Cu₂O Nanoparticles: A Simple Synthesis, Characterization and Its Photocatalytic Performance toward Methylene Blue

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Cuprous oxide nanoparticles (Cu₂O-NPs) were fabricated by a simple solution-phase reduction route with a one-step reduction method. The used original chemicals were the copper sulfate and the sodium sulfite. The physicochemical properties of Cu₂O-NPs were investigated by different methods such as XRD, Raman, SEM, and UV-Vis spectra. The results show that the molar ratio of precursors ([CuSO₄]/[Na₂SO₃]) not only affects crystal structure and morphology but also affects the crystallinity of crystals and optical characteristics of Cu₂O-NPs samples. The photocatalytic activity of Cu₂O-NPs was evaluated by the removal of methylene blue (MB) aqueous solution under visible light irradiation. The result shows that good photocatalytic activity with the MB degradation is higher than 98% under visible light irradiation for 40 minutes and the rate constant of 0.11281 min⁻¹. [doi:10.2320/matertrans.MT-MN2019039]

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1. Introduction

Cuprous oxide (Cu₂O) is a p-type semiconductor with a bandgap energy of about 2.17 eV, which is a narrow gap energy and is suitable for photochemical reactions in the visible light region.¹⁻³⁾ Moreover, Cu₂O is easy to make, abundant in nature, inexpensive, readily available, safe, and nontoxicity.^{4,5,9-12)} Due to the attractive properties of Cu₂O has attracted significant interest for many applications such as photocatalysis,⁴⁻⁷⁾ gas sensing,^{1,8)} solar energy conversion.^{4,5,9)}

Several methods have been described for the synthesis of Cu₂O, such as solvothermal synthesis¹³⁾ solution-phase reduction,¹⁾ the hydrothermal method,^{3,14,15)} SILAR method,¹²⁾ electro-deposition,¹⁶⁾ chemical bath deposition.¹⁷⁾ Among these various techniques, the solution-phase reduction is one of the most efficient fabrication methods because of simple production, low cost, high purity, and the high productivity of the products.

Liao *et al.* prepared Cu₂O nanospheres by hydrazine hydrate reduction of copper acetate.¹⁰⁾ Guo *et al.* were successfully prepared Cu₂O via a convenient liquid phase reducing method using sodium dodecyl sulfate (SDS) and copper chloride as beginning chemicals.¹⁾ Xue *et al.* have been successfully fabricated Cu₂O micro-nano particles using copper sulfate solution, sodium hydroxide solution, and glucose.⁴⁾ Kumar *et al.* obtained Cu₂O from copper nitrate with using L-ascorbic acid or L-glutamic acid as a reducing agent.¹⁷⁾ Cuprous oxide nanoparticles were (Cu₂O-NPs) prepared with usual precursor chemicals as sodium borohydride and origanum Vulgare leaf extract which have a role of a reducing agent and an oxidizing agent, respectively.¹⁸⁾

The novelty of our article is shown in the method of prepared single-phase Cu₂O NPs by a simple and easy solution-phase reduction route using the CuSO₄ and Na₂SO₃ precursors. In which, sodium sulfite (Na₂SO₃) as a reducing

agent which has outstanding advantages compared to other used reducing agent due to inorganic precursor, and it is less expensive and less harmful than other organic precursors like hydrazine hydrate, L-glutamic acid, sodium dodecyl sulfate. Besides, the Na₂SO₃ also acts as a complex agent to control free copper ions concentration and convey stability in the prepared solution. The photocatalytic activity of Cu₂O NPs in the decomposition of methylene blue (MB) aqueous solution under visible light irradiation has been mentioned in our study. Also, the photocatalytic mechanism of Cu₂O NPs toward MB dye is analyzed in the article.

In this paper, Cu₂O nanostructures have been synthesized by a simple reduction method with the use of CuSO₄ and sodium sulfite (Na₂SO₃) inorganic chemical precursors that are easy to find. The easy process for the fabrication of Cu₂O NPs materials in our study shows further possibilities for practical applied research.

2. Experiment

2.1 Cu₂O cuprous oxide preparation

The used chemical precursors include the copper sulfate (CuSO₄) (99.99%, China-AR) and sodium sulfite (Na₂SO₃) (99.99%, China-AR). The cuprous oxide (Cu₂O) nanoparticles were prepared by a wet reduction of the copper sulfate (CuSO₄) and sodium sulfite (Na₂SO₃). First, 8.56 g of CuSO₄ was dissolved in 40 ml of deionized water. This solution was added with different volumes of Na₂SO₃ 0.1 M with the molar ratio of [CuSO₄]/[Na₂SO₃] is 1:05; 1:10 and 1:15 under magnetic stirring for 15 mins. The mixed solution was then heated from room temperature 85°C and maintain at this temperature for an hour for reaction. A red precipitate was formed indicating that this product was Cu₂O particles. Then, the precipitate was filtered and washed several times with deionized water and alcohol until the washing solution had reached a neutral pH of 6.5–7. The washed product was then dried at 90°C for 24 h. The prepared samples were named C105, C110, and C115 corresponding to the molar

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ratio of [CuSO₄], and [Na₂SO₃] is 1:05; 1:10 and 1:15, respectively.

2.2 Characterization techniques

The structure and phase composition of crystals were recorded with an X'pert Pro (PANalytical) using the Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$), scanning rate was $0.03^\circ/2 \text{ s}$ from the $2\theta \approx 25^\circ$ to 75° . Crystal analysis was carried out using HighScore Plus software with the ICDD database. The micro Raman spectrum was determined by Renishaw Invia Raman Microscope using 633 nm laser at a power of 6.25 mW and Leica NPLAN L50x/0.50 BD Microscope. The morphology of Cu₂O NPs was measured by a scanning electron microscope SEM images using Tabletop Microscope HITACHI TM4000Plus. The diffusion reflectance spectra of samples were determined with a JASCO V-750 using the integrating sphere (ISV-922) of 60 mm. The scan rate was 200 nm/min and UV-Vis bandwidth was 0.5 nm.

2.3 Experiment photocatalytic activity

The photocatalytic properties were studied through the removal of the methylene blue on Cu₂O NPs samples in solution. The MB (C₁₆H₁₈CN₃S) is a water-soluble cationic organic. It is toxic and common in the composition of textile wastewater. In the experiments, 10 mg/L of MB solution was put into a quartz photoreactor of 100 mL capacity in which the reaction is performed at room temperature. Before irradiation, 0.02 g as-prepared catalyst was dispersed into the MB solution of 80 ml. Next, this mixture solution was stirred in the dark for about 10 mins to reach the absorption-desorption equilibrium. The visible light source was taken from a compact lamp (Compact 250W- Rang Dong, Viet Nam). Photocatalytic reaction was carried out for 40 mins under visible light irradiation. Each time, 5 ml of the supernatant solution was extracted from the mixture solution of catalyst and MB and was measured the absorbance on a spectrometer (Agilent 8453) at 664 nm.^{19,20)}

The degradation degree of MB (D) was determined by the eq. (1):^{4,6,18,31)}

$$D = [(C_0 - C_t)/C_0] \times 100\% \quad (1)$$

In which, C_0 - the initial concentration of MB (mg/L), C_t - the concentration of MB at time t (mg/L) of the photocatalytic reaction.

3. Results and Discussions

The XRD diffraction patterns were used to investigate the structures and purity phase composition of Cu₂O NPs. Figure 1 shows the XRD patterns of Cu₂O nanoparticles synthesized. The peaks were found including (110), (111), (200), (220), (311) phase orientation which are determined to be the Cu₂O phase (matched with JCPDS 05-0667). The strong peak at (111) phase orientation shows that the preferred crystal orientation of Cu₂O NPs is cubic. No possible impurities diffraction peaks of CuO and/or Cu are found. Therefore, in this experimental condition, the pure Cu₂O NPs samples were obtained.

The average crystallite size was calculated according to the Scherrer equation.^{1,21-24)}

Fig. 1 XRD pattern of Cu₂O nanoparticles synthesized (a) C105, (b) C110 and (c) C115.

Table 1 The values of the crystallite size, D scherrer, D Williamson-Hall, dislocation density and microstrain calculated from X-ray diffraction plot for the Cu₂O-NPs C105, C110 and C115.

Sample name	D Scherrer (nm)	D Williamson-Hall (nm)	Dislocation density (δ) 10 ¹⁴ /m ²	Microstrain (ε)
C105	10.4	46.2	0.047	0.002011
C110	15.1	138.7	0.005	0.015281
C115	5.7	86.7	0.013	0.023806

$$D = (K \times \lambda) / (\beta \times \cos \theta) \quad (2)$$

Where D was the average crystallite size, $K = 0.90$ which was a constant, λ was the wavelength of the incident radiation in nm ($\lambda = 1.54060 \text{ \AA}$), θ was the Bragg angle taken in radians, and β was the line width at half maximum height in radians.

The lattice parameters of samples were calculated according to the Williamson-Hall eq. (3) and (4):²⁵⁻²⁷⁾

$$\delta = \frac{1}{d^2} \quad (3)$$

$$\beta \times \cos \theta = \frac{0.9 \times \lambda}{D} + 2\epsilon \times \sin \theta \quad (4)$$

Where, δ is a dislocation, ϵ is a microstrain.

The lattice parameters are shown in Table 1. The data in Table 1 shows that the crystallite size of grain increases and the strain in the crystal lattice decrease when the molar ratio [CuSO₄]/[Na₂SO₃] increases from 1:05 to 1:10. But when the molar ratio [CuSO₄]/[Na₂SO₃] increases from 1:10 to 1:15, the crystallite size decreases whereas the microstrain in the crystal lattice increases with the increase of molar ratio. The result obtained from the Scherrer method also shows a similar trend of crystallite size. The large crystallite size implies the high crystallinity of Cu₂O NPs.

The good crystallization of Cu₂O NPs is also identified by Raman spectra. The Raman spectra of Cu₂O NPs for different molar ratio [CuSO₄]/[Na₂SO₃] is presented in Fig. 2. In Fig. 2, the characteristic peaks of Cu₂O is obtained. The band at $\sim 218 \text{ cm}^{-1}$ is attributed to the second-order overtone mode 2Eu. Raman-allowed mode F_{2g} (514 cm^{-1}), one red-allowed

Fig. 2 Raman spectra of Cu_2O nanoparticles synthesized (a) C105, (b) C110 and (c) C115.

Fig. 3 SEM image of Cu_2O nanoparticles synthesized: (a) C105, (b) C110 and (c) C115.

mode TO, 650 cm^{-1} , are detected.^{24,28} These results of Raman analysis are consistent with the analytic results from XRD patterns.

The SEM images of the samples are presented in Fig. 3. The C105 sample (Fig. 3(a)) appears to have spherical morphology with a diameter of $1\text{--}2\text{ }\mu\text{m}$. The C110 sample (Fig. 3(b)) has uniformly octagonal nanoparticle morphology with a medium size of $1\text{--}2\text{ }\mu\text{m}$. The C115 sample (Fig. 3(c)) also has octagonal morphological nanoparticles, but the particle size is larger than that of the C110 sample. The dimension of the Cu_2O NPs is evenly distributed potential for photocatalytic applications with high surface area. This suggests that the sample with the molar ratio $[\text{CuSO}_4]/[\text{Na}_2\text{SO}_3]$ precursors of 1:10 has the highest cuprous oxide nanoparticles (Cu_2O NPs).

The diffuse reflectance spectra of Cu_2O NPs are shown in Fig. 4. We see that the edge of the diffuse reflectance spectra of samples is red-shifted when the Cu_2O NPs molar ratio $[\text{CuSO}_4]/[\text{Na}_2\text{SO}_3]$ increasing. The higher Cu_2O NPs molar ratio $[\text{CuSO}_4]/[\text{Na}_2\text{SO}_3]$, the further shift. This shift is assigned to the transformation from Cu_2O to Cu.

The optical bandgap of the samples was determined through extrapolation using the Kubelka-Munk method. The Kubelka-Munk method describes the relationship of the diffuse reflection function to the incident photon energy according to eq. (5):

Fig. 4 Reflectance spectra Cu_2O nanoparticles synthesized: (a) C105, (b) C110 and (c) C115.

$$[F(R)h\nu] = A(h\nu - E_g)^2 \quad (5)$$

where, $F(R)$ is the diffuse reflection function, R is the data of the diffuse reflectance, A is an arbitrary coefficient, $h\nu$ is the incident photon energy and E_g is the optical band gap of Cu_2O NPs. $F(R)$ is determined according to eq. (6):²⁹

$$F(R) = \frac{(1 - R)^2}{2R} \quad (6)$$

$h\nu$ is the incident photon energy; A is an arbitrary coefficient; E_g is the optical band gap of the sample.²⁹

Thus, the optical bandgap of Cu_2O can be evaluated from the plot $[F(R)h\nu]^2$ vs. $(h\nu)$ Kubelka-Munk method. Figure 5 shows the plot of $[F(R)h\nu]^2$ vs. $(h\nu)$. The extrapolated optical bandgap of C105, C110 and C115 are 2.03, 2.00 and 1.98 eV, respectively. All the values are in the visible range, but we note that the optical bandgap of sample reduction with the molar ratio $[\text{CuSO}_4]/[\text{Na}_2\text{SO}_3]$ increases.

The experiments of photocatalytic activity for degradation of MB dyes on our Cu_2O NPs catalyst under visible light irradiation with the desire to bring practical applications in wastewater treatment.

Figure 6 indicates the absorption spectra of C110 sample for the decomposition of the MB organic dye solution with the exposure of the visible light. The maxima absorption peak of MB at $\lambda \approx 664\text{ nm}$ was used for this photo-degradation investigation. As seen in Fig. 6 the absorption peak decreases continuously with time of visible light illumination. This indicated that there was a decomposition of the MB solution in the experimental system. The intensity in the absorbance spectra of MB solution decrease with radiation time indicates the degradation of dye with the exposure of the visible-light.

The photocatalytic performance of the C105, C110 and C115 samples in the reaction of the MB decomposition is calculated based on the change of the absorption peak intensity of MB dye solution which is correlated with the MB dye concentration. As shown in Fig. 7(a), The C105, C110 and C115 samples have photocatalytic activities in MB under visible-light irradiation for 40 min. The C110 sample shows photocatalytic performance about 98% higher than 92% and 95% of C105 and C115 samples, respectively. The photodegradation efficiency of MB on the C110 sample was the highest. Results show that the improved photocatalytic activity of the C110 sample due to the interaction between the

Fig. 5 The plot of $[F(R)hv]^2 - (hv)$ of Cu₂O nanoparticles synthesized: (a) C105, (b) C110, (c) C115.

Fig. 6 The absorption spectra of C110 sample using the MB with the exposure of the visible light.

effective surface area of the C110 catalyst and the MB molecules is greater than that compared to other samples.

The relationship between kinematic data on the catalyst is shown in Fig. 7(b). The photo-oxidation kinetics model of pigments has been verified that is following the Langmuir-Hinshelwood kinetic equation. The Fig. 7(b) shows that plots of regression logarithmic curves between the concentration of normalized MB vs. the reaction time approximates with linear line. This indicates that the kinetics of MB degradation on the photocatalysts are first-order reaction kinetics:³⁰⁾

$$\ln(C/C_0) = k_{app}t \quad (7)$$

In which, C_0 - the initial concentration before illumination ($t = 0$), C - the concentration of the MB dye solution at every illumination time (t) and k_{app} - rate constant which characterizes the optical decomposition of dyes.

The C105, C110 and C115 samples have the correlation coefficients R^2 of 0.989, 0.984 and 0.933, respectively. This

Fig. 7 (a) Degradation curve of methylene blue and (b) The plots of kinetic linear simulation to determine the rate constant (k) for the photodegradation of methylene blue.

Table 2 Compare the MB decomposition efficiency of the prepared photocatalytic samples with this of the references.

Samples	photocatalyst concentration (g/L)	MB concentration (mg/L)	degradation efficiency (%)	irradiation time (min)	degradation rate constant (min^{-1})	irradiation source
Cu ₂ O-NPs (C110 sample -this study)	0.25	10	98	40	0.11281	250W compact lamp (Rang Dong Viet Nam)
Cu ₂ O Spheres (90 nm) [18]	3.15	5	63	80	0.0087	The room's natural light
Cu ₂ O Spheres (200 nm) [18]	3.15	5	44	80	0.0057	The room's natural light
TiO ₂ (19.1 nm) [6]	0.5	10	-	-	0.03558	125W high-pressure mercury lamp
0.16%Cu ₂ O-TiO ₂ (19.4 nm) [6]	0.5	10	-	-	0.09641	125W high-pressure mercury lamp
Degussa P25 [6]	0.5	10	-	-	0.08155	125W high-pressure mercury lamp
Cu ₂ O Spheres (1000 nm) [31]	9	10	90	50	5.095	300W tungsten lamp ($\lambda > 350$ nm)
Ag/Cu ₂ O [31]	20	10	96.5	120	1.365	500W xenon lamp ($\lambda > 400$ nm)
Cu ₂ O/ZnWO ₄ [31]	100	10	90	90	1.054	300W xenon lamp ($\lambda > 420$ nm)

confirms that the plots are linear lines that fit the data of the experiment. The kapp value is determined according to the slope of the plots of linear line. In the Fig. 7(b) shows that the value of kapp of C105, C110 and C115 samples are about 0.04866/min, 0.11281/min and 0.05681/min. The rate of C110 is 2 times greater than of C105 and C115 samples.

The MB decomposition efficiency and degradation rate constant of prepared Cu₂O NPs photocatalytic samples in our study show higher MB degradation efficiency in comparison with other studies. The comparison of MB decomposition efficiency and decomposition kinetics over prepared photocatalytic samples in this study compared with the studies in the references is shown in Table 2.

The prepared Cu₂O NPs samples have a bandgap edge of 1.98–2.03 eV which corresponding to the wavelength of 611–626 nm. Thus, these Cu₂O NPs materials are capable of stimulating light working in the visible region for photo-sensitive reactions. The mechanism of the blue methylene dye decomposition reaction is proposed according to the following reactions. The simplified schematic diagram of the energy band structure of electron-hole pair separation in Cu₂O NPs for degradation of MB dye under visible light irradiation shows in Fig. 8.^{1,3,4,31)}

Fig. 8 Simplified schematic diagram of the energy band structure and electron-hole pair separation in Cu₂O NPs for degradation of MB dye under visible light irradiation.

When Cu₂O nanoparticles are excited by light with energy which is greater than the bandgap energy of the material, there will be the separation of the photogenerated electron and hole pairs in the conduction regions (CB) and valence regions (VB), respectively. Then the photogenerated holes in the VB will readily react with hydroxyl ions to form hydroxyl radicals ($\cdot\text{OH}$) (eq. (8)). photoexcited electrons in the CB will react with dissolved O₂ to superoxide radicals O₂^{•−} (eq. (9)). These O₂^{•−} can further react with H₂O to increase the $\cdot\text{OH}$ hydroxyl radicals concentration (eqs. (11)–(16)). These hydroxyl radicals are responsible for MB oxidation to form degradation products which are H₂O and CO₂.

4. Conclusion

The cuprous oxide (Cu₂O) nanoparticles are synthesized by a simple reduction method at 85°C with different molar ratios as [CuSO₄]/[Na₂SO₃] (1:05, 1:10 and 1:15). The results show that the molar ratio [CuSO₄]/[Na₂SO₃] not only affects crystal structure and morphology but also affects the optical characteristics as well as surface crystallinity of Cu₂O NPs samples. The crystallite size calculated by the scherrer and Williamson-Hall equations ranges from 10–150 nm. These crystallite particles have uniformly octagonal morphology with medium size of 1–2 μm (according to SEM results). The sample with the molar ratio [CuSO₄]/[Na₂SO₃] precursors of 1:10 (C110 sample) has the highest uniformly octagonal cuprous oxide nanoparticles. The photocatalytic efficiency of the C110 sample was determined to be

remarkable which is higher than 98% under visible light irradiation for 40 minutes and with the rate constant of 0.11281 min^{-1} .

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