

Example of research paper on hydrothermal synthesis of shape-controllable copper ...

[Technology](#), [Innovation](#)



1. ABSRACT

The purpose of this experiment was two-fold. Firstly it was to synthesize shape-controllable Copper Oxide (Cu_2O) under alkaline conditions by using hydrothermal methodology. Secondly it was to measure and evaluate its application for photocatalytic degradation of direct blue dye 53 also commonly known as Direct Blue 53 or Evans Blue. Materials used for the first step were Cu_2O and the two reactants, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH . The temperature during the hydrothermal process was raised from 80°C to 140°C . Two products were synthesized: a) the Cu_2O nanorod and b) a mixture of Cu_2O nanorod and Cu_2O nanocubes.

Hydrothermal temperature was found to be an essential factor in the synthesis process. The function of the change in hydrothermal temperature was to facilitate shape-control and therefore determine the shape of Cu_2O as a nanorod or a nanocube. The products of the synthesis were characterized using four measurements: a) X-ray Diffraction (XRD), b) Ultraviolet and Visible spectroscopy (UV-Vis), c) Transmission Electron Microscopy (TEM) and, d) surface area. The application of Cu_2O as a catalyst for the degradation of direct blue dye with visible light was observed and measured.[2]

2. THEORY

Azo (blue) dyes have many practical purposes in the industrial and in the medical fields. The azo dyes are used in clothing manufacturing but the waste product after being used to dye clothing needs to have toxicity of

the dye neutralized so that waste product entering community water streams will not damage the environment. Azo dyes are also important in the medical profession in what is called “ photodynamic therapy” which is a “ treatment for tumors and certain diseases.”[1] As with industrial waste, medical waste should not be toxic when it enters the community whether by routes of water or through landfills. Therefore neutralizing toxicity is very important Figure 1 shows the chemical structure of the diazo dye, DB53 used in the experiment. Notice that that it is benzedine in nature (6 benzene structures) and that there are four molecules of Figure 2-1. Chemical Structure of DB53 (Diazo dye Direct Blue). [1]

NaSO₃ which characterizes the species as a “ sodium salt of a sulfonic acid.” [2] Figure 2 shows the structure of the hydrazone tautomers that cause the ‘ shoulder’ or the ‘ blue shift’ on the absorbance spectra which is particularly pronounced on the uv-visible light spectra when Figure 2-2. Equilibrium reaction between the azo and hydrazone tautomers. [2]

the dye is in the methanol diluents. . Isak et al. researched the photo-properties of DB53 and the results of their work is displayed in Table 2.

Note that λ_{max} is the maximum absorbance wavelength, ϕF is the fluorescence quantum yield and mfw stands for Mean Fluorescence wavelength. The low concentration limit is designated by LCL and expressed as molarity.

Figure 3 displays the absorbance from the visible spectra of DB53 at the same time comparing the three diluents that were used: a nonionic detergent (TX), aqueous, and methanol. Isak et al. have explained that this is the typical expected spectra for DB53 because the “hydrazne is the predominatnt tautomeric species in solution.” [1] The TX and methanol peaks each show a slight shoulder (blue shift) but the methanol spectra in particular demonstrates this dimension while another important point is the longer wavelengh measuered in the TX diluent than the methanolic peak which is “the main aborbance peak.” [1]

Figure 2-3. “Visible absorbance spectra of DB53 (Evans Blue) in aqueous TX (non-ionic detergent), aqueous, and methanolic solutions.” ([2] p. 81).

Figure 4 displays the fluorescence data in the three different diluents. Isak et al. have explained the significance of this spectra as once again being characteristic of the hydrazone tautomer. [2] (see Fig. 1) These results are important for this laboratory experiment because it was useful in deciding which diluent would be most suitable. Methanol was chosen.

Figure 2-4. Fluorescence spectra of DB53 (Evans Blue) In aqueous TX (non-ionic detergent), aqueous, and methanolic solutions. ([2] p. 83)

3. INTRODUCTION

The purpose of this experiment was two-fold. Firstly it was to synthesize shape-controllable Copper Oxide (Cu_2O) under alkaline conditions by using hydrothermal methodology. Secondly it was to measure and evaluate its application for photocatalytic degradation of direct blue dye 53. There are

several reasons this is important research in removing toxic elements from industrial wastes so in order to protect the environment. For example, there need to degrade blue dye used in clothing manufacturing as efficiently and cost-effectively as possible so toxic waste does not reach water supplies.

Hydrothermal synthesis has been shown to be a good methodology for creation of catalysts having crystalline nanomaterials. [2] [3] [4] Simple reducing agents reacted with Cu(II) (Cu^{+2}) salts have been found to successfully create different morphologies of Cu_2O nanocomposites who exhibit crystalline shapes ranging from “nanocubes to hexapods.” [6] Li and Zhang successfully synthesized “ Cu_2O - TiO_2 nanocomposites” using “homogeneous hydrolysis followed by solvothermal crystallization and ethylene glycol-thermal reduction process.” [7] Basu (et al.) synthesized “truncated Cu_2O cubes with well-defined morphology” from the a prepared reducing agent of a precursor Cu(II)-EDTA and glucose. [6] The synthesis was done under alkaline conditions with a short period (less than 5 minutes) of microwave irradiation. [6] The authors concluded that the passive medium, dilute H_2SO_4 , was very satisfactory. [6] They observed the “undisturbed reaction mixture showed oscillatory behaviour (clock reaction) even after one month. [6] This is in contrast to their experiments which did not create the oscillatory behavior in acidic dilutions unless MB was present. [6] The researchers concluded that “synthesized Cu_2O truncated cubes” are suitable for creating a clock reaction when MB is present under highly acidic conditions. [6] The primary reactions were a) the oxidation of Cu(I) to Cu(II) and b) the reduction of MB at $\text{pH} = 1$. [6] Srivastava (et al.) reached a similar

conclusion that the alkaline conditions (using methanol) for the preparation of the catalyst CuO a) “ exhibited better catalytic activity” and b) achieved the “ highest rate of methylene blue degradation.” [4] The rate of reaction, reactions to hydrothermal control, reaction rate and concentration of oxidants and reductants was reviewed in the literature in order to design this experiment.

4. EXPERIMENTAL INSTRUMENTATION AND PROCEDURES.

This experiment was undertaken in order to better understand the effect on cupric oxides photocatalytic efficiency with change in the hydrothermal temperature. Data was also gathered in order to evaluate the impact of the size of surface area, the surface texture, and the band gap energy on the diazo blue dye, Direct Blue 53 (DB53). The experiment was carried out using chemical reagents that had an analytical grade. In the process of the experiment, cupric oxide synthesis took place using the following: 200 mg poly ethylene glycol (PEG) which has a Molecular Weight (MW) of 20 000; 180 mg copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) dissolved in 200 ml H_2O with stirring. A magnetic stirrer was used for thirty minutes in order to ensure complete dissolution of the PEG and CuCl_2 . The amount of 2 mL of NaOH (6M) was added, drop-wise, into the solution during the magnetic stirring. At the end of the first 30 minute stirring period the $\text{Cu}(\text{OH})_2$ solution was colored blue and a portion had precipitated out. Another 30 minute timed stirring was started. And then 2 ml of 14 M hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) solution was added drop wise into the solution . The precipitate gradually changed colour and became red. Once the reduction by the N_2H_4 was

complete the solution was in a gel phase and still coloured red. The red gel was placed into an autoclave. It was heated for 10 hours at four different temperatures (80, 100, 120 and 140 oC). Precipitates were formed so those were filtered, washed with distilled water several times, and next they were dried in a vacuum oven at 60 oC for 3 hours.

Characterization techniques

A Bruker Axix D8 was used with a Cu K α radiation which is equal to $\lambda = 1.540 \text{ \AA}$ for x-ray diffraction (XRD) analysis. The duration was over a 2θ collection range of 10-80oC. and it was done at room temperature.

All samples were treated under vacuum at 200°C for 2 hours. And then a Nova 2000 series Chromatech apparatus at 77K was used to calculate the specific surface area from the measurement of the of N₂-adsorption spectra.

A UV-Visible diffuse reflectance spectra (UV-Vis-DRS) in air (room temperature) was used to determine the Band Gap of the samples which had measured within the 200-800 nm wavelength range after measurement in a UV/Vis/NIR spectrophotometer (V-570, JASCO, Japan).

A JEOL-JEM-1230 transmission electron microscope (TEM) recorded the electron transmissions after prepared samples were suspended in ethanol. Next ultrasonication for 30 min. Followed. And then a small amount of solution was placed on a carbon coated copper grid, dried and then loaded into the TEM.

Photocatalytic test

The application of synthesized nanocomposite for the photodegradation of pure DB53 dye was investigated under visible light. An annular batch reactor consisting of a horizontal cylinder was used in the photocatalytic testing part of the experiment. This consisted of irradiation of the photocatalyst with a blue fluorescent lamp (150 W) which had been doubly covered with a UV cut filter. Confirmation was made so that it was known that the detection limit was under 0.1 mW/cm² of a UV radiometer. The weights of the catalysts were measured and recorded. Then the catalyst was suspended into 300-ml of 100 mg/L pure DB53 dye solution with a neutral pH (pH ~7). An isothermal reaction at 25 °C proceeded. Reaction mixture samples were taken several time intervals until the end of the total reaction time after one hour. A UV JASCO (V 570) was used to measure the unreacted concentration of the DB53. The following equation determines the percent removal efficiency of the DB53.

5. RESULTS AND DISCUSSION

X- Ray Diffraction Analysis

approximation of the mean crystallite size was made using the Scherrer formula and evaluating the broadening of the peaks. The Full Width at Half Maximum (FWHM) can be fit by accommodating 111 peaks to the Sherrer formula with reference to varying hydrothermal temperatures. At temperatures (80, 100, 120 and 140 °C) the corresponding crystallite size in nm is 19.3, 26.0, 26.3 and 31.5 nm, respectively (Table 5-1).

Fig. 5-1. XRD patterns of Cu₂O samples prepared at different hydrothermal temperatures: 80, 100, 120 and 140 °C

TEM Observation

Figure 5-2 displays the TEM images of the Cu₂O samples and their appearance at different hydrothermal temperatures. From left to right the four images correspond to the four different hydrothermal temperatures of 80, 100, 120 and 140 °C. The first image on the right shows nanorod shapes which are very similar to one another (80 °C). The second image from the right an increase to 100 °C shows the development of heterogeneity as nanorod and nanocube shape were forming. At 120 °C the heterogeneity is more distinct although it still shows a combination of nanorod and nanocube shapes. At 140 °C the mixture is again homogenous but the shapes are nanocubes as opposed to the nanorods which were evident at the lowest hydrothermal temperature of 80 °C. The definite shape changes in the four phases in relationship with the four hydrothermal temperatures clearly indicate the importance of hydrothermal temperature on the shape which is produced.

Fig. 5-2. TEM of the Cu₂O samples prepared at different hydrothermal temperatures

Specific surface area analysis

The adsorption/desorption of N₂ was used to measurement of the synthesized Cu₂O samples' mesoporosity and textural properties. Liquid N₂ was use at a temperature of –196 °C. Fig. 5-3 a through d. show N₂ adsorption-desorption isotherms for the 4 samples. Typical type II sorption

behaviours were graphed of the isotherms. This indicates that there was no impact from the changes in the hydrothermal temperature.

Fig. 5-3. N₂ sorption isotherms of the Cu₂O samples prepared at different hydrothermal temperatures.

UV-vis absorption spectra

Figure 5-4 displays the wavelength versus the absorption for the samples at the four experimental temperatures. The shape the graph for each temperature is very similar. The difference is in how the absorbance increases from the highest temperature 140o C to the lowest temperature 80o C. This is reported to be typical of the blue shift which occurs in nanosystems experiencing such a quantum change in structure

An estimate of the optical band gap is obtained using the following equation.

$$\alpha(h\nu) = A(h\nu - E_g)^{m/2} \quad [12]$$

“ Where A is a constant, α is the absorption coefficient, and m equals 1 for a direct transition. The energy intercept of a plot of $(\alpha h\nu)^2$ versus $(h\nu)$ yields the E_g for a direct transition.” [12] [5] [7]

Fig. 5- 4. UV-vis absorption spectra of the Cu₂O samples prepared at different hydrothermal temperatures

Photocatalytic activity analysis

The photocatalytic analysis results are shown in Fig. 5-5. The DB53 diazo dye degradation is graphed at the four experimental hydrothermal temperatures with respect to time. The environmental conditions were under visible light.

The longer the solutions were irradiated the more degradation was observed. Total (degradation = 100 %) DB53 photocatalytic degradation was observed after sixty minutes at the 80o C hydrothermal temperature. At 100o C degradation was measured at approximately 88 percent, at 120o C measured approximately 80 percent degradation and at 140o C the dye demonstrated a degradation of approximately 69 percent. Because increased thermal temperatures cause reduced surface areas then a decrease in active sites on particles' surface follows. The following equation was used to explain this situation where R equals rate of degradation equal to kinetic energy multiplied by the concentration of DB53.

$$R = k [\text{direct blue dye}] \quad [1]$$

Fig. 5-5. Photocatalytic degradation of direct blue dye with Cu₂O at four different hydrothermal temperatures.

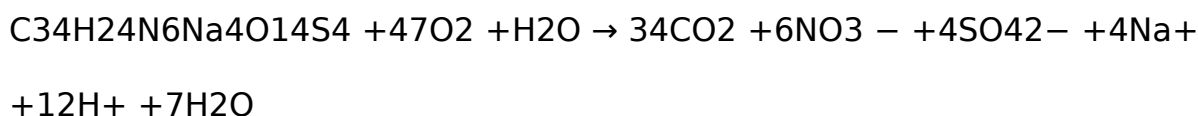
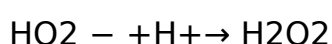
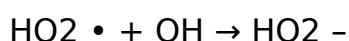
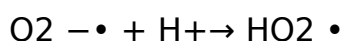
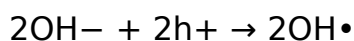
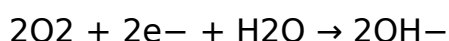
The absorbance edge of Cu₂O products was identified by UV-Vis spectra to be located in the range of 506 to 564 nm. This fits a supposition that Cu₂O “is excited by visible light and generated the electron-hole pair.” [1]

Mohammed (et al.) have observed that as Cu₂O grain size decreases, specific surface area increase which improves the ability of Cu₂O to catalyze degradation. [1] (See the Appendix cupric acid for photograph and list of its chemical properties.) Repeated trials under visible light were made. For the first six cycles the degradation was 100 percent effective. Further recycling of the photocatalyst decreased the effectiveness to only 3 percent after seven cycles. [1] this demonstrated that the photocatalyst had been

successfully separated and the use of recycling the photocatalyst has real potential.

The ability to act as a semi-conductor of Cu₂O is due to its ability to rise to a higher energy state under visible light; this leads to electrons releasing from the surface, causing excitement leading to a valence band gap. The 'hole' in the gap exhibits high oxidation capabilities and so it can remove an electron from a hydroxide ion in an aqueous solution while at the same time the hydroxide takes an electron creating a highly unstable hydroxide ion radical. (Fig. 5-6)

Fig. 5-. 6. The basic of photocatalytic process



where E is energy"

Kinetic of direct blue dye with Cu₂O

Figure 5-7 shows the DB53 kinetic reaction orders in a graph of reaction time against log [DB53]

Here is the equation used for calculating the various ratios of catalyst/ direct blue dye solution. [1]

$$\text{Log } [C]_t = -(k)(t) + \text{Log } [C]_0 \quad [1]$$

The concentrations at the initial phase and after time are designated as $[C]_0$ and $[C]_t$. These time conditions for the concentration of DB53 can also be described at $[C]$ at zero time and at some duration of illumination time passed. The rate constant 'k' is equal to the appropriate rate constant (min^{-1}). Figure 5-7 shows the graphic representation of the reaction time in minutes versus the $\text{Log } [C]_t$ for the 4 hydrothermal temperatures used in the experiment. The results are also listed in Table 5-1. First order kinetics can be recognized from Figure 5-7. The first order kinetics of DB53 and rate constants plotted show a range of 100×10^{-4} to $330 \times 10^{-4} \text{ min}^{-1}$.

Fig. 5-7. Reaction kinetic of DB53 (Direct Blue dye 53)

Conclusions

This experiment used four different hydrothermal temperatures in order to control the morphology of Cu_2O . The initial materials were $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH . The four different temperatures were 80, 100, 120 and 140°C . At the temperature of 80°C the shape was nanorods and the surface area was $40.1 \text{ m}^2/\text{gm}$; the band gap measured 2.20 eV . Through the four phases of the four temperatures the morphology changed from nanorod to a mixture of nanorods and nanocubes until finally at the highest temperature only nanocubes were evident. Hydrothermal temperature change had impacts not only on the shape but also on the surface area of the particles and the

measure of the band gap in synthesized Cu₂O. DB53 underwent photocatalytic experiments which determined that a future use for Cu₂O as a photocatalyst could be very practical for neutralizing toxic dyes in industrial wastes, as a water purifier, and neutralizing toxic dye in medical wastes. Interestingly the catalyst recycles with 100 percent efficiency for six cycles. And then the seventh cycle still demonstrated degradation of 96 percent efficiency. After the seventh recycling the usefulness as a degradation photocatalyst quickly deteriorated.

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[12] 256: 134-138.

Appendix

Figure 1. Ball-and-stick model of the unit cell of copper(II) oxide, CuO (Mills, 2007)

Figure 2. Section of Crystal Structure of CuO (Mills, 2007)