Transformation of Nanostructures Cu$_2$O to Cu$_3$Se$_2$ through Different Routes and the Effect on Photocatalytic Properties

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1. INTRODUCTION

Nowadays, one of the world’s biggest problems is environmental pollution, in which water contamination has increased exponentially in recent years. One of the common contaminants in water flows is organic dyes, which are used mainly as coloring agents in textile, cosmetics, paper, pharmaceutical, and other industries. Methylene blue (MB) is a heterocyclic aromatic molecule with a complex aromatic structure, which is very stable. This dye can provoke numerous effects on the health of humans and animals, causing an increase in heart rate, allergic problems, nausea, and vomiting.

Several methods have been studied and reported for the elimination of contaminants in wastewater, such as photocatalytic degradation, adsorption, electrocoagulation, and membrane for water evaporation. Among these methods, photocatalytic degradation has been well studied and recognized as one of the best due to its advantages such as simple operation and high efficiency. Various semiconductors like metal oxides, metal chalcogenides, and carbon nanostructures have been extensively studied. Within this area, copper selenide is a p-type semiconductor, which has attracted attention in recent years due to its active band gap energy in the visible range of the solar spectrum. The band gap of copper selenide depends on its structure, phase, and stoichiometry, the band gap energies reported for Cu$_3$Se$_2$, Cu$_2$Se, Cu$_2$Se$_2$, Cu$_2$Se, and Cu$_2$Se$_2$ are 1.65–1.85, 1.49, 1.98, 2.0, and 2.17 eV, respectively. Copper selenide can be used in different applications such as solar cells, supercapacitors, optoelectronic systems, and photocatalysis under natural sunlight.

There are several methods for the synthesis of CuSe materials, such as thermolytic, ultrasonic, microwave, electrochemical, and hydrothermal processes. In the present investigation, we report a simple route for the preparation of copper selenide (Cu$_3$Se$_2$) from Cu$_2$O hexapods. The focus of this research was to obtain a material that is easy to synthesize, inexpensive, and active under natural sunlight for dye removal. That way, the possibility of using this material as a photocatalyst for the removal of methylene blue in water solution was studied.

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2. EXPERIMENTAL SECTION

2.1. Materials. All of the reagents were purchased from Sigma-Aldrich and used as received without further purification process. Copper chloride (CuCl₂, 97% purity), sodium citrate (Na₃C₆H₅O₇, 99% purity), dextrose (C₆H₁₂O₆), and potassium bicarbonate (KHCO₃, 99% purity) were used to synthesize Cu₂O hexapods. Copper selenide materials were obtained by the reaction of Cu₂O with selenium ions in a solution obtained by mixing sodium sulfite (Na₂SO₃, 98% purity) and selenium powder (Se, 99.5% purity). Methylene blue (C₁₆H₁₈ClN₃S·xH₂O) and methanol (CH₃OH, 99.9% purity) were used for the photocatalytic experiments.

2.2. Synthesis of the Catalysts. 2.2.1. Step 1: Cu₂O Hexapods Synthesis. The synthesis of Cu₂O hexapods was similar to that in our previous work; briefly, 1.125 g of CuCl₂, 1.35 g of Na₃C₆H₅O₇, 1.05 g of C₆H₁₂O₆, and 7.5 g of KHCO₃ were dissolved in 75 mL of deionized water with magnetic stirring. After 30 min of magnetic stirring, the solution was transferred to a Teflon-lined autoclave system and heated at 120 °C for 16 h. The obtained red powder was washed three times with deionized water and dried at 110 °C overnight in a conventional oven.

2.2.2. Step 2: Selenium Ions Synthesis. A solution of selenium ions was used to interact with the hexapods of Cu₂O. The Se²⁻ solution was prepared by mixing 12.6 g of Na₂SO₃ and 1 g of selenium powder in 100 mL of deionized water. The solution was heated at 80 °C for 4 h under vigorous magnetic stirring. After this, the solution was left to rest before being used in experiments.

2.2.3. Step 3: Synthesis of Copper Selenide Materials. Copper selenide materials were synthesized by the following two routes (see Figure 1):

(I) CuSe-A by chemical reaction: 0.1 g of Cu₂O hexapods was mixed with 30 mL of the Se²⁻ solution for 5 h.

(II) CuSe-H by hydrothermal process: first, 0.1 g of Cu₂O hexapods were mixed with 20 mL of the Se²⁻ solution, and then the suspension was placed in a Teflon-lined autoclave at 120 °C by 5 h.

The obtained powders were black-purple in both solutions and were recovered, washed twice with deionized water, and dried at 110 °C overnight.

2.3. Characterization. The morphology of the Cu₂O hexapods and the copper selenide materials (CuSe-A and CuSe-H) was studied by scanning electron microscopy (SEM) using a Philips-ESEM 30 instrument. X-ray diffraction (XRD) was employed to study the crystalline structure of the materials using a Rigaku D-Max 2100 X-ray diffractometer. An Oceans Optics UV–visible spectrometer was used to study the optical properties of the materials. For X-ray photoelectron spectroscopy (XPS) measurements, a Thermo Scientific Escalab 250Xi spectrometer with monochromatized Al Kα radiation (1486.6 eV) was used, and the binding energies were referenced to the C 1s peak at 284.8 eV.

2.4. Photocatalytic Experiments. Copper(I) oxide hexapods and copper selenide materials (CuSe-A and CuSe-H) were applied as photocatalysts for decolorization of methylene blue (MB) under sunlight (100°23′17″ W and 20°35′17″ N, 1820 m above sea level average solar irradiation of 5.9 kWh/m²-day, and an average solar radiation index of 984 W/m²) on a sunny day for 4 h. This experiment demonstrates its use under real conditions. The experiment involves addition of 0.025 g of photocatalyst materials in a 50 mL solution of methylene blue (0.02 mM) in 100 mL beakers. Then, the beakers were placed under sunlight, and the samples were periodically taken every hour to measure their optical absorption spectra. The photodegradation efficiency of methylene blue in solution (D) was calculated using the following equation:

\[ D = \frac{C_o - C}{C_o} \times 100\% \]

where D is the decolorization efficiency of the catalyst (CuSe-A and CuSe-H), C₀ is the initial concentration of MB, and C is the concentration of MB at a different time. The MB concentrations were determined from the optical UV–vis absorption spectra.

3. RESULTS AND DISCUSSION

3.1. Structural Results. Figure 2 shows the structural analysis of the Cu₂O hexapods obtained by the hydrothermal
process. Figure 2a shows the SEM image where the formation of six-pointed stars of size between 3 and 6 μm can be observed in each of the peaks; most of the hexapods synthesized show a smooth and regular surface. In the XRD analysis (Figure 2b), cuprite phase (Cu2O) formation is observed, with peaks at 29.5, 36.4, 42.2, 52.4, 61.3, and 69.5° corresponding to the (110), (111), (200), (211), (220), and (310) planes of the cubic phase (JCPDS 05-0667). It is also possible to observe the presence of two peaks at 43.3 and 50.4°, which correspond to the (111) and (200) planes of the metallic copper cubic phase (JCPDS 89-2838).

The X-ray diffraction (XRD) patterns of copper selenide (Cu3Se2) are shown in Figure 3. Figure 3a (CuSe-A) shows the presence of the peaks corresponding to combined phases of umangite (Cu3Se2) and cuprite (Cu2O). Figure 3b (for CuSe-H) shows peaks corresponding only to the umangite phase. These XRD results suggest that the complete conversion of hexapods from Cu2O to Cu3Se2 was achieved only through the hydrothermal process, whereas with the chemical reaction methodology, a Cu2O/Cu3Se2 mixture was obtained. The previous supposition is in agreement with the SEM analysis (Figure 4). Figure 4a,b shows the morphology images of CuSe-A, where the formation of bulges and blocks on the surface of the Cu2O hexapods can be observed, in which the smooth surfaces show that the hexapods were not completely converted to the Cu3Se2 umangite phase. On the other hand, Figure 4c,d (CuSe-H SEM images) shows the hexapods formed by particles and “blocks” without any visible smooth surface.

These results lead us to conclude that the best route to synthesis is by the hydrothermal method, with the variables of pressure and temperature being an ideal combination for the reduction of Cu2O and the insertion of Se to the original structure of the hexapods. In the case of the chemical reaction method, the used combination of ion concentration and time does not provide enough energy to penetrate the entire structure of the hexapod and reduce the Cu2O beyond the surface level.

The band gap energy values were calculated using UV spectroscopy and the Kubelka–Munk equation (Figure 5). According to the calculations, CuSe-H has the lowest band gap energy of 2.11 eV, followed by the Cu2O sample with a value of 2.25 eV, and finally CuSe-A with a higher value of 2.67 eV. Through this analysis, it is determined that although all of the samples can work under solar irradiation, the lower band gap of CuSe-H provides an advantage due to the lower energy needed to generate the electron–hole pair.30–32

The XPS analysis of the Cu2p, Se3d, and O1s regions of the samples (CuSe-A and CuSe-H) is shown in Figure 6. The broad Cu2p3/2 peak and the shake-up satellite feature were deconvoluted into four peaks, marked as peaks CuI and CuII in Figure 6b and as Se(I) and Se(II) in Figure 6c. The main peak at 932 eV (CuI) is due to the copper selenides phases, broadly defined as Cu2−xSe,33−35 while the signal at 933.8 eV (CuII) corresponds to the Cu3Se2 phase.24 Finally, the satellite peaks36−38 at 941.5 and 947.3 eV can be observed in both samples. In the Se3d spectrum, the main peak at around 55 eV in both samples can be deconvoluted into four peaks (Figure 6c,d). The peaks at 53.3 and 54.1 eV originate from Se3d5/2 and Se3d3/2 of the copper selenide phases, respectively, while the peaks at around 54.3 and 55.8 eV could be elemental selenium from the precursor.39−41 Finally, the peak at approximately 58.4 eV could be ascribed to Se4+ of SeO2.42−44 The Se(I) signal,
corresponding to the copper selenide phases, is higher for CuSe-H than for CuSe-A. Similarly, a high signal is observed for the elemental selenium and selenium oxide phases in the CuSe-A sample. These results confirm that a higher extraction of the Cu3Se2 phase is achieved with the hydrothermal process compared to the agitation process. The chemical composition analysis performed with the XPS technique is shown in Table 1, where the presence of selenium is observed in CuSe-A and CuSe-H, as expected. A greater quantity of selenium was found in CuSe-H (18.14 atom%) than in CuSe-A (11.61 atom%). The higher oxygen content in CuSe-A (69.87 atom%) is attributed to the presence of the Cu2O and SeO phases found by XRD and XPS, respectively. The lower amount of oxygen in CuSe-H (44.13 atom%) is due to the absence of the Cu2O phase in the hexapods as well as the higher conversion of the Cu3Se2 phase, which leads to a lower amount of SeO in the final material.

3.2. Photocatalytic Results. Figure 7 shows the results of MB removal as a consequence of the interaction with photocatalytic materials. The absorbance peak of the MB solution is located at 664 nm with a small shoulder at 615 nm, which correspond to the conjugation system and dye dimmers. As shown in Figure 7a, the intensity of the absorbance of MB decreased at different levels after 240 min under sunlight irradiation in the presence of CuSe-H, Cu2O hexapods, and CuSe-A photocatalysts. These results indicate good MB degradation performances under sunlight irradiation of the three samples. In the presence of the CuSe-H photocatalyst, the decrease in the absorbance band is sharper, and a blue shift from 664 to 635 nm was also observed. The hypsochromic shifts and rapid decrease of the absorption band are attributed to the effective degradation of methylene blue by N-demethylation, which means that CuSe-H is a better photocatalyst for the degradation of MB under solar irradiation. This better photocatalytic effect of CuSe-H can be followed in Figure 7b by the normalized concentration (C/C0), and in Figure 7c by the decolorization of the MB solution. CuSe-A and Cu2O show a similar behavior, reaching decolorization efficiencies of 50.1 and 53.7%, respectively. In contrast, CuSe-H shows a 77.8% decrease in the normalized concentration in the first hour, which is seen by a decolorization efficiency of 77.8% in the first hour and reaches 92.4% at the end of the experiment.

The kinetic rate constants (k) were calculated using the data from Figure 7a,b and are displayed in Figure 7d,e. A first-order equation was used for the CuO and CuSe-A data, while the
CuSe-H data were fitted to a second-order reaction.47 The equations are presented in Table 2, where \([C]_0\) is the initial dye concentration and \([C]_t\) is the concentration of the dye at time \(t\) of irradiation. The kinetic rate constant of CuSe-H \((5.493 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1})\) is an order of magnitude higher than those of CuSe-A and Cu2O hexapods \((2.99 \times 10^{-3} \text{ and } 3.11 \times 10^{-3} \text{ min}^{-1}, \text{ respectively})\).

To explain the photocatalytic behavior of the samples, the band position diagram was constructed using the absolute electronegativity of Mulliken48,49 (Figure 8) and the band gap energy values calculated by UV spectroscopy (Figure 5). The conduction band (CB) and valence band (VB) edges were calculated using the following equations

\[
E_{\text{CB}} = X - E_g + 0.5E_g
\]

\[
E_{\text{VB}} = E_{\text{VBM}} - E_g
\]

where \(E_{\text{CB}}\) and \(E_{\text{VB}}\) are the edge potentials of the CB and VB, respectively, \(X\) is the geometric mean of the Mulliken’s electronegativities of the constituent atoms, \(E_g\) is the energy of free electrons on the hydrogen scale \((4.5 \text{ eV vs normal hydrogen electrode (NHE)})\), and \(E_g\) is the band gap energy of the sample. The \(E_{\text{CB}}\) and \(E_{\text{VB}}\) values were −0.29 and 1.95 eV for Cu2O, and −0.56 and 1.55 for Cu4Se2, respectively.

With the calculated band edges, the following mechanism for the photodegradation of the dye on the CuSe-H sample is proposed. The photodecolorization of the MB solution is initiated by the excitation of the photocatalyst by sunlight irradiation (eq 6), and the generated electrons interact with molecular oxygen \((O_2)\) to produce free oxidative radicals \((O_2^-)\) (eq 7) and hydrogen peroxide \(H_2O_2\) (eq 8), which can react to obtain hydroxyl radicals \(^{•}OH\) (eqs 9 and 10). Therefore, the photodecolorization is carried out by the holes generated by photoexcitation and by the generated \(H_2O_2\), \(O_2^-\), and \(^{•}OH\) radicals. The involvement of these radicals helps explain the observed rapid kinetics (eqs 10–13).

\[
\text{Ph} + \text{hv}(\geq E_g) \rightarrow \text{Ph}(e_{\text{CB}}^-) \quad (6) \\
*\text{Ph}: \text{photocatalyst: CuSe} - \text{H} \\
*E_g: \text{energy gap} \\
\text{e}_{\text{CB}}^- + O_2 \rightarrow O_2^- \quad (7) \\
\text{e}_{\text{CB}}^- + O_2^- + 2H^+ \rightarrow H_2O_2 \quad (8) \\
H_2O_2 + e_{\text{CB}}^- \rightarrow 2OH^- \quad (9) \\
H_2O_2 + \text{MB} \rightarrow \text{products} \quad (10) \\
O_2^- + \text{MB} \rightarrow \text{products} \quad (11) \\
O_2^- + \text{MB} \rightarrow \text{products} \quad (12) \\
H_2O_2 + \text{MB} \rightarrow \text{products} \quad (13)
\]

In the case of Cu2O, due to its CB and VB values, it is not capable of generating \(O_2^-\) radicals, so the photodecolorization takes place only with the holes generated in the photoexcitation and

Table 1. Cu, O, and Se Contents (atom %) in Cu2O Hexapods and the CuSe-A and CuSe-H Photocatalysts, According to XPS Analysis

| sample                   | Cu (atom %) | Se (atom %) | O (atom %) |
|--------------------------|-------------|-------------|------------|
| Cu2O hexapods            | 28.42       | NA          | 71.57      |
| CuSe-A                   | 18.51       | 11.61       | 69.87      |
| CuSe-H                   | 37.72       | 18.14       | 44.13      |

Figure 6. High-resolution XPS spectra of the Cu2p (a, b) and Se3d (c, d) regions of the CuSe-A and CuSe-H photocatalysts.
any OH$^-$ radicals from the water. Finally, the CB of CuSe-A is higher than that of Cu$_2$O, even though it contains Cu$_3$Se$_2$. The photogenerated electrons move to the CB of the Cu$_2$O and do not react with O$_2$ to generate the O$_2$•$^-$ radical. Thus, the photodecolorization mechanism for CuSe-A is the same as for Cu$_2$O, which explains their similar behavior and performance.

### 4. CONCLUSIONS

The Cu$_3$Se$_2$ materials were successfully synthesized from Cu$_2$O hexapods by two synthesis routes and applied for the photodegradation of the methylene blue solution. The achievement of the Cu$_3$Se$_2$ phase was confirmed by XPS and XRD studies, showing that the hydrothermal route showed a total conversion of the Cu$_2$O phase to Cu$_3$Se$_2$. The SEM study showed the formation of Cu$_3$Se$_2$ particles on the Cu$_2$O hexapods in the CuSe-A sample, while in the CuSe-H sample, a smooth surface was observed. The CuSe-H material showed a higher efficiency for MB degradation, reaching 92% discoloration under solar radiation in a total time of 4 h. The improvement in photocatalytic efficiency of the CuSe-H material is due to the generation of O$_2$•$^-$ radicals and OH$^-$ radicals, which degrade the methylene blue molecule faster than the Cu$_2$O and CuSe-A samples. With the results obtained, it was possible to meet the objective of obtaining a cheap and active material under natural sunlight for the removal of dyes in water.
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Notes

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