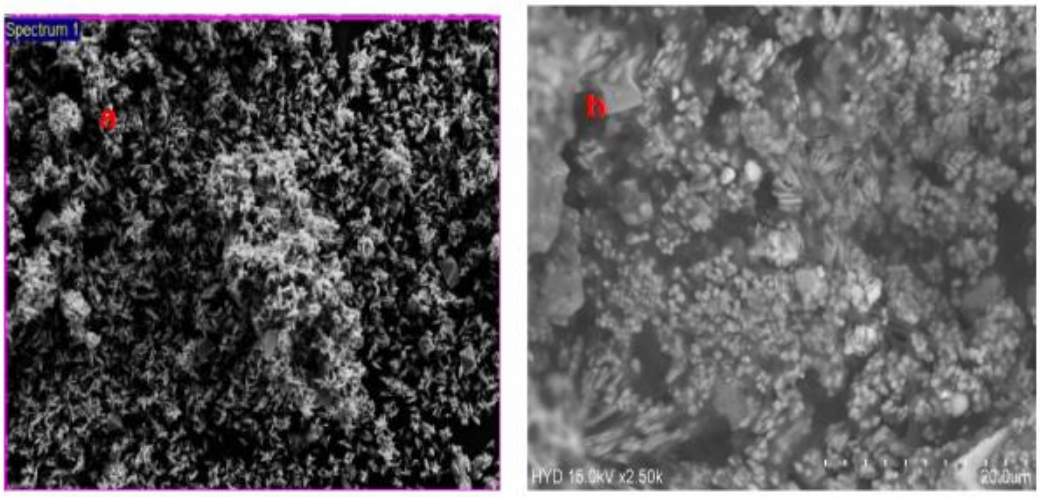

Fig. 1: SEM images of (a) pure CuO and (b) CuO-ZnO nanostructure.

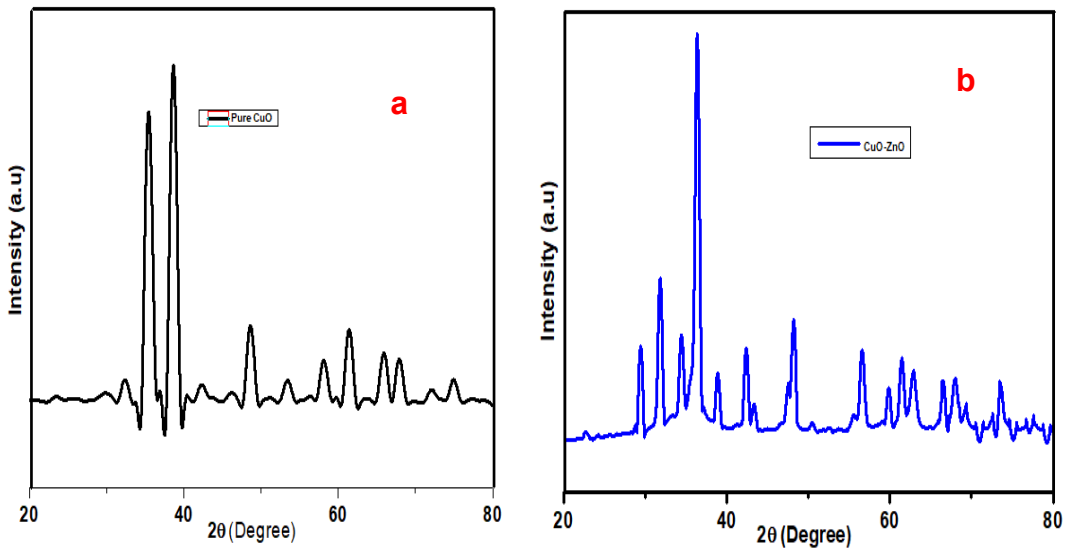

Fig. 2: XRD pattern of (a) pure CuO and (b) CuO-ZnO nanostructure.

Fig 1. displays the morphology of both pure CuO and CuO-ZnO nanostructures. Pure CuO had uniformly distributed nanoflakes. The morphological size changes to tiny nanorods and bubbles after ZnO doping. The CuO-ZnO nanostructures surface area grew. Doping could increase the distance between particles, creating micropores that enhance catalytic activity. Pore formation may also result from the evolution of emissions at elevated temperatures[7].

Fig. 2 shows the powder XRD diagrams of samples of pure CuO and CuO-ZnO nanostructure oxide. Fig 2(a) shows the CuO XRD pattern. Peak values measured 2θ at around 35° and 38°, corresponding to peaks (002), (111), confirmed for monoclinic (JCPDS card no.48-1548)[13,15]. CuO Peak intensity changes after ZnO doping; hexagonal ZnO with confirmed peaks at 32.07° (010) and 36.53° (011) are supported by JCPDS no. 96-101-1259[3].

EDX spectra, as shown in fig. 3, provide information about the sample's purity and the synthesized CuO and CuO-ZnO nanostructures elemental composition. The EDX spectra of CuO-ZnO nanostructure consist of peaks that are unique to Cu, O and Zn. The purity of the nanomaterials was confirmed by the absence of any extra peaks beyond the ones that were predicted. Zn-O peak presence confirms the effective doping of the CuO lattices. The atomic and weight % of pure CuO and CuO-ZnO nanostructure are given in table 1.

The pure CuO and CuO-ZnO nanostructure FTIR spectra are shown in fig 4. The broadband wave numbers between 3430 and 3475 cm^{-1} show a substantial intramolecular hydroxyl group (OH) interaction. The presence of the carboxylic compound was established by the O-H stretching vibrations at approximately 2930 cm^{-1}.

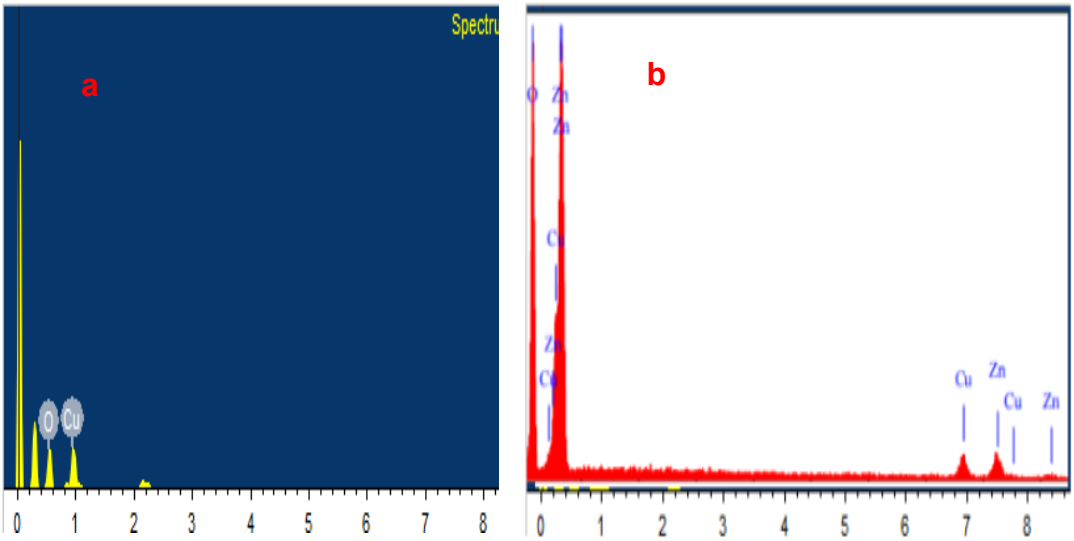

Fig. 3: EDX spectra of (a) pure CuO and (b) CuO-ZnO nanostructure.

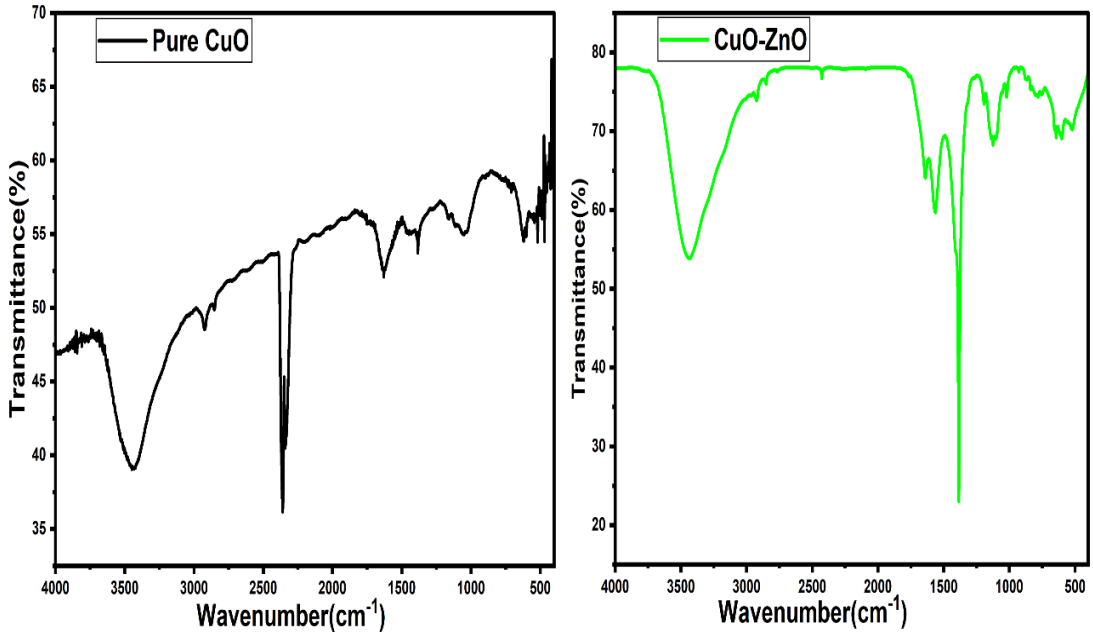

Fig. 4: FTIR of pure CuO and CuO-ZnO nanostructure.

Table 1
Weight and Atomic % of elements in pure CuO and CuO-ZnO nanostructure.

Sample	Element	Weight%	Atomic%
Pure CuO	O K	33.56	68.40
	Cu L	66.44	31.60
CuO-ZnO	O K	24.61	57.09
	Cu L	71.02	41.46
	Zn L	4.37	1.44

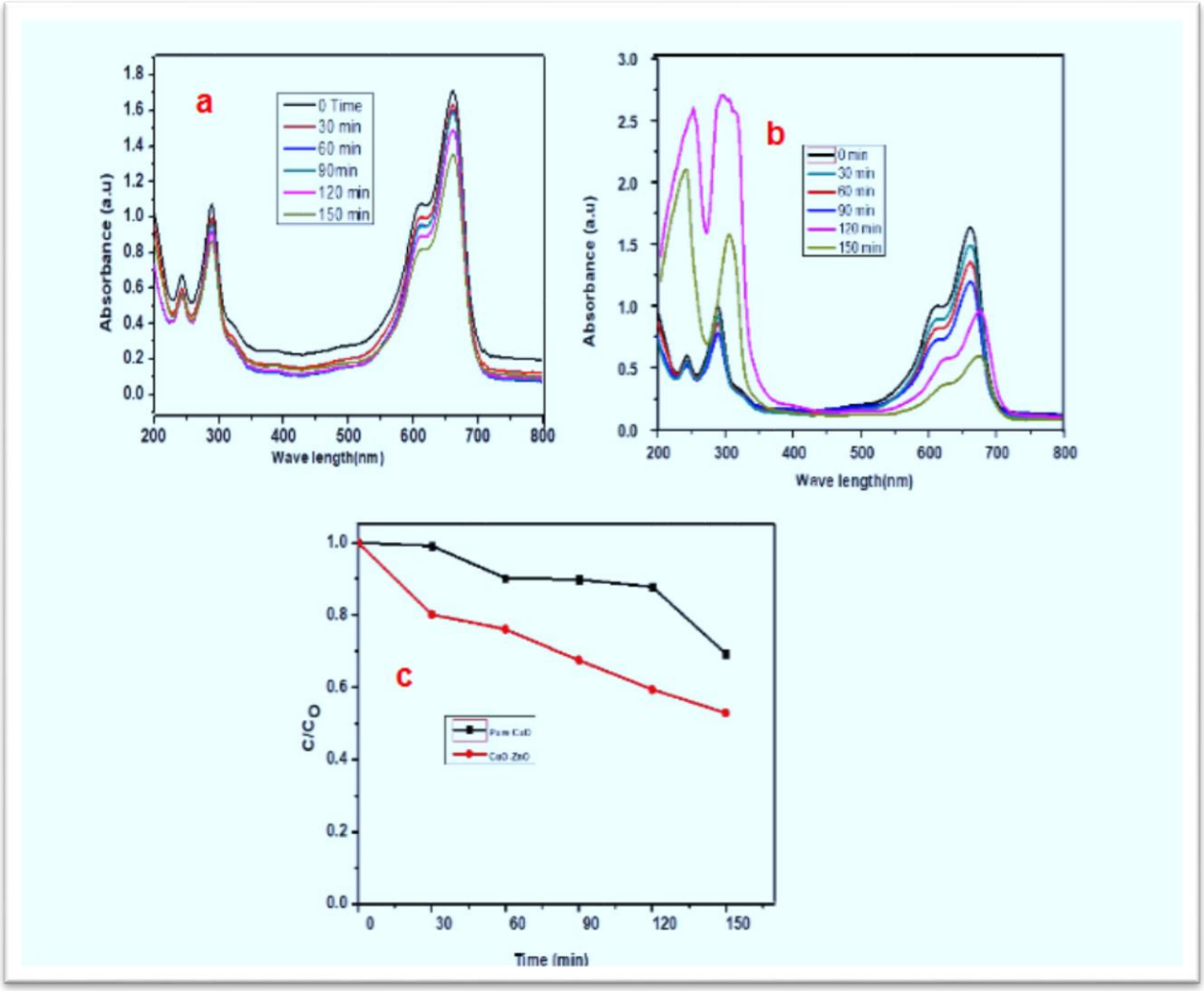

Fig. 5: UV-Visible absorption spectra showing the photodegradation of methylene blue (MB) dye using (a) pure CuO and (b) CuO-ZnO nanostructure. (c) Plot of C/C_O as a function of irradiation time under sunlight exposure.

The interactions of C–N stretching vibrations are represented by the peaks that emerged at approximately 1650 and 1350 cm^{-1}. At 620 cm^{-1}, peaks represent absorption peak of pure CuO. 480 cm^{-1} attributes stretching vibration of ZnO peak[4,18,19]. Because of the interactions between Zn and Cu ions and compounds, a shift in the locations of the CuO-ZnO nano structure peaks was identified at 635 and 487.7 cm^{-1}, relative to pure sample between 800 to 400 cm^{-1}.

According to FTIR results, which also show that all of the synthesized materials exhibit characteristic metal-oxygen vibrations and surface functional groups that promote the production of reactive oxygen species for photocatalysis and antibacterial activity.

Catalytic properties of CuO and CuO-ZnO nanostructure (Catalytic reduction of methylene blue): Prepared CuO and CuO-ZnO nanostructures were used as a catalyst to break down MB organic dye. The UV–visible absorption spectra of aqueous MB are displayed in fig. 5. Three bands were visible in the spectrum at 240, 280 and 660 nm. There was a modest decrease in the peak intensity of

MB dye absorption. It comes to the conclusion that the pure CuO could not completely degrade the color. Additionally, we conducted studies using CuO-ZnO nanostructure to reduce MB. At first, there was a high intensity of absorption peaks at 240, 280 and 660 nm. When compared to pure CuO, the intensity dropped off quickly as the duration increased.

The inclusion of ZnO greatly accelerated the degradation of MB dye. A plot between C/C_0 and reaction time was displayed in fig. 5(c). In this formulation, C_0 represents initial concentration of methylene blue at t=0 (before irradiation) and C represents the concentration at various irradiation times (min). It gives the apparent rate constant (min^{-1}) of the photodegradation reaction. The photodegradation rate constant is higher for CuO-ZnO nanostructure compared to pure CuO nanostructure.

CuO and ZnO formed a heterojunction, which assisted the separation of photogenerated carriers. The band gaps of CuO and ZnO were 1.4 and 3.23 eV respectively. During sunlight irradiation, CuO and ZnO were excited to generate electrons and holes at the conduction band (CB) and the valence band (VB) respectively, since the band positions of ZnO were below the CB and VB of CuO. The photoexcited electrons transferred from CuO to ZnO, whereas the holes migrated from ZnO to CuO.

Then, oxygen molecules in dye solution reacted with electrons to generate superoxide radical ($\bullet O_2^-$) and the holes combined with H_2O to produce hydroxyl radical (•OH). Moreover, MB was directly oxidized by the holes at the VB of CuO[1,17].

Conclusion

The hydrothermal synthesis of pure CuO and CuO-ZnO nanostructure is demonstrated in this work. The XRD analysis reported the CuO-ZnO nanostructure's as hexagonal form. The produced nanostructure's elemental compositions (Zn, Cu and O) were verified using the EDX spectrum. CuO-ZnO nanostructure demonstrates excellent photodegradation for methylene blue dye elimination efficiency.

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