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Enhanced photocatalytic activity of Cuprous Oxide nanoparticles for malachite green degradation under the visible light radiation

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Abstract

Photocatalysis provides excellent potentials for the complete removal of organic pollutants in environmentally friendly ways and sustainable means of technology. It has been noted that under UV-visible light irradiation, nanostructured semiconductor metal oxides photocatalysts can degrade different organic pollutants. Taking into consideration of the photocatalytic activity, the present study deals with the synthesis of cuprous oxide (Cu₂O) nanoparticles (NPs) by the sonochemical method and characterized for their physicochemical, optical, and photocatalytic properties. The powdered X-ray diffraction (XRD) analysis confirmed for the cubic phase crystalline structure while the Field emission scanning electron microscopy (SEM) supported for the icosahedron morphology. The bandgap of the synthesized Cu₂O NPs was found to be 2.26 eV, which is the suitable bandgap energy so as to achieve the enhanced photocatalytic degradation efficiency. On testing for the degradation of Malachite green (MG) as a model pollutant, the synthesized Cu₂O NPs demonstrated a high degradation efficiency under visible light irradiation. The observed results suggest that the synthesized Cu₂O NPs are attractive photocatalysts for the degradation of toxic organic wastes in the water under visible light. Further investigation confirmed for the photocatalytic reduction of 4-nitrophenol (4-NP) into 4-aminophenol (4-AP) under aqueous conditions with visible light.

1. Introduction

Nowadays, Cuprous(I) oxide (Cu₂O) nanoparticles (NPs) have achieved excellent properties as it supports a wide range of applications like optoelectronics, catalysis, sensors, solar energy, batteries, energy storage, etc [1]. Moreover, it is naturally available abundantly, non-toxic in nature, chemically stable and hence suits well for the photocatalytic applications. Since the main limitation of the commonly used photocatalytic materials is that the excited electron-hole pairs are not with the effective band gap separation and this leads to the fast recombination rate which tends to reduce the photocatalytic activity. But these drawbacks can simply be overcome by the incorporation of Cu₂O NPs as photocatalysts taking advantage of its excellent photocatalytic activity. The Cu₂O NPs show different crystal faces and exhibit different physical and chemical properties such as stability, catalytic activity, etc [2–4]. According to different researchers, there are various semiconducting materials including CuO, Fe₂O₃, TiO₂, and ZnO where they can also be used as photocatalysts uses UV radiation provided by the UV lamps in order to obtain sufficient energy for the formation of oxide radicals [5]. The photocatalysis is a process that involves the break down or decomposition of various dyes, organic dirt, and biological species such as harmful fungi and viruses on surfaces using UV or visible light irradiation to make it



clean [6, 7]. By keeping in view of the harmful effects of industrial effluents that pollute the water streams, most of the industrial processes in the developed countries are designed to limit or purify the dye contained products especially before they actually can get released into the water bodies [8, 9]. The commonly available technologies for the dye contained water purifications on an industrial scale include membrane technology, precipitation, chemisorption, sand filtration, photocatalysis, etc [10, 11]. The photocatalysis process is considered to be a more proficient method owing to its effective utilization of highly available solar energy and formation of non-toxic mineralized products (such as H₂O, CO₂, etc). Thus, the designing of visible light-active photocatalyst materials is the most important objective among scientific community for the disinfection of microorganisms and to treat the hazardous pollutants in a sustainable ways [12–14]. In this paper, we report the facile synthesis, characterization and visible-light photocatalytic degradation of the perforated Cu₂O NPs synthesized by the sonochemical process. The synthesized Cu₂O NPs were examined by several techniques to investigate the crystal structures, morphologies, optical, compositional, and photocatalytic properties.

2. Materials and experimental methods

2.1. Chemicals

Copper acetate monohydrate (Cu(CH₃COO)₂.H₂O), absolute ethanol, glucose, and sodium hydroxide (NaOH) were purchased from Sigma Aldrich and were used as received. All chemicals and solvents were used without any further purifications and the solvents used were of the highest analytic grade.

2.2. Synthesis of Cu₂O NPs

In a typical synthesis, about $0.25 \text{ M Cu}(\text{CH}_3\text{COO})_2$ and 100 mL of absolute ethanol solution were taken in a 250 ml beaker and ultrasonicated for 10 min Then, 50 mL of 1 M NaOH was added to the above solution and ultrasonicated (probe ultrasonicator, sonics Vibra cell, 20 kHz, 50% amplitude) for 15 min and observed to see the turning of reaction mixture into dark intense green colour. Now 1.0 mmol of D-glucose was added to the above solution and ultrasonicated for another 30 min. Finally, a dark red coloured precipitate was obtained which indicates the formation of Cu₂O NPs. The precipitate was filtered, washed, and dried under vacuum at room temperature [15]. Figure 1 shows the schematic representation of the synthesis of Cu₂O NPs and the synthesis reactions for the formation of the Cu₂O particles are given below.

$$\begin{aligned} & \text{Cu}(\text{CH}_3\text{COO})_2 + \text{NaOH} \rightarrow \text{Cu}(\text{OH})_2 + \text{CH}_3\text{COONa} \\ & 2\text{Cu}(\text{OH})_2 + \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{Cu}_2\text{O} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}_2\text{O} \end{aligned}$$

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3. Results and discussion

3.1. Physicochemical characterization of Cu₂O NPs

The Cu₂O NPs were prepared by the sonochemical method in the presence of some external compounds like glucose where the characteristic functional groups were identified by the FTIR spectroscopy as shown in figure 2(a). From figure 2(a) the observation of broad bands at 3496 cm⁻¹ 1413 cm⁻¹ can be linked to the H-OH stretching and COO⁻ stretching vibrations, respectively. Further, the band at 611 cm⁻¹ was ascribed to the vibrational mode of Cu–O in the Cu₂O phase [16]. Similarly, the Raman spectrum for the Cu₂O NPs at room temperature is shown in figure 2(b) where the band at 218 cm⁻¹ refers to the 2E_U Raman-active phonon mode and the other band at 330 cm⁻¹ can be attributed to the A_{2U} phonon modes [17]. The bands at 420 and 510 cm⁻¹ are attributed to multiple phonon scattering processes and the intense band at 618 cm⁻¹ is attributed to the infrared allowed mode of the Cu₂O NPs. Thus from the comparative analysis of FTIR and Raman spectroscopy bands, it can be confirmed for the formation of Cu₂O material with a moisture on its surface.

The optical properties were investigated using the UV–vis DRS analysis where the results were plotted and shown in figure 3(a). From the figure, it can be seen that the absorption maximum is observed at 590 nm for the Cu₂O sample which is obvious for the Cu₂O NPs in the visible region [18]. This strong absorption of Cu₂O NPs is attributed to the electron excitation from the valence band (VB) of Cu to the corresponding conduction band (CB). As shown in figure 3(b) which represents the Tauc plot, the band gap value of Cu₂O NPs was found to be 2.26 eV and with this band energy value, the enhanced photocatalytic activity can be expected.

The structure and phase composition of Cu₂O NPs were investigated by the powdered XRD analysis in the 2θ range of 10° - 70°. As can be seen in figure 4, the diffraction peaks with respective intensities for Cu₂O NPs at 29.7°, 36.4°, 42.5° and 61.4° corresponding to (1 1 0), (1 1 1), (2 0 0), and (2 2 0) planes of cubic crystal structure





of Cu₂O, and further they are well matched with the reported literature and standard JCPDS card (No.65-3288) [19].

More information about the morphological properties of the as-synthesized Cu₂O NPs was deliberated by the FESEM analysis and the images are shown in figures 5(a), (b). From figure 5, the Cu₂O particles are exhibiting the uniform icosahedron morphology where the NPs were observed to be aggregated in nature (figure 5(a)). The surface morphology of Cu₂O NPs in the magnification of 2 μ m scale (figure 5(b)), further confirmed for the icosahedron morphology and aggregated micron crystallites formation [20]. According to FESEM micrograph results, the diameters are roughly estimated from micrographs of the samples within the ranges from 5 to 2 μ m.

The TEM analysis and the corresponding SAED pattern for the Cu_2O NPs are shown in figures 6(a), (b) respectively where the Cu_2O NPs were identified again in the icosahedral shape with no sharp edges (figure 6(a)). The Cu_2O particle size was determined to be in the broad range of 20–95 nm. Also, the SAED pattern (figure 6(b)) showed that the Cu_2O NPs comprised the small nanocrystalline structures which maintain orientation different from the single crystal diffraction pattern. From the analysis, it can be confirmed that the Cu_2O NPs are crystalline in nature, which was earlier proposed by the XRD pattern (figure 4).

3.2. Photocatalytic degradation of Cu₂O NPs

For the photocatalytic activity testing, the Cu_2O NPs are being used to evaluate the degradation property of malachite green (MG) in an aqueous medium under visible light illumination. In a typical photocatalytic experiment, 10 mg L⁻¹ MG aqueous solution was selected as a model pollutant and its degradation in the

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presence of UV light determines the efficiency of our Cu₂O sample where the optical absorption was measured to study the photocatalytic degradation process. For the study, a 10 mg of Cu₂O NPs were taken in 250 ml of MG dye (1×10^{-3} M) and was sonicated for 45 min for the complete dispersion. Approximately 15 mg of catalyst powder was added to the beaker containing 100 mL of MG solution, followed by 20 min stirring in darkness to create an adsorption-desorption equilibrium between the MG dye and the synthesized Cu₂O surface. The MG dye and the catalyst mixture were allowed to stir in the dark for 20 min before subjecting to the visible light irradiation to ensure the adsorption equilibrium. The samples were taken in a 5 mL sample holder at 15 min intervals during irradiation time and their absorbance was recorded at 615 nm, corresponding to the highest absorption wavelength of MG UV–vis using UV-3600 Cary 8453 UV–vis spectrophotometer [21]. Figures 7(a), (b) summarizes the MG percentage versus treatment time in the range of 0–45 min under the visible-light treatment in the absence and presence of Cu₂O NPs. We identified the adsorption-desorption equilibrium reaction of MB can be determined within the 45 mins period where the catalytic study in the absence of the Cu₂O catalyst (figure 7(b)) did not show a significant effect of the product formation. However, for the same reaction in the presence of the catalyst, we found some significant effect with respect to the time (figure 7(b)).

The good photocatalytic reactivity of Cu₂O NPs denoted C_t/C_0 between the residual concentration and the initial concentration of MG. The ratio of C_t/C_0 depends on the dye irradiation time figure 8(a). As shown in figure 8(a) which compares the effect of C_t/C_0 with time, it can be observed that there is a good linear correlation between (C_t/C_0) and the reaction time (t) for the presence and absence of the catalyst.





$$E = (C_t - C_0 / C_0 \times 100)$$
(1)

Where, E corresponds to the degradation efficiency, C_0 for the initial absorbance, C_t - absorbance after complete degradation. The degradation efficiency without the catalyst during 5 min is 1.39% and at 45 min, it is 21.39%; with the presence of catalyst, the efficiency at 5 min is 11.59% and at 45 min, it was observed to be 91.89% and these significant changes in the efficiency confirms for the good photocatalytic efficiency as shown in figure 8(b). The observation of such activity of the Cu_2O NPs might be due to the reduction in the penetration of light into the photocatalyst and further generation of larger amounts of photons adsorbed onto the catalyst surface. From the analysis, the observation of a very high significance (about 92% at 45 min) by the Cu_2O NPs confirms the excellent photodegradation capability towards the MG dye solution [22].

The kinetic studies of the MG have a high performance of the photocatalytic activity of Cu₂O NPs for firstorder kinetic model the equation (2).

$$\ln \left[C_t / C_o \right] = K_{app}^{\ t} \tag{2}$$

Where, K_{app} stands for the apparent rate constant, C_0 and C_t for the absorbances at zero and after the t time (min) respectively.

Further, figure 9 shows the comparison of the changes in the concentration of MG dye $(\ln(C_t/C_0))$ with respect to time (0–45 min) in the presence and absence of the Cu₂O catalyst. From the figure, it can be seen that there is no significant change for the reaction occurring in the catalyst absence, while significant decrease in the MG dye concentration was observed for the catalyst presence and this effect is getting increased with increase of reaction time.



This greater degradation efficiency of Cu₂O NPs under visible light is mostly attributed to their unique structure with high specific areas and excellent optical absorption behavior. The photocatalytic mechanism depends on the wavelength of the light, pollutant and the sample catalyst. During the photocatalytic degradation of phenol and MG separately, on irradiation of the aqueous catalyst with the visible light energy greater than the energy gap, the electrons are subjected to the pumping to the CB and this creates the holes. The electrons in the CB reduces the dye directly or react with dissolved oxygen species to form superoxide ion (O_2^-) or participates in a reaction with electron acceptors (like O_2) absorbed on the surface of the catalyst. The holes which are generated in the mechanism can oxidize the water molecules into OH⁻ radicals or react with OH⁻. When these hydroxyl radicals get combined with other oxygen containing oxidant species ($\cdot O_2^-$), they undergoes a heterogeneous photochemical degradation process which has the capacity to easily degrade the organic dye substrates. Figure 10 shows the schematic representation of the effective separation of electrons among CB and VB and the unique role played by the heterojunction structure towards the scavenging of photoexcited electron (e^{-}) and hole (h^{+}) pairs. So in the present case, the Cu₂O NPs being the major constituents showed some strong absorbance characteristics under the visible light region. Following the light absorption, the electrons in the VB of Cu₂O will be migrated to the CB and inturn, the holes are shifted to the VB. The available free electrons in the Cu₂O's CB are quickly captured by the adsorbed O_2 and generates the highly reactive superoxide radicals (O_2^-), and holes in the Cu₂O's VB reacts with the adsorbed H_2O or OH^- to form the other extremely reactive $\cdot OH$ radicals in aqueous solution [23-25].

3.3. Catalytic reduction of Cu₂O NPs

In order to test the catalytic efficiency of the synthesized Cu₂O NPs, the particles were tested based on the reduction of 4-nitrophenol (4-NP) to 4- aminophenol (4-AP) in the presence of aqueous sodium borohydride (NaBH₄) as a model. The success of the reaction was evaluated with the help of UV–vis spectroscopy and by the measurement of absorbance peak for 4-AP at 263 nm under acidic or neutral conditions. With this technique, the disappearance of 4-NP's absorption peak (at 400 nm) and the appearance of 4-AP's peak (263 nm) confirm for the catalytic reduction [26]. Figure 11 shows the Cu₂O mediated catalytic conversion of 4-NP into 4-AP over a 45 min period where it can be observed that the NPs are highly active towards the conversion of nitro groups into amino even at room temperature conditions. Since the addition of NaBH4 to the reaction mixture causes the alkalinity and so a slight shift to the peak at 400 nm can be expected due to the generation of 4-NP ions [27]. From the comparison of absorption peaks, it can be observed that there appears the weakening of absorption peak at 400 nm and concomitant increase in the intensity of peak at 263 nm with respect to an increase in the time. This confirms that the prepared Cu₂O particles are effective towards the reduction of 4-NP into 4-AP and can be used explored on an industrial scale or for other compounds for the economical means of the conversion of nitro to amino groups.



4. Conclusion

In summary, the Cu₂O NPs were synthesized by a simple and efficient sonochemical technique using glucose as a reducing agent. The spectroscopic and microscopic results revealed for the successful formation of Cu₂O NPs. The bandgap of the Cu₂O NPs was found to be 2.26 eV which supports the enhanced photocatalytic performance. On testing under visible light irradiation, the Cu₂O NPs found to exhibit high photodegradation activity towards the degradation of MG dye and that too shows enhanced degradation in a short time. Also, the prepared Cu₂O NPs showed very promising catalytic activity towards the reduction of 4-NP to 4-AP. These results indicate that the Cu₂O NPs can further be incorporated in the photocatalytic activity devices for adapting suitable bandgap energy and also for reducing the nitro groups simultaneously.

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