Photocatalytic effect of CuO nanostructures under sun light irradiation for environmental application

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Abstract:

The current study focuses on creating copper oxide nanostructures using a hydrothermal process, examining the fundamental characteristics of CuO nanostructures, and analysing the photocatalytic behaviour of CuO samples. SEM-assisted morphological analyses showed that CuO developed anoflakes structures. The x-ray diffraction (XRD) pattern confirms the modest variances in peak positions. The photo catalytic performance of the samples examined during the methylene blue (MB) dye degradation indicates that samples perform better.

Keywords: Morophology, CuO, Methylene blue, Photo catalysis

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Introduction

Environmental pollution is a serious problem for current and future generations because it is linked to saviour health problems, loss of biodiversity and destruction of ecosystem. Contamination problems caused in large part by human activities have become more severe due to unbridled materialism after the industrial revolution. Unplanned industry growth, the use of antiquated waste processing techniques, and ineffective waste disposal have all led to harm with long-term negative effects by continuously allowing poisons to permeate into nature, water, and soil [1-3]. Due to their distinctive electrical, optical, magnetic, and biological properties, metal oxide nanostructures have attached much attention and young researchers in recent decades. Pollutants are converted into harmless substances such as CO_2, H_2O, and others photo catalysis. It allows the use of light to accelerate catalytic reactions and has garnered widespread praise as the most beneficial method [4]. The use of process engineering techniques for photocatalysis has shown that heterogeneous photocatalysis is most common due to its improved stability, the ease of product separation, and the simplicity of photo-catalyst recycling. On the surface of semiconductor materials (photocatalyst), photoinduced chemical reactions are also involved. A photocatalyst that emits light larger than or equal to the energy of its bandgap leads electrons to migrate from the valence band (VB) to the conduction band (CB), leaving positive holes (h +) in VB. Conversely, the CB bands can receive negative electrons without damaging semiconductor. The most powerful photocatalysts are often semiconductors because of their high band width energy and distinctive electrical arrangement with occupied with the VB and the unoccupied CB [5]. The anticipated photo-catalytic activities for the elimination of diverse organic contaminants were delivered by semiconductors due to their ability to distinguish between electronic, light absorption, charge transfer, and porous structural features.

Metal oxide nanostructures are used in a variety of products, including pigments, fluids, catalysts, sensors, and the controlled administration of medication. Metallic nanoparticles are common and have become promising materials for environmental cleaning because of their small bandwidth, low cost, non-toxic nature, chemical stability, and thermal stability [6]. Transition metal oxides (TMOs), including TiO_2, ZnO, MnO_2, SnO_2, WO_3, and CuO, have recently drawn a lot of interest from the research community due to their remarkable physical

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and chemical properties [7-15]. Because of their amazing qualities such as biocompatibility, high stability, and cost effectiveness, metal oxide nanostructures are largely favoured in a variety of applications, including photocatalytic investigations. Copper oxide (CuO) is a P transition metal semiconductor (TMS) with a low bandgap and good stability. As the structure and morphology is one of the key factors influencing the many physical and chemical properties displayed by the semiconducting sample, tuning the morphology and understanding the science underlying its development seem to be of utmost importance [7]. CuO is a semiconductor with an indirect gap and optical band width energy of 1.5 eV, making it ideal for sunlight absorption [16]. CuO has additionally been used to photocatalyst the breakdown of organic contaminants. Even though CuO has received a lot of attention as a useful photocatalyst, its photocatalytic abilities for the degradation of pollutants are directly correlated with the method of manufacture, particle size, and shape. Therefore, it is both theoretically and practically significant to explore the synthesis and applications of CuO [17-18]. Sol-gel, chemical precipitation technique, ball milling, microwave-assisted procedure, ultrasonication, hydrothermal, combustion, and mechanical alloying are a few of the various ways utilized to generate metal oxide nanostructures [7-11]. Due to its simplicity and other benefits including the low-temperature need and possibility for large-scale production, the hydrothermal approach has been regarded as the most promising method for the controlled synthesis of CuO nanostructures. Here, we describe a straightforward hydrothermal method for producing very stable CuO nanostructures with enhanced surface areas. The photocatalytic activity of these nanostructures on organic pollutants like methylene blue has also been studied. Using a recycling experiment, the stability of the CuO catalyst was evaluated.

2 Experiments

2.1 Materials

Materials: Copper acetylacetonate, Sodium hydroxide, distil water, ethanol

2.2 Synthesis of CuO nanostructure:

Synthesis route from precursors of copper acetyl acetonate [$Cu(C_5H_7)_2$ in the first approach 3-gram copper acetylacetonate used with 0.3-gram Sodium hydroxide (NaOH) and distilled water as solvent. These solutions will keep in stainless steel autoclaves at three different

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temperatures 150 °C for 10 hours then allow cool to room temperature naturally. A dark precipitate will collect after being filtered and wash with distilled water and absolute ethanol to remove the residue of inorganic/organic impurities. . The final products dried at 60°C for 20h under ambient air**.**

2.3 Material characterizations

To determine the crystal phase CuO photocatalyst powders, X-ray powder diffraction (XRD) analysis was carried out at room temperature) with Cu Kα radiation (λ = 0.15406 nm), over the 2θ collection range of 0–80◦. The FE-SEM (Field Emission Scanning Electron Microscope) images and EDX (Energy-dispersive X-Ray) spectra were obtained from ZEISS-LEO SUPRA-55 and JEOL-JCM-6000 plus, Surface morphology of the sample was studied by atomic force microscopy (AFM). The UV-Visible investigations of the synthesized photo-catalysts were finished on Carry-60 UV/Vis spectrometer.

2.4. Photo-catalytic degradation

The degradation of MB-dye in the presence of visible light radiations was used to test the photocatalytic capability of pure CuO nanostructures. It was done by using a UV cut-off filter to remove UV light from the sun spectrum. To create an equilibrium between the MB-dye and photo-catalyst, 5 mg of pure CuO was added to a 5-ppm solution of MB-dye, and the two substances were then mixed together in the dark for 60 minutes. In order to analyse the photo catalytic process, the photocatalytic reaction vessel was placed under visible sunlight while being constantly stirred after the dark reaction. The 5 mL suspension was removed from the reaction vessel after 30 minutes and centrifuged for 3 minutes to separate the photocatalyst. The residual MB-concentration dye's was calculated using its absorption spectra around 595 nm. The developed photocatalysts' ability to degrade or decompose was calculated.

3. Result and discussion

Structural analysis

The main characteristic diffraction peaks of the samples are consistent and the corresponding 2θ is also consistent, indicating that the sample. Consistent with the peaks of the copper oxide standard Fig. 1 shows the XRD spectrum of sample, which has CuO synthesis at 150 ^{0}C hydrothermal temperatures. The sample shows distinct peaks at 2θ around 35.5°, 38.9°,48.5°,

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58.5°, 62.°, 67, 68, 73°,76°C, can be assigned to (002), (111), (− 202), (202), (− 113), (− 311), (− 220), (311), (− 222) reflections, respectively of the monoclinic structure of CuO phase, in agreement with JCPDS card No.45-0937 [19, 20], No peaks of impurities could be detected, suggesting the high purity. The average crystallite sizes of the CuO nanostructures were calculated using the Scherrer equation given below, K = βcosθ/kλ; where, k is a material constant called shape factor, λ is the wavelength of x-ray source used, β is the full width at half maxima of the XRD peak in radians and θ is the diffraction angle [21]. The average crystallite size as calculated using Scherer's equation. The results show that by increasing the in-situ hydrothermal temperature, the XRD peaks increase in intensity and their FWHM reduces, indicating an improvement in the crystallinity of the samples synthesis at elevated temperature. Atomic diffusion is responsible for the temperature-related growth in crystallite size. Diffusion is the progressive movement of atoms from one lattice position to another from an atomic perspective. In actuality, the atoms within solid materials are constantly shifting places. An atom needs enough energy to break bonds with its neighbouring atoms and then exert enough lattice distortion during the displacement in order to make such a motion. The atoms gather enough energy as the temperature rises to allow for diffusive motion, which leads to a growth in size [22].

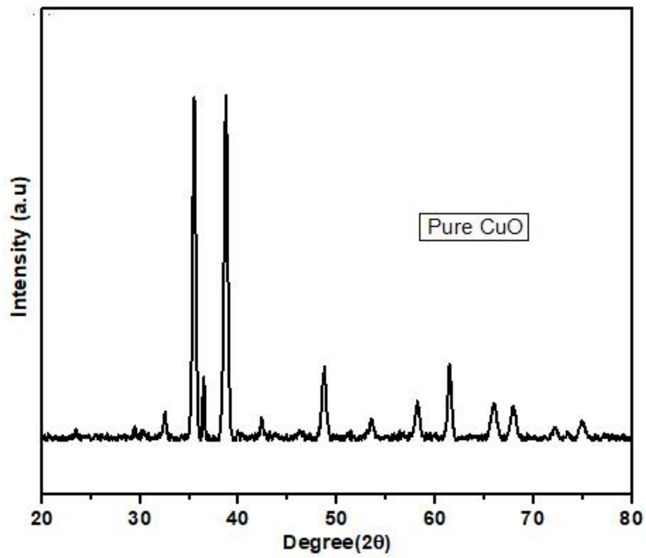

Fig 1. XRD pattern of CuO nanostructure at 150°C.

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The development of CuO nanoflakes shapes was confirmed by the results of field emission scanning electron microscopy (FESEM). At the sample exhibits aggregated nanoflakes. Nanoflakes need energy to move in order to combine nearby crystallites and generate crystallinity. Since crystal development and rearrangement of crystallinity are not achievable at extremely low temperatures, temperature variation can provide the thermal energy needed for crystal formation [22].

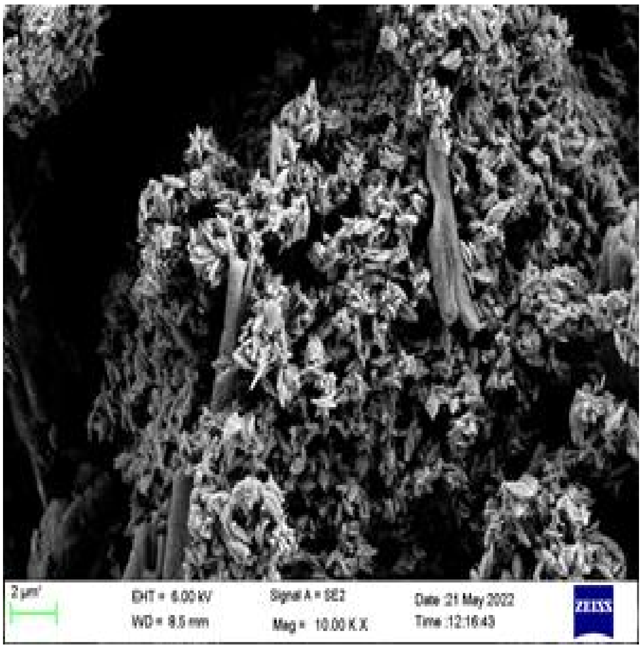
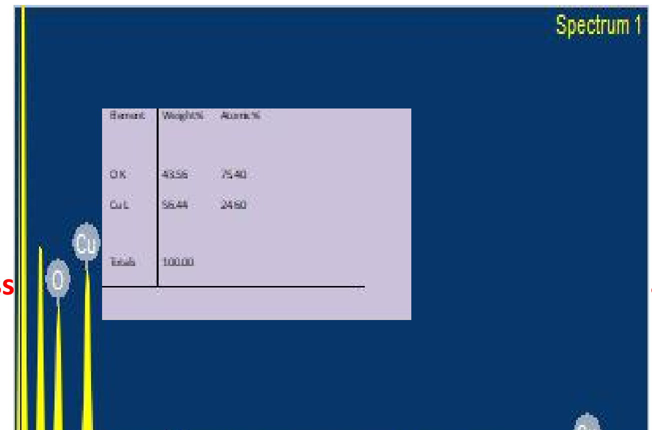


Fig 3. FESEM images of CuO nanostructure.

EDX analysis of the synthesized CuO nanostructures was used to confirm their elemental composition and purity (Fig 4). The copper peaks centered on 0 keV and 8 keV and the oxygen peak centred on 0.8 keV as shown in Fig 4. The weight present compositions of Cu and O of CuO nanostructures shown in Fig 4. The EDX spectra revealed the high purity of CuO nanostructures.



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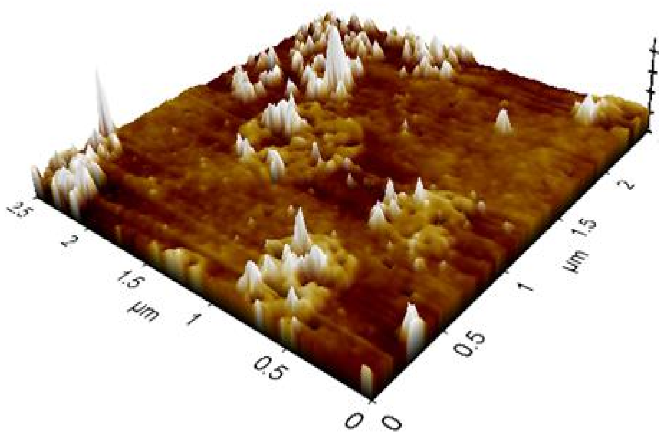

Fig 5. AFM images of CuO nanostructure.

Fig. 5 displays 3D atomic force microscopy (AFM) images that were captured in contact mode. In Fig 5 continuous and tiny nanostructure grains at 150^{o}C are visible.

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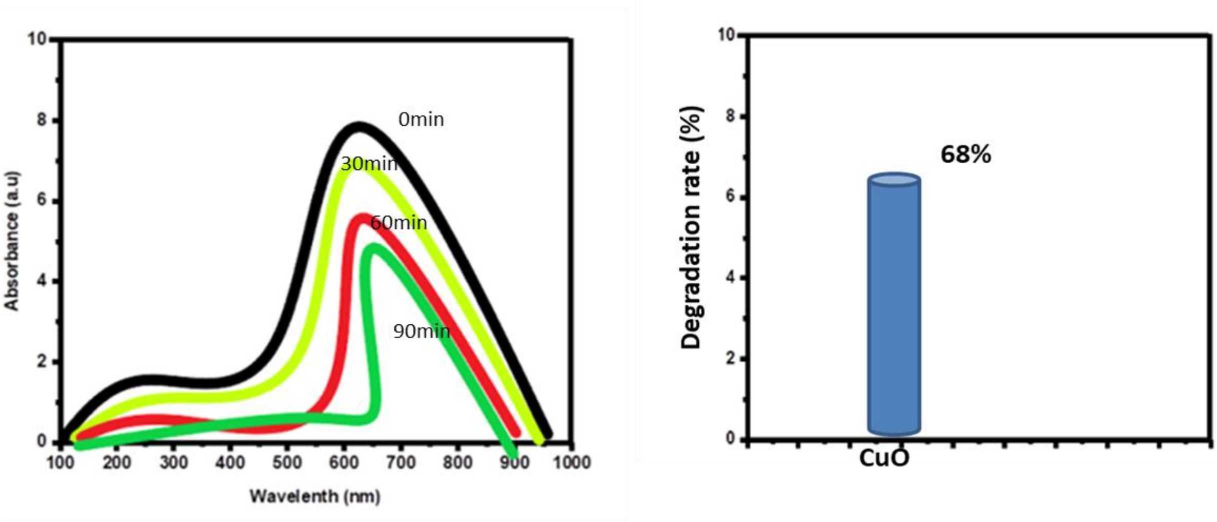

Fig 6.. Absorption spectra of MB dye with Degradation efficiency (%) CuO nanostructure .

To assess the photocatalytic capabilities of CuO nanostructures under sunlight illumination, the photo-degradation of MB was carried out. Figure 6 displays the spectrum fluctuation in MB dye absorption at various time intervals (a–c). .CuO photocatalysts with 1.7 eV bandgaps have CB and VB potentials of 0.46 V and 2.16 V, respectively, which are higher than the usual redox potential and adequate for releasing the OH and O_2 radicals needed for photodegradation [23,24].

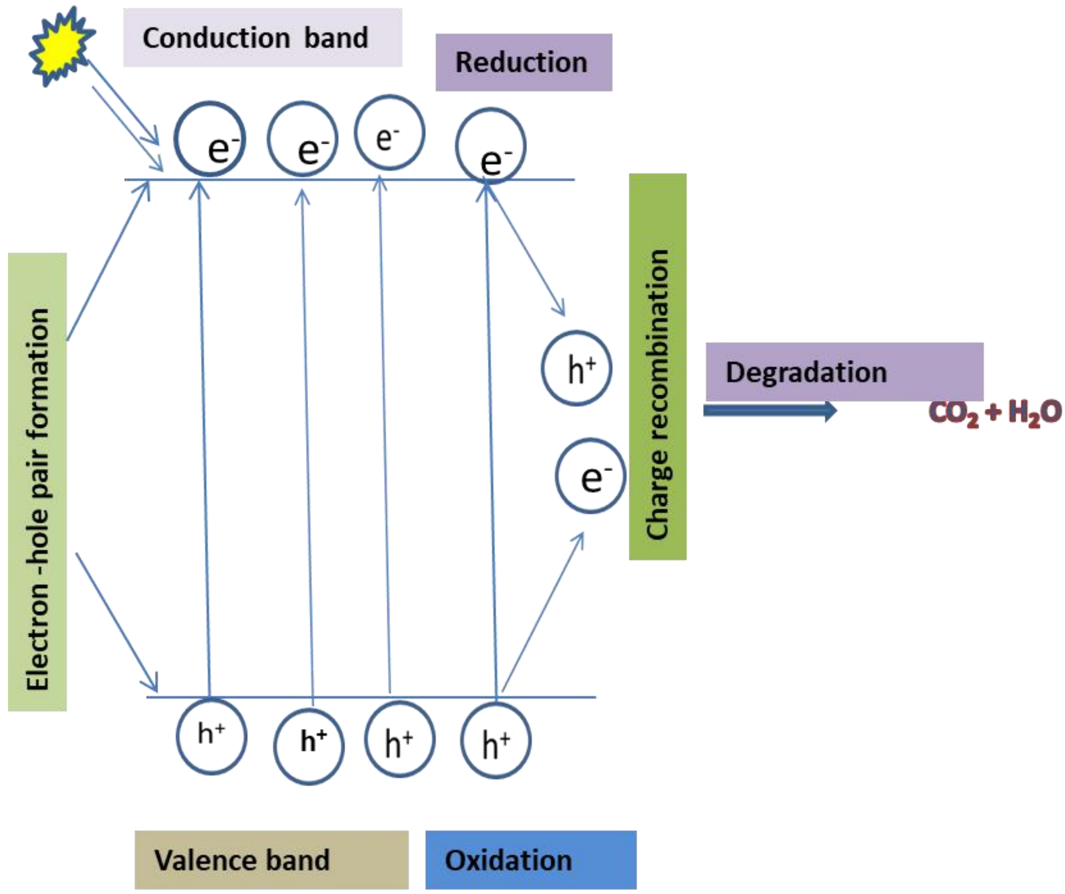

Fig 7. Photo catalysis mechanism diagram.

An e- from a filled VB excites an empty CB when light is flashed on a photocatalyst, forming e- h+ couples. At the photocatalyst surface, oxidation and reduction take place. Photogenerated e- and h+ are transferred to the catalyst's surface and engage in redox reactions. Photogenerated e- reacts with oxygen (O_2) to produce less toxic superoxide anions, whereas h+ reacts with water or hydroxide ions to produce the most reactive hydroxyl radicals, radical oxidative process, and ultimately hydrogen peroxide. Hydroxyl radicals are created when hydrogen peroxide and superoxide radicals interact. During the degradation reaction, these hydroxyl and superoxide radicals interact with the dyes and transform them into intermediary substances. In the end, these chemicals are changed or decomposed. This photo catalysis theory draws on earlier research [25–28]. Comparing the current work's CuO nanostructures to other metals oxide listed in Table1.

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Table1. Photocatalysis efficiency of different metaloxides.

S.no	Catalyst	Efficiency	Reference
1.	CuO	50%	29
2.	NiO	65%	30
3.	ZnO	10.71%	31
4.	WO_3	65%	32
5.	CuO	68%	Present

Conclusions

Innovative nanostructure CuO prepared using hydrothermal approach. The compositions, morphologies, and photocatalytic activity of material was examined. Due to the sample's favourable morphologies and high surface area, the CuO photocatalyst synthesised at 150 was discovered to have the maximum photocatalytic activity. This was attributed to a synergistic effect on the particular adsorption property and effective electron-hole separation at the CuO photocatalyst morphology. This research may offer fresh perspectives on the creation of innovative sunshine photocatalysts. In a sense, the efficient photodegradation dye by CuO photocatalyst under sunlight is a very fascinating aspect in the photocatalytic domain.

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