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Mo-doped CuO Nanomaterial for Photocatalytic Degradation of Water Pollutants Under Visible Light

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Abstract: Recently, metal oxide-based nano-photocatalysts have gained a great deal of attention in waste water remediation due to their outstanding properties. In this report, a novel Mo-doped CuO nanomaterial was successfully prepared and utilized for the degradation of methylene blue water pollutant. The molybdenum content was varied from 1–5 wt.% to obtain the desired modified CuO based nanomaterials. The crystalline structures of as prepared materials were investigated using the XRD technique, which explored the successful fabrication of monoclinic-structure-based CuO nanomaterials. For morphological studies, SEM and HRTEM were used, which proved the successful preparation of nanoparticles-based material. SAED was used to check the crystallinity of the sample. EDX and XPS analyses were performed to evaluate the elemental composition of Mo-doped CuO nanomaterials. The optical characteristics were explored via UV-vis and PL techniques. These studies showed that the energy bandgap of CuO decreased from 1.55 eV to 1.25 eV due to Mo doping. The photocatalytic efficiency of Mo-doped CuO nanomaterials was evaluated by degrading methylene blue (MB) under visible light-irradiation. Among different Mo-doped CuO based nanomaterials, the 4 wt.% Mo-doped CuO sample showed the highest degradation activity against MB dye. These results verified that the optimized material can be used for photocatalytic applications, especially for the purification of waste water.

Keywords: nanostructured; Mo-CuO; sol-gel; photocatalysis; methylene blue

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1. Introduction

Fresh water is crucial for the existence of life. About 70 percent of the Earth is covered by water, but a very small portion of this (2.5%) percentage is available for different purposes. Uncontrolled population growth in the world has proliferated the industrial revolution, which has caused the pollution of land and water bodies, especially by industrial wastes, which are highly toxic and hardly degradable [1]. Most textile industries use large amounts of water in the process of dyeing and cleaning. During the manufacturing of textile items, 50 percent of dyes are mixed into wastewater. The dissemination of this contaminated wastewater into the environment is a major source of pollution. Residential wastewater includes poisonous species released from non-fabricating actions, including deadwood, contagions, dangerous microorganisms, germ-free crops, wastage of cleaners, etc. The appearance of this untreated surplus of water is a substantial cause of water pollution [2]. Researchers have identified in earlier studies that several management agencies have used different schemes for the recycling of discarded water, using approaches that are physical, biological, and chemical in nature [3]. The choice of scheme used depends

on the source of the wastewater, either from industries and houses or from pharmaceutical products containing effluents, and thus the nature of pollutants in water and the related treatment techniques may differ from each other [4].

Among the different treatment approaches, photocatalysis is the best technique for water purification. It is a method in which light energy is absorbed for the production of electron/hole pairs, which then starts redox reactions. These reactions happen at the same time on the surface of the photocatalyst material [5]. In recent years, photocatalysis has been developed as a versatile technique in many applications, including self-sterilizing, self-cleaning of glasses, water splitting, antifouling coatings, oxidation of organic contaminations, decomposition of crude oil and polyaromatic hydrocarbons, etc. [6]. The photocatalytic process is separated into two categories, which are homogenous and heterogeneous photocatalysis, depending on the phase state of the components. Homogeneous photocatalysis is disadvantageous, as it occurs at low pH values, whereas for the precipitation and removal of ions from systems, high pH values are required [7]. On the other hand, in heterogeneous photocatalysis, a wide range of reactions occur, such as oxidation, exclusion of pollutants, isotopic exchange, detoxification, hydrogen removal, etc. [8,9].

In photocatalysis, many metal oxides, such as TiO_2 , ZnO , MoS_2 and CuO , have been used for waste water treatment [10–12]. Among these, CuO has distinctive features, such as low cost, non-toxicity, and highly stable nature under light irradiation; thus, it is used frequently in photocatalysis [13]. CuO is a transition metal oxide with a monoclinic structure. Copper (Cu) possesses different oxidation states, such as Cu^{1+} , Cu^{2+} , and Cu^{3+} , which make it equally promising for both hole and electron doping [14]. Nowadays, CuO is used as photocatalyst, antioxidant, drug delivery agent, and imaging mediator in the field of biomedicine [15]. Furthermore, in industrial fields, CuO is extensively used as a p-type semiconductor in photocatalysis, batteries, solar cells, gas sensors, and field emitters [16–18].

Previously, different researchers have worked to improve the photodegradation activity of CuO by doping it with different elements. For example, Shaban et al. investigated the influence of Fe doping on CuO and found higher activity due to Fe doping [19]. Nuengruethai et al. prepared Ce-doped CuO nanostructures and evaluated their photocatalytic activity against methylene blue (MB) [20]. Similarly, Devi et al. optimized the photodegradation activity of CuO by doping it with Tb. They used a combustion method to fabricate these monoclinic Tb-doped CuO nanoparticles. The enhanced surface area played an important role in improving degradation activity against different dyes [21].

In this study, we prepared Mo-doped CuO nanomaterials using a sol-gel method by varying the content value by 1–5 wt.%. The prepared photocatalytic material showed enhanced optical and photocatalytic properties due to the Mo doping.

2. Results and Discussion

2.1. XRD Spectroscopy

XRD spectroscopy was employed to examine the crystalline nature of the prepared nanomaterials. From the XRD patterns shown in Figure 1, it is clear that CuO nanoparticles showed a highly crystalline nature. Sharp peaks were obtained at 38° and 36° , corresponding to diffraction from the (111) and (002) planes. Further peaks were attained at 33° , 49° , 53° , 58° , 62° , 66° , 68° , 72° and 75° were consistent with the diffraction for planes 110, 020, 202, $\bar{1}13$, $\bar{3}11$, 220, 311, and 222, separately, according to JCPDS data card no. 80-1916 [22]. It can be observed that by doping Mo in CuO , the peaks' intensities were gradually decreased with an increasing content of Mo. In order to confirm this change, the crystalite size of the samples were calculated using the Debye Sherrer formula, as given in Equation (1).

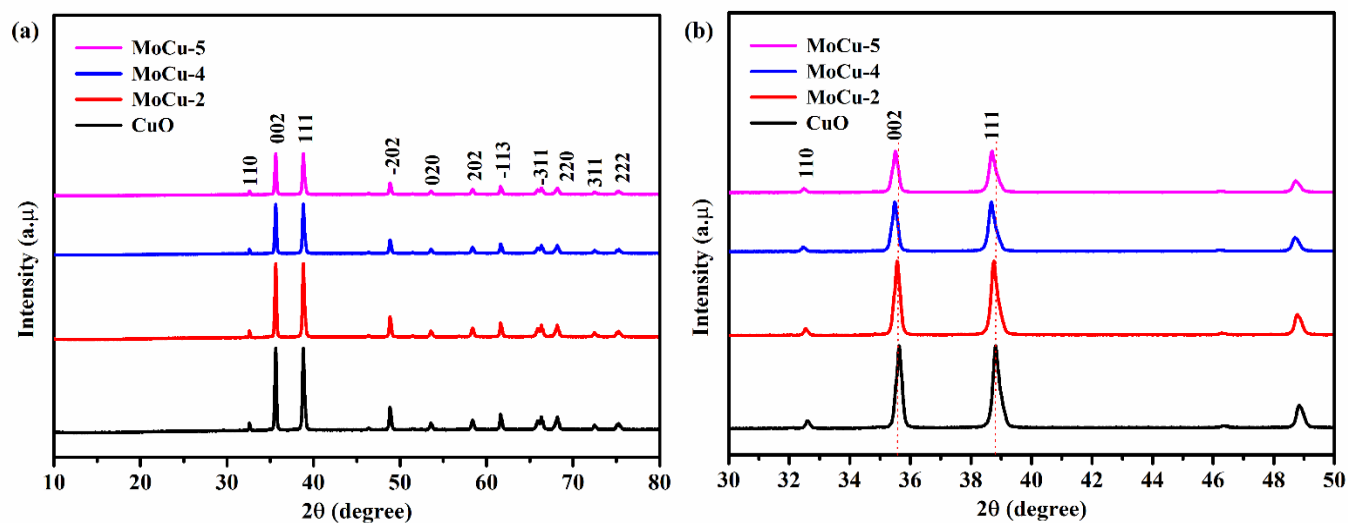


Figure 1. XRD pattern of pure CuO, MoCu-2, MoCu-4, and MoCu-5 samples. (a) 2θ (degree) from 10–80; (b) 2θ (degree) from 30–50.

$$D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (1)$$

Here, $\lambda = 1.54056 \text{ \AA}$ is the X-ray's wavelength, " β " is the full width at half maximum, and " θ " is the Bragg's angle of the diffraction peak in radians [23]. Using the above equation, the average crystallite sizes for the pure CuO and Mo-doped CuO samples were found to be 17.9 and 12.9 nm, respectively. This clearly shows that the crystallite size of CuO was decreased due to Mo doping, which could be attributed to the difference between the ionic radii of Mo and Cu, which are 0.068 nm and 0.073 nm, respectively.

2.2. SEM and EDX Analysis

SEM was utilized to analyze the morphological properties and size estimation of the prepared nanostructures. The SEM images of CuO and MoCu-4 are shown in Figure 2a,b, respectively. Figure 2a shows a material with randomly distributed nanoparticles on its surface, and some spaces for the smooth diffusion of ions. Figure 2b shows an SEM image of the MoCu-4 sample. It can be observed that, after Mo doping, the material was converted into uniformly distributed nanosized particles. The average particle sizes of the CuO and MoCu-4 samples are in the range of 65–75 nm and 30–40 nm, respectively. This development of nanoparticles improved the surface properties, active surface area, and a large number of active sites for the attachment and degradation of toxic dye molecules.

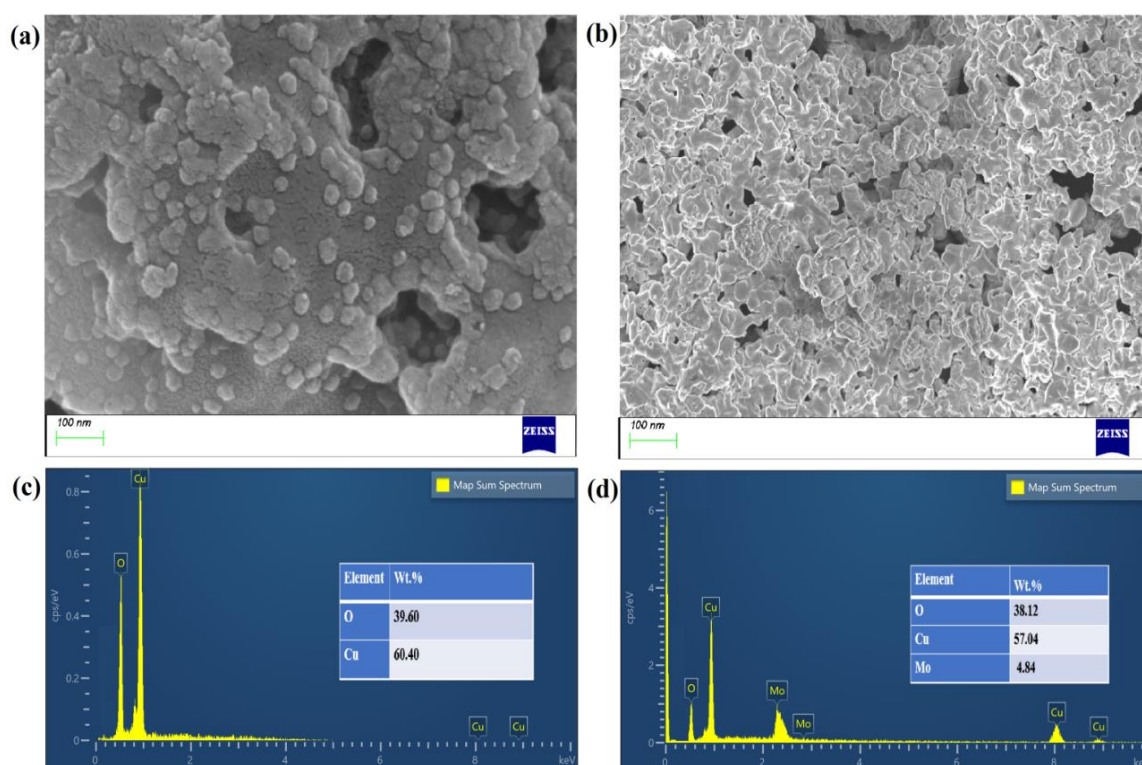


Figure 2. SEM images of (a) pure CuO (b) MoCu-4 samples, EDX of (c) pure CuO and (d) MoCu-4 sample.

The elemental composition of the prepared samples was determined through EDX analysis. EDX plots of CuO and MoCu-4 are shown in Figure 2c,d. One can observe only peaks related to Cu and O in Figure 2c; thus, expressing the elemental purity of pristine CuO. On the other hand, signals related to Cu, O, and Mo appeared in the EDX plot of MoCu-4, and are shown in Figure 2d. This showed the successful doping of Mo in the CuO crystalline lattice. The weight percentages of Cu, O, and Mo in the MoCu-4 sample were 38.12, 57.04, and 4.84, respectively. These values are approximately in agreement with the used weight percentages during the synthesis process.

2.3. HRTEM and SAED Studies

For further confirmation of the prepared MoCu-4 sample, and to support the SEM results, HRTEM images were also obtained and are shown in Figure 3a,b.

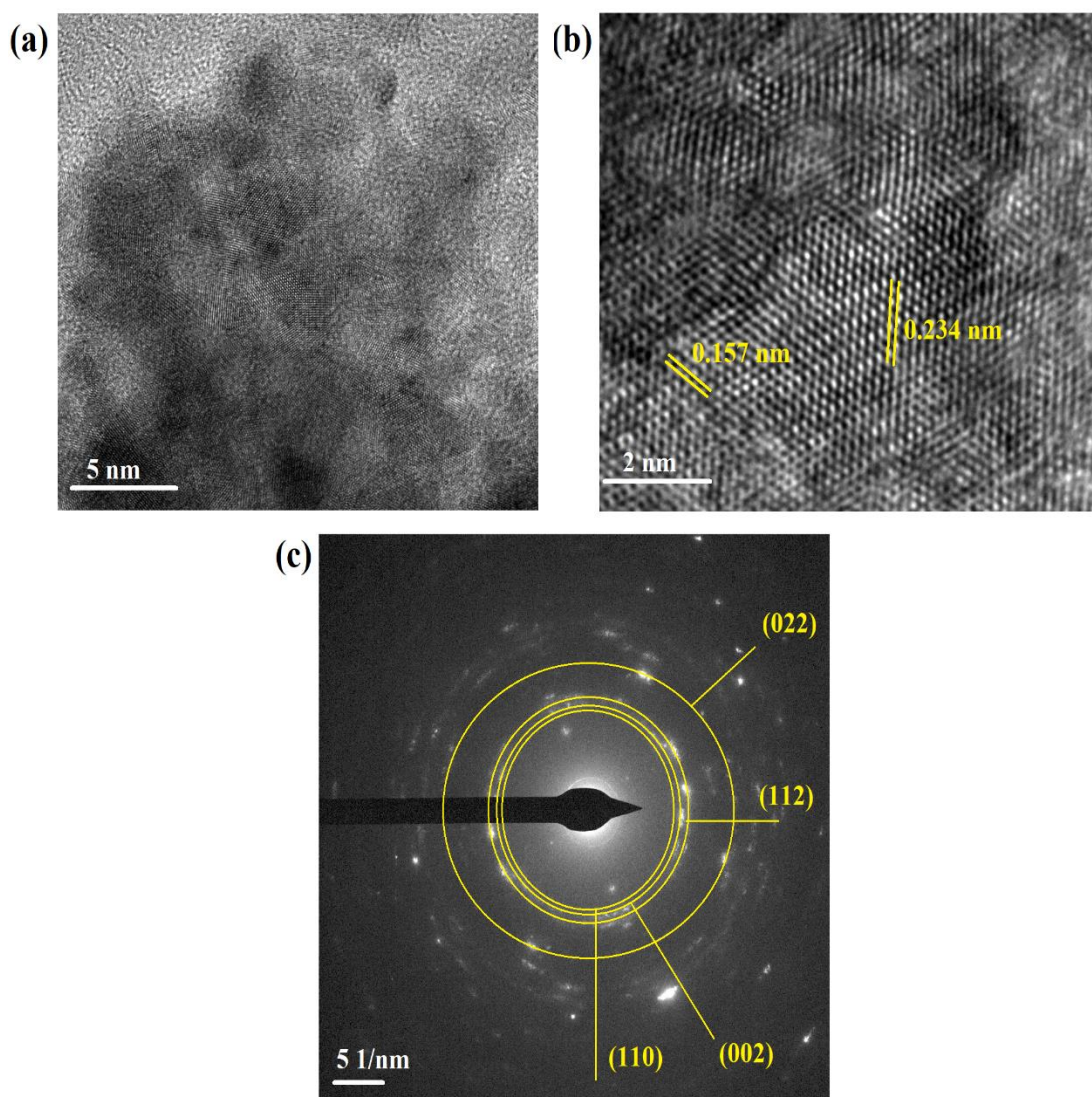


Figure 3. (a) HR-TEM image of MoCu-4, (b) HRTEM image of MoCu-4 and (c) SAED pattern of MoCu-4 sample.

The micrograph shown in Figure 3b shows the inter planar spacing of 0.234 nm and 0.157 nm, corresponding to the (1 1 1) and (202) crystalline planes of the monoclinic structure of CuO. Furthermore, the SAED (selected area electron diffraction) pattern, which was obtained for the MoCu-4 sample, is shown in Figure 3c. From this, it is clear that this sample is polycrystalline in nature.

2.4. XPS Analysis

In Figure 4a–d, the XPS results for the MoCu-4 sample are shown, which show the existence of the constituent elements, which were copper (Cu), molybdenum (Mo), and oxygen (O), along with carbon (C) shown as a reference in Figure 4a. In Figure 4b, the peaks shown at 933.4 eV and 952.6 eV are related to Cu 2p_{3/2} and Cu 2p_{1/2}, which are the features of the Cu²⁺ ions [24]. Furthermore, the presence of CuO was also confirmed by the appearance of peaks with binding energies of 942.11 eV and 962 eV [25]. Figure 4c shows two peaks at binding energies of 231.49 eV and 234.79 eV, which can be indexed to Mo 3d_{3/2} and Mo 3d_{5/2}, thus demonstrating the successful doping of the CuO crystalline lattice [26]. Figure 4d demonstrates the high-resolution XPS spectrum of O 1s with one peak at 530.52 eV [27].

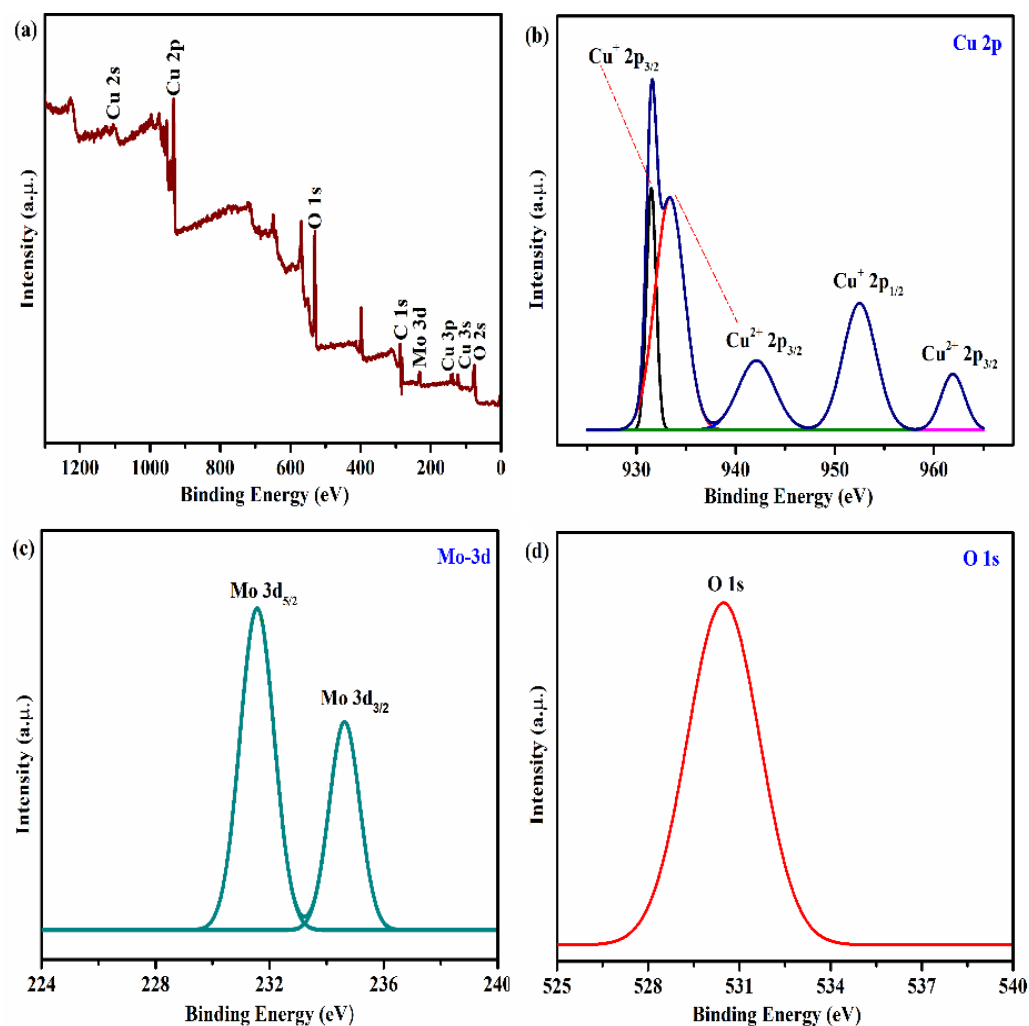


Figure 4. (a) XPS survey spectrum for MoCu-4, high resolution XPS spectra for (b) Cu 2p, (c) Mo-3d and (d) O 1s.

2.5. UV-Visible Spectroscopy

For an efficient photocatalyst material, a narrower optical bandgap is essential to exhibit the highest photodegradation activity under irradiation with visible light. To investigate the optical properties of CuO and Mo-doped CuO, absorption spectra were obtained within the wavelength range of 750 nm to 1100 nm and are shown in Figure 5a. The optical band gap values of these samples were found using the Tauc relation, which is given in Equation (2) [28].

$$(ah\nu)^2 = A(h\nu - E_g) \quad (2)$$

Here, " E_g " stands for optical bandgap energy, " ν " is the frequency, " h " is Planck's constant, and " A " is a constant that relies on transition probability [29]. The estimated bandgap value for pure CuO was 1.55 eV and for the MoCu-4 sample it was 1.25 eV (shown in Figure 5b). This clearly shows a decrease in the band gap energy of CuO due to Mo doping. By decreasing the band gap, the catalyst absorbs more light and electrons jump easily from the valance band to the conduction band. Electron and hole pairs form, which are required for the dye degradation process.

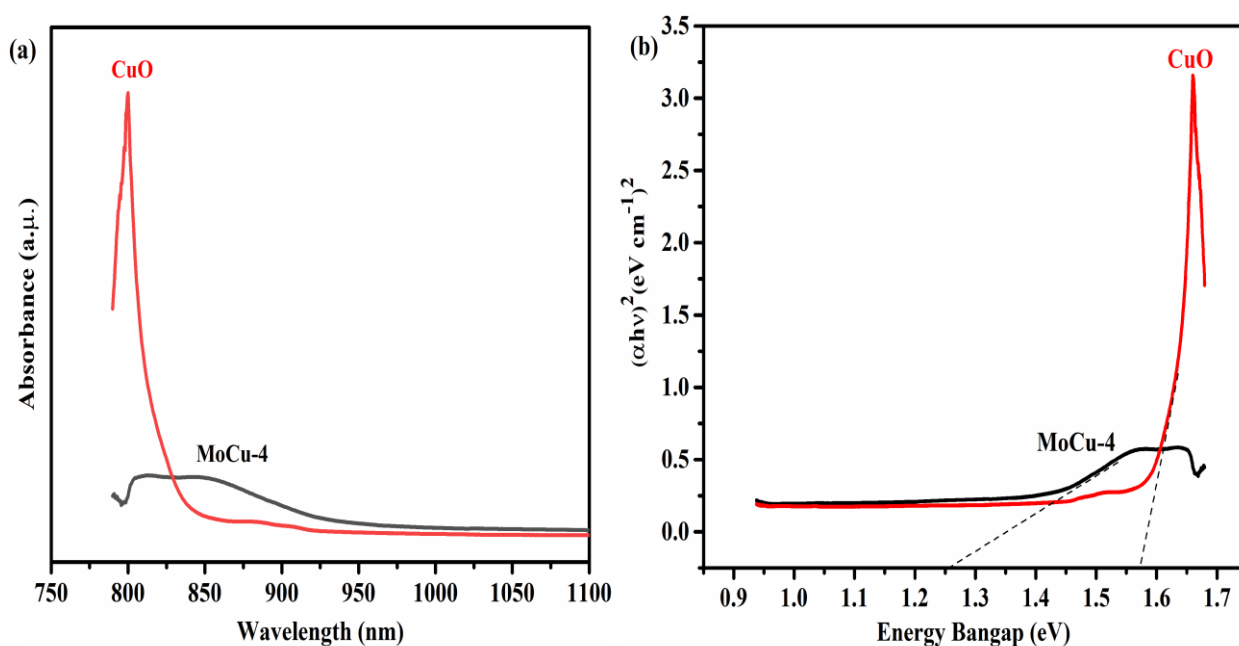


Figure 5. (a) UV-vis absorbance of pure CuO and MoCu-4 samples and (b) Tauc plot of pure CuO and MoCu-4 samples.

2.6. Photoluminescence Spectroscopy

PL emission spectra show the proficient separation of electron/hole pairs and their recombination rate [30,31]. Figure 6 shows the emission spectra corresponding to pure CuO, MoCu-1, MoCu-2, MoCu-3, MoCu-4, and MoCu-5 samples.

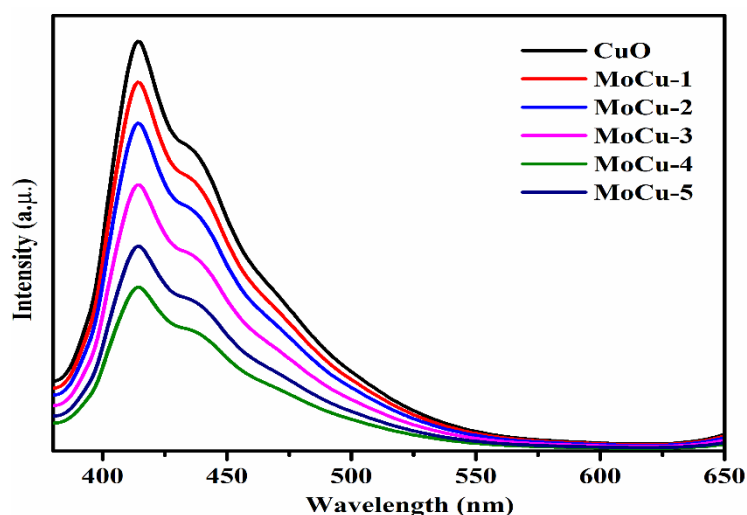


Figure 6. PL spectra for pure CuO, MoCu-1, MoCu-2, MoCu-3, MoCu-4, and MoCu-5 samples.

The spectrum for pure CuO showed the highest peak intensity, while the MoCu-1, MoCu-2, MoCu-3, and MoCu-4 samples showed a gradual decrease in peaks heights, exhibiting good separation of electron hole pairs and the availability of band levels for the easy migration of electrons; however, the MoCu-5 sample showed a higher PL emission intensity, which confirmed that 4 wt.% is the optimum level for Mo doping in CuO.

2.7. Photocatalytic Activity

The photocatalytic activity of pure CuO and Mo-doped CuO samples was investigated by approximating the degradation of MB dye under visible light irradiation, $\lambda \geq 420$ nm, as shown in Figure 7a–c.

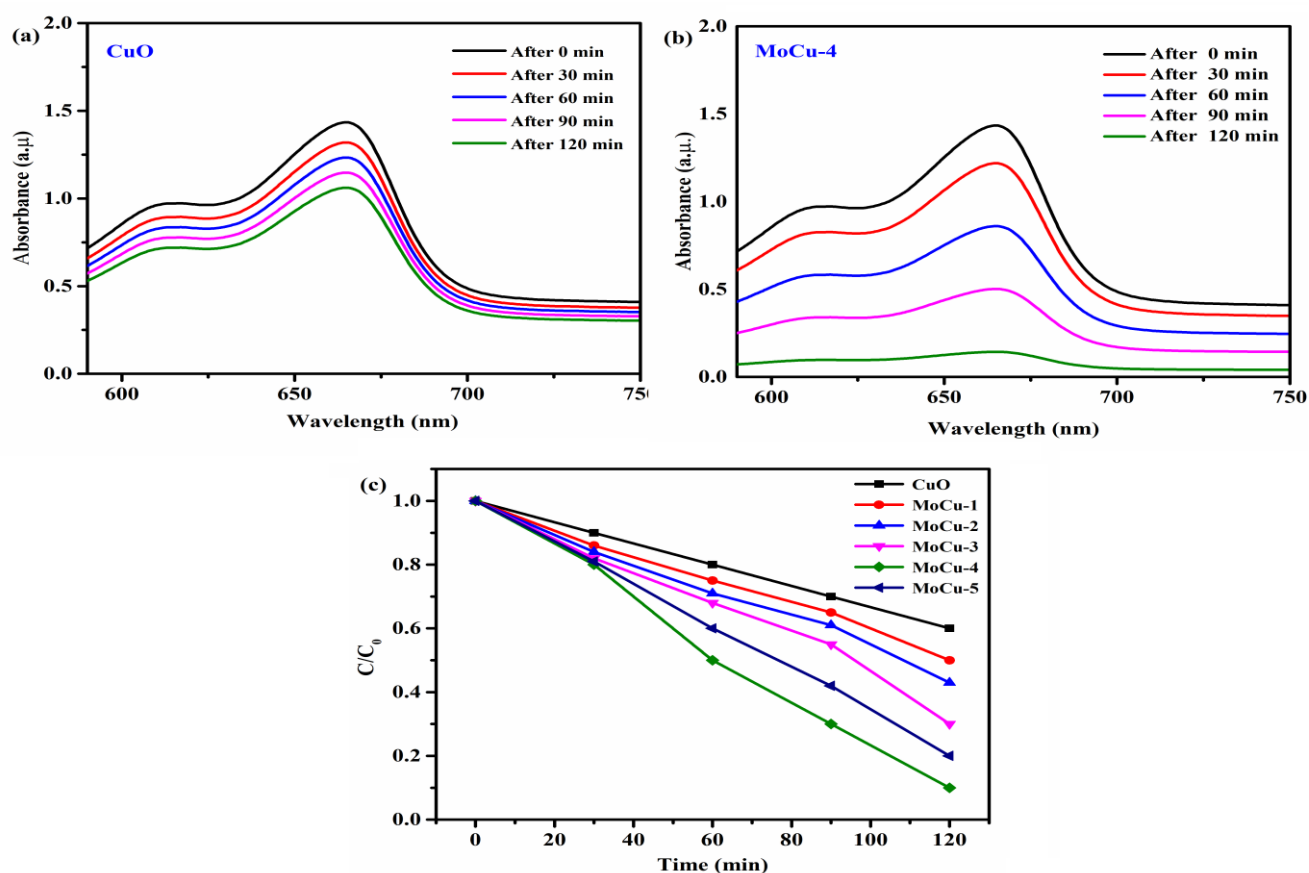


Figure 7. Photocatalytic activity absorption spectrum of (a) pure CuO, (b) MoCu-4 sample, and (c) photodegradation activity of pure CuO, MoCu-1, MoCu-2, MoCu-3, MoCu-4, and MoCu-5 samples.

The obtained absorption spectra in the degradation of methylene blue using CuO and MoCu-4 samples are shown in Figure 7a,b. Surprisingly, the absorbance of MB was noticeably reduced after 120 min for sample MoCu-4 (Figure 7b) in comparison to pure CuO (Figure 7c). Moreover, Figure 7c, shows a comparison of the photocatalytic performance of different photocatalysts under visible light irradiation. The pure CuO nano-material exhibited very low performance under visible light irradiation. After doping CuO with molybdenum, the photocatalytic activity of the materials was enhanced significantly. The MoCu-4 sample showed the best performance, and demonstrated a 90% decrease in MB after 120 min of irradiation. The 4 wt.% Mo doped CuO demonstrated a higher photocatalytic activity than the pure CuO as well as all the other doped materials. Furthermore, the MoCu-5 sample showed a lower performance than the MoCu-4 photocatalyst, as confirmed by PL spectroscopy (Figure 6), which confirmed the low activity of the sample.

3. Experiment

3.1. Materials and Method

A simple sol-gel method was used to prepare the Mo-doped CuO nanoparticles. During the synthesis, ammonium molybdate ((NH₄)₆Mo₇O₂₄) and copper nitrate (Cu(NO₃)₂) were used as sources of copper and molybdenum, which were purchased from Sigma-Aldrich. Citric acid (C₆H₈O₇) was used for chelation. All reagents were used as received without further purification. Stoichiometric amounts of ammonium molybdate, copper nitrate, and citric acid were dissolved in distilled water (H₂O) for the formation of a homogeneous solution. The molar ratio among the nitrates and citric acid was 1:1 and the prepared solution was kept under stirring at 60 °C until the formation of a gel occurred.

This gel was dried at the same temperature and then ground using a mortar to obtain a powdered form of the material. This powder was further calcined at 550 °C in a box type heating furnace for 2 hours. After cooling to room temperature, the obtained powder was further ground using a mortar to obtain fine nanoparticles. All concentrations were prepared by adopting the same synthesis method, and the 1–5 wt.% Mo-doped CuO samples were labeled as MoCu-1, MoCu-2, MoCu-3, MoCu-4, and MoCu-5. Moreover, pristine CuO was obtained in the absence of a molybdenum source.

3.2. Characterization

The size of crystallite of the samples and the structural properties were investigated via XRD diffraction. Cu-K α radiation with a wavelength of 1.5406167 Å was used to probe the samples at a scanning rate of 0.02 °/s in the 2 θ range from 10 to 80. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) were used for the morphological study of the samples. Energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) were used to evaluate the elemental composition and purity of the samples. Ultraviolet visible spectroscopy (UV-vis) and photoluminescence (PL) spectroscopy were used to study the optical properties of the prepared samples.

3.3. Photocatalytic Property

The photocatalytic degradation activity of the prepared samples was investigated against methylene blue. For this, a homogeneous solution was obtained by mixing 2 mg of methylene blue in 500 mL of distilled water. Six beakers, each with 50 mL of solution were prepared and 20 mg of CuO was added to each beaker. Five beakers out of the six were 1–5 wt.% of Mo. The obtained final solutions were stirred for 30 min in a dark environment to attain adsorption–desorption equilibrium. Then, the prepared final solution was kept in a photocatalytic reactor and 3 mL of each sample solution was taken out after 0, 30, 60, 90, and 120 min, which were also centrifuged to eliminate the photocatalyst. The degraded amounts of methylene blue were then measured in each sample using a spectrometer. The percentage decrease in the absorption of dye on the surface of the catalyst was a measure of degradation efficiency. Due to the introduction of the catalyst, the maximum absorption value was observed at the wavelength calculated using Equation (3).

$$\% \text{ Degradation} = ((C_0 - C_t)/C_0) \times 100 \quad (3)$$

Here, C_0 and C_t are the initial and after time “ t ” concentrations of the dye [32].

4. Conclusions

In summary, the optical and photocatalytic activity of CuO was tuned by fabricating Mo-doped CuO nanomaterials. The structural, morphological, and optical properties were investigated using different techniques. The results showed that all these properties were improved after doping CuO with molybdenum. Furthermore, the photocatalytic activity results for the degradation of MB dye showed that the Mo-doped CuO nanomaterials were effective photocatalysts. Among all samples, MoCu-4 demonstrated an excellent photocatalytic performance in the degradation of MB dye. Hence, this sample can be ideally employed for the purification of water by degrading methylene blue present in it.

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