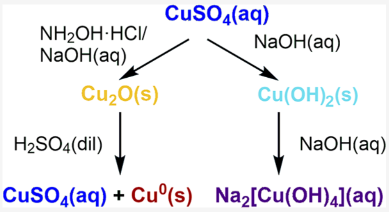
JOURNAL OF CHEMICAL EDUCATION

Copper–Oxygen Compounds and Their Reactivity: An Eye-Guided Undergraduate Experiment

Matilde Fondo*

Cite This: *J. Chem. Educ.* 2023, 100, 4791–4795



ABSTRACT: The chemistry of Cu^I and Cu^{II} is rich, and these oxidation states can be converted into each other by using quite mild or more strong oxidizing or reducing agents, depending on the starting materials and reaction conditions. Thus, this work describes an easy way to obtain yellow copper(I) oxide from copper(II) sulfate, using hydroxylamine hydrochloride as a reductant. In addition, the aqueous chemistry of Cu^{II} is very abundant, and in basic media, it perfectly exemplifies the chemistry of any transition metal having amphoteric hydroxides. For this purpose, copper(II) hydroxide is prepared from copper(II) sulfate by addition of basic medium. The insoluble amphoteric hydroxide reacts again with a solution of sodium hydroxide to form the corresponding water-soluble sodium tetrahydroxocuprate(II). Finally, an experiment is carried out to demonstrate the instability of Cu^I in aqueous acid medium, which disproportionates to form Cu^0 and the corresponding water-soluble copper(II) salt. This set of experiments has been designed to be performed in a single 3–4 h laboratory session, and it has been tested several times with second-year undergraduate chemistry students at the University of Santiago de Compostela (Spain).

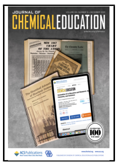
KEYWORDS: *Undergraduate, Inorganic Chemistry, Laboratory Experiment, Copper Chemistry, Yellow Copper(I) Oxide, Amphoteric Character, Disproportionation*

INTRODUCTION

Characteristic aspects of the descriptive inorganic chemistry of metals are often an arduous subject for students of the degree in Chemistry. Therefore, it is of great interest to carry out laboratory experiments that help them to consolidate concepts related to the reactivity of metals and their compounds. In this way, copper in massive form is a quite noble metal, though less so than others,[1] and it resists atmospheric attack, covering itself in the long term with a green patina.[2−4] Under more aggressive conditions, copper reacts readily. Thus, the chemistry of copper involves oxidation–reduction reactions, which give rise to different oxidation numbers (commonly +I and +II), and these can be converted into each other. The stability of these oxidation states both in solid state and in aqueous solution is different, with Cu^{II} being the most stable species in both media. Thus, Cu^I compounds can be isolated by reduction from more stable Cu^{II} precursors. In this way, many methods have been described for obtaining copper(I) oxide from copper(II) salts. In the more classical syntheses (not electrochemical or hydrothermal), maybe the most used reductants are sugars (making use of the well-known behavior of Benedict's reagent or Fehling's solution),[5−8] but other reductants such as ascorbic acid,[6,9] hydrazine,[10] sodium borohydride,[11] or hydroxylamine[12] have also been employed. Among these synthetic methods, the simplest ones, and therefore the easiest to implement in an undergraduate laboratory, typically lead to brick-red Cu_2O nanoparticles, whose color is reminiscent of Cu^0 metal itself. Some other experiments also described the identification of the yellow form of the oxide but in the course of other investigations, which were not aimed at isolating the oxide itself.[12,13] Accordingly, a simple and straightforward method of synthesizing yellow Cu_2O nanoparticles would be of great interest, so that students can visualize that a strong reductant can reduce Cu^{II} to Cu^I, not to Cu^0.

Besides, it should be noted that Cu^I classic compounds can only be isolated in the solid state, given that Cu^I disproportionates in aqueous solution,[14] and this is a characteristic that Cu^I shares with Au^I. Unlike Cu^I, the chemistry of Cu^{II} in aqueous solution is rich, forming different species depending on the pH of the medium, a feature common to many other d-block metals in the +II or +III oxidation states. In this respect, the amphoteric character of copper(II) hydroxide is remarkable, which in a strong basic medium leads to the isolation of tetrahydroxocuprate(II) ($[Cu(OH)_4]^{2-}$). This exemplifies the reaction of amphoteric metal oxides or hydroxides with a strong base, which gives rise to oxoacid salts where the metal forms part of the oxoacid group.

Received: June 30, 2023
Revised: October 14, 2023
Accepted: October 19, 2023
Published: November 8, 2023



https://doi.org/10.1021/acs.jchemed.3c00634

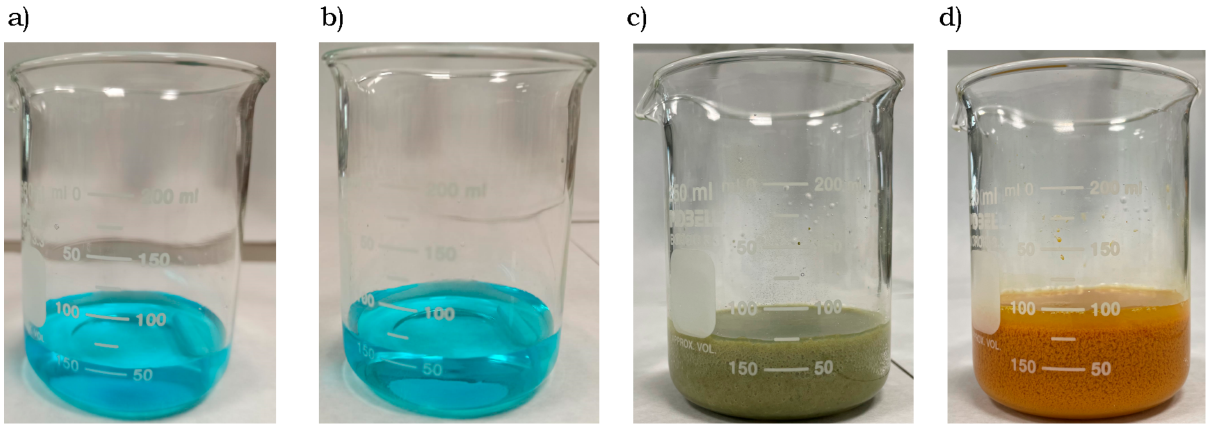


Figure 1. (a) The solution of copper(II) sulfate. (b) The solution of copper(II) sulfate after addition of the solution of hydroxylamine. (c) The solution of copper(II) sulfate and hydroxylamine after the addition of a small quantity of the NaOH solution. (d) The solution of copper(II) sulfate with hydroxylamine after completing the addition of the NaOH solution.

EXPERIMENTAL OVERVIEW

The following three experiments are proposed for undergraduate chemistry students: experiment 1, obtaining of yellow copper(I) oxide using hydroxylamine; experiment 2, reactivity of copper(II) sulfate in basic medium; experiment 3, reactivity of copper(I) oxide with sulfuric acid and identification of the final solid. All of these experiments can be carried out in a single laboratory practice session, in a maximum time of about 4 h. The detailed implementation of the three experiments is described in the Supporting Information. In addition, other methods of synthesis of copper(I) oxide, but in this case of brick-red color, are also included in the Supporting Information.

DISCUSSION

Experiment 1

The first experiment, the obtaining of yellow copper(I) oxide, illustrates the interconversion of the two common oxidation states of copper. Thus, this is a redox reaction, where the copper(II) sulfate acts as an oxidant toward the strong reducing agent hydroxylamine, as shown below (eq 1).

$$\underset{\text{oxidant}}{2CuSO_4\cdot 5H_2O(s)} + \underset{\text{reductant}}{2NH_2OH\cdot HCl(s)} + 6NaOH(s)$$

$$\Big\downarrow H_2O(l)$$

$$Cu_2O(s) + N_2(g) + 2NaCl(aq) + 2Na_2SO_4(aq) + 17H_2O(l) \qquad (1)$$

$$\left[\, Cu^{2+} + 1e^- \rightarrow Cu^+ \,\right] \times 2 \qquad E^{o}\ Cu^{2+}/Cu^+ = 0.153\ V$$

$$2NH_2OH + 2OH^- \rightarrow N_2 + 4H_2O + 2e^- \qquad E^{o}\ N_2/NH_2OH = -3.84\ V$$

$$2Cu^{2+} + 2NH_2OH + 2OH^- \rightarrow 2\,Cu^+ + N_2 + 4H_2O$$

The copper(I) oxide can show different colors due to the different particle size[13] obtained depending on the experimental conditions, and the use of hydroxylamine is important for isolating the yellow form of the oxide. Although the most common methods for obtaining Cu_2O with more typical reductants could, in theory, also enable the isolation of the yellow form of the oxide, the use of hydroxylamine is advantageous. First of all, it does not give colored products in solution (as can occur, e.g., with ascorbic acid or glucose), which facilitates visual examination and interpretation of the reaction results by the students. Second, this reducing agent is sufficiently reactive to eliminate the heating required by many other reductants. Finally, it has much greater stability compared with other reductants for synthesis at room temperature (e.g., sodium borohydride), and its solutions can be stored for months without changes, which is useful for reproducible and cost-effective teaching experiments.

The reaction of Cu^{2+} with hydroxylamine only takes place in a basic medium. This is clearly observed because the mixing of the blue copper(II) sulfate solution (color due to the presence of the $[Cu(OH_2)_6]^{2+}$ cation) and the colorless hydroxylammine solution does not lead to changes in color or physical states. The solid only begins to precipitate when the sodium hydroxide aqueous solution is added (Figure 1 and Figure S1).

The Cu_2O suspension obtained is left to stand, and supernatant water is decanted. Then, the solid is washed with water to eliminate the possible salts (NaCl and Na_2SO_4) that can impurify the product, before being filtered by gravity (Figure S2). Subsequent washes with ethanol and diethyl ether are intended to encourage drying of the final product.

Experiment 2

The second experiment explores the reactivity of copper(II) sulfate in a basic medium. The first part of this illustrates the typical reaction of a soluble salt of a transition metal in a basic medium. Thus, this is an exchange reaction, where the most insoluble species is formed. In this case, this species is the light blue copper(II) hydroxide, as shown in the reaction below.

$$CuSO_4\cdot 5H_2O(s) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + Na_2SO_4(aq) + 5H_2O(l) \qquad (2)$$

Accordingly, this reaction is very easy to track, as we go from observing the blue copper(II) sulfate solution (Figure 1) to a suspension with the light blue solid (Figure 2).

The copper(II) hydroxide has amphoteric character, and it redissolves in a strong basic medium. Therefore, the addition of more sodium hydroxide produces the soluble sodium tetrahydroxocuprate(II), according to the following Lewis acid–base reaction:

$$\underset{\text{Lewis acid}}{Cu(OH)_2(s)} + \underset{\text{Lewis base}}{2NaOH(aq)} \rightarrow Na_2[Cu(OH)_4](aq) \qquad (3)$$

The progress of this reaction can also be followed visually, since as the soluble sodium tetrahydroxocuprate(II) is formed, the copper(II) hydroxide dissolves, and the suspension of the

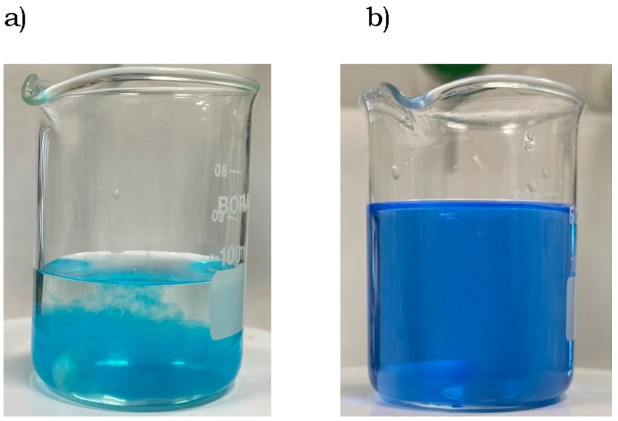


Figure 2. (a) The solution of copper(II) sulfate after the addition of a few drops of NaOH solution, showing the precipitation of copper(II) hydroxide. (b) The solution of $Na_2[Cu(OH)_4]$ formed after the addition of the whole NaOH solution to the precipitated copper(II) hydroxide.

light blue solid is transformed into a darker blue solution (Figure 2).

The temperature, the concentration of the original copper(II) sulfate solution, and the addition rate of the sodium hydroxide solution are fundamental factors in this reaction. If a very concentrated $CuSO_4$ solution has been used to precipitate the copper hydroxide, if the solutions are hot, or if the base is added too fast, dark insoluble aggregates (CuO) are produced according to eq 4.[15−19]

$$Na_2[Cu(OH)_4](aq) \rightarrow CuO(s) + 2NaOH(aq) + H_2O(l) \quad (4)$$

Accordingly, it is very important to add the cold NaOH solution to the copper(II) sulfate solution dropwise and with stirring.

Experiment 3

The third experiment illustrates the disproportionation of Cu^I species in aqueous solution, which can be easily inferred from the reduction potentials of the pairs Cu^{2+}/Cu^+ and Cu^+/Cu^0 (eq 5). Thus, the reaction of copper(I) oxide, which is a weak base, in the presence of dilute sulfuric acid should give rise to an acid−base reaction. However, a redox process occurs (eq 5), due to the instability of Cu^I in water, according to the following reaction:

$$\begin{array}{lll}
\text{Oxidation} & Cu^+ \longrightarrow Cu^{2+} + 1\,e^- & E^o\ Cu^{2+}/Cu^+ = 0.15\ V \\
\text{Reduction} & Cu^+ + 1e^- \longrightarrow Cu^0 & E^o\ Cu^+/Cu^0 = 0.52\ V \\
\hline
 & 2\,Cu^+ \longrightarrow Cu^{2+} + Cu^0 &
\end{array}$$

$$Cu_2O(s) + H_2SO_4(aq) \longrightarrow Cu^0 + CuSO_4(aq) + H_2O(l) \quad (5)$$

It is very easy to verify that this rapid reaction has taken place, since the dark yellow solid Cu_2O (Figure 1) disappears, and a reddish solid (Cu^0) and a blue solution (due to the presence of $[Cu(H_2O)_6]^{2+}$) are formed (Figure 3).

Besides, the identification of copper metal can be made by adding a small quantity of concentrated nitric acid to a spatula tip of the solid copper, observing the release of brown NO_2 gas, and the formation of the typical blue solution of copper(II) nitrate according to the following reaction.

$$\underset{\text{reductant}}{Cu(s)} + \underset{\text{oxidant}}{4HNO_3(conc)} \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l) \quad (6)$$

$$\begin{array}{c}
Cu \longrightarrow Cu^{2+} + 2e^- \\
\left[NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O\right] \times 2 \\
\hline
Cu + 2NO_3^- + 4H^+ \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O
\end{array}$$

Another indication that the reddish solid is copper can be obtained by adding concentrated hydrochloric acid over it. In this case, as copper itself is more oxidizing than the proton, no reaction will be observed. The same is true for water, a medium with which copper metal does not react in the short term.

■ LABORATORY IMPLEMENTATION

I have conducted these three experiments in six different years for a group of 18−20 second year undergraduate chemistry students, who were taking a course on metals and their compounds. The experiments were carried out individually during a 3−4 h laboratory session. All students could complete the experiments successfully, and changes in color and/or solubility helped them to see if their experiments were on track. The part they reproduced the worst, and in which approximately 10% of the students failed, is in obtaining sodium tetrahydroxycuprate(II) from copper(II) hydroxide. In this part, the rush to finish means that they do not let the sodium

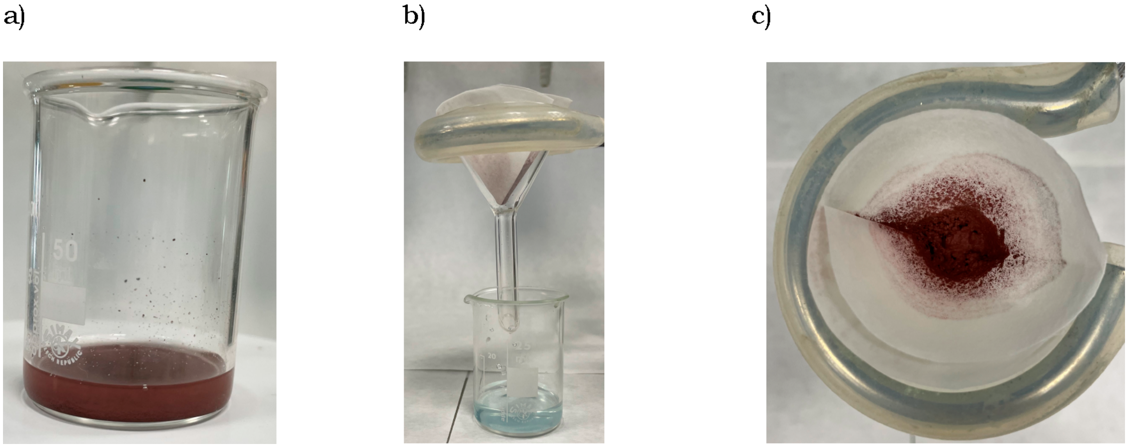


Figure 3. (a) The suspension obtained after the addition of 2 M H_2SO_4 to Cu_2O. (b) The filtrate of the suspension, showing the pale blue color of the diluted solution of $CuSO_4$. (c) The solid obtained after filtering the suspension, showing the typical color of copper.

hydroxide solution cool once it has been prepared (remember that dissolving NaOH in water is an exothermic process) or they add this solution too quickly to the $Cu(OH)_2$ suspension, which leads them to obtain dark CuO particles (eq 4),[15−19] which are not amphoteric and thus do not redissolve in a basic medium.

Since this experiment is short, they can repeat it and thus observe that in chemistry it is fundamental to follow exactly the indications of the experiments and that small variations can lead to frustrating outcomes. In this way, the experiments were optimized over the years, so that the experimental conditions described herein are the most suitable ones to make these experiments fully reproducible. Therefore, 100% of the students end up obtaining the expected results, all of them at the first attempt, except, as I have just mentioned, the obtaining of sodium tetrahydroxycuprate(II). In addition, this work also includes a reaction in which the limiting reagent is not the metal salt. Usually, undergraduate students consider that the metal salt is always the limiting reagent, and this is a good example to show that this does not have to be the case.

Before the students perform this lab practice, one should make sure that they know the chemistry involved in the experiments (answering the questions proposed in the Supporting Information), which will help them to grasp the concepts related to the reactivity of copper and its compounds. In general, students give reasonable explanations for the results and observations.

HAZARDS

Rubber gloves and safety glasses shall be worn. It is advised that all experiments be conducted in a fume hood. If hoods are not available for all students, the reactions may be carried out outside the hood, except for the synthesis of copper(I) oxide and the copper tests with concentrated nitric acid and concentrated hydrochloric acid, which must be carried out in the fume hood.

Hydroxylammine hydrochloride is irritating to the eyes, skin, and respiratory tract.[20] The substance may cause effects on the blood and may result in the formation of methemoglobin. However, this substance can only be absorbed into the body by inhalation of its aerosol, through the skin, and by ingestion. Inhalation risk is insignificant, given that its evaporation at 20 °C is negligible. Accordingly, there is no risk if gloves and glasses are worn, and the aqueous solutions of this species are relatively safe for teaching. Tumors have been detected in experimental animals but may not be relevant to humans; however, this only occurs after long-term or repeated exposures. The substance is very toxic to aquatic organisms. Therefore, it is necessary to use the exact amount of this substance and ensure that none of it is wasted. If this reagent is not to be used, there is an alternative in the Supporting Information for the obtaining of brick red Cu_2O.

$CuSO_4$ is harmful if swallowed and can causes serious eye damage. It is very toxic to aquatic life with long lasting effects. Accordingly, the solution generated in the Cu_2O dismutation process must be discarded in a metal waste container, never in the aqueous solution waste container. HNO_3(c), HCl(c), and NaOH cause eye and skin damage, while the obtained Cu_2O only is harmful if swallowed.

SUMMARY

The three experiments described herein are very illustrative of the descriptive chemistry of copper and, hence, of the chemistry of many other transition metals. Typical reactions, such as acid−base processes in which an amphoteric metal oxide or hydroxide behaves as an acid, are exemplified in one of these experiments. In addition, it is also intended to familiarize the student with the different stability of metal species in the solid state and in solution, and with the processes of dismutation. These experiments, in which the transformations can be easily observed simply by means of changes in color and/or physical states, also help the student to grasp the redox concepts. All of the experiments are low-polluting. In fact, the solvent is always water. All of them are very easy to perform, with it being feasible to do the three experiments in a 3−4 h laboratory session.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.3c00634.

> Reagents and materials, detailed experiments, and some considerations to take into account in the experimental process (PDF)

AUTHOR INFORMATION

Corresponding Author

Matilde Fondo − *Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain;*
orcid.org/0000-0002-7535-946X;
Email: matilde.fondo@usc.es

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jchemed.3c00634

Notes

The author declares no competing financial interest.

REFERENCES

(1) Wang, H. Chapter 9 - Noble Metals. In *Membrane-based separations in metallurgy*; Jiang, L-Y, Li, N., Eds.; Elsevier: 2017; pp 249−272.

(2) Graedel, T. E.; Nassau, K.; Franey, J. P. Copper Patinas Formed in the Atmosphere − I. Introduction. *Corros. Sci.* **1987**, *27* (7), 639−657.

(3) Strandberg, H. Reactions of Copper Patina Compounds − I. Influence of Some Air Pollutants. *Atmos. Environ.* **1998**, *32* (20), 3511−3520.

(4) Strandberg, H. Reactions of Copper Patina Compounds − II. Influence of Sodium Chloride in the Presence of Some Air Pollutants. *Atmos. Environ.* **1998**, *32* (20), 3521−352.

(5) Khan, R.; Ahmad, R.; Rai, P.; Jang, L.-W.; Yun, J.-H.; Yu, Y.-T.; Hahn, Y.-B.; Lee, I.-H. Glucose-assisted synthesis of Cu_2O shuriken-like nanostructures and their application as nonenzymatic glucose biosensors. *Sens. Actuators B: Chem.* **2014**, *203*, 471−476.

(6) Ma, P.; Zhang, C.; Dou, B.; Yi, X.; Bin, F.; Liang, W. Synthesis of Cu_2O micro/nanocrystals for catalytic combustion of high-concentration CO: The crucial role of glucose. *Chemosphere* **2023**, *314* (51), 137720.

(7) Jiménez-Rodríguez, A.; Sotelo, E.; Martínez, L.; Huttel, Y.; Ujué-González, M.; Mayoral, A.; García-Martín, J. M.; Videa, M.; Cholula-Díaz, J. L. Green synthesis of starch-capped Cu_2O nanocubes and their application in the direct electrochemical detection of glucose. *RSC Adv.* **2021**, *11* (23), 13711−13721.

(8) Song, L.; Huang, Y.; Dong, J.; Zhu, B.; Huang, W. Shape-controlled syntheses and redox activity differences of Cu_2O particles as an undergraduate laboratory experiment. *J. Chem. Educ.* **2022**, *99* (4), 1788−1793.

(9) Chang, I.-C.; Chen, P.-C.; Tsai, M.-C.; Chen, T.-T.; Yang, M.-H.; Chiu, H.-T.; Lee, C.-H. Large-scale synthesis of uniform Cu_2O

nanocubes with tunable sizes by in-situ nucleation. *CrystEngComm* **2013**, *15* (13), 2363−2366.

(10) Wang, W.; Wang, G.; Wang, X.; Zhan, Y.; Liu, Y.; Zheng, C. Synthesis and characterization of Cu_2O nanowires by a novel reduction route. *Adv. Mater.* **2002**, *14* (1), 67−69.

(11) Du, B. D.; Phu, D. V.; Quoc, L. A.; Hien, N. Q. Synthesis and investigation of antimicrobial activity of Cu_2O nanoparticles/zeolite. *J. Nanoparticles* **2017**, *4*, 1−6.

(12) Huang, W.-C.; Lyu, L.-M.; Yang, Y.-C.; Huang, M.-H. Synthesis of Cu_2O nanocrystals from cubic to rhombic dodecahedral structures and their comparative photocatalytic activity. *J. Am. Chem. Soc.* **2012**, *134* (2), 1261−1267.

(13) Markina, N. E.; Pozharov, M. V.; Markin, A. V. Synthesis of copper(I) oxide particles with variable color: demonstrating size-dependent optical properties for high school students. *J. Chem. Educ.* **2016**, *93* (4), 704−707.

(14) Holleman, A. F.; Wiberg, E. *Inorganic Chemistry*, 1st ed.; Academic Press: Berlin, 2001; pp 1253−1254.

(15) Schlur, L.; Bonnota, K.; Spitzer, D. Synthesis of $Cu(OH)_2$ and CuO nanotubes arrays on a silicon wafer. *RSC Adv.* **2015**, *5* (8), 6061−6070.

(16) Cudennec, Y.; Lecerf, A.; Gérault, Y. Synthesis of $Cu(OH)_2$ and CuO by soft chemistry. *Eur. J. Solid State Inorg. Chem.* **1995**, *32* (10), 1013−1022.

(17) Cudennec, Y.; Riou, A.; Gerault, Y.; Lecerf, A. Hypothèse cristallochimique des mécanismes deformation de CuO(s) et de $Cu(OH)_2$(s) à partir de $Na_2Cu(OH)_4$(s). *A. C. R. Acad. Sci. Paris, Śerie IIc, Chimie/Chemistry* **2000**, *3*, 661−666.

(18) Cudennec, Y.; Lecerf, A. The transformation of $Cu(OH)_2$ into CuO, revisited. *Solid State Sci.* **2003**, *5* (11−12), 1471−1474.

(19) Goncharova, D. A.; Kharlamova, T. S.; Lapin, I. N.; Svetlichnyi, V. A. Chemical and morphological evolution of copper nanoparticles obtained by pulsed laser ablation in liquid. *J. Phys. Chem. C* **2019**, *123* (35), 21731−21742.

(20) European Chemical Agency (ECHA); https://echa.europa.eu/substance-information/-/substanceinfo/100.024.362.