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Demonstration

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Synthesis of Copper(I) Oxide Particles with Variable Color: Demonstrating Size-Dependent Optical Properties for High School Students

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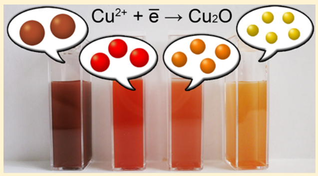
Ⓢ *Supporting Information*

ABSTRACT: We suggest the use of a simple and cheap synthesis of micro- and nanosized copper(I) oxide particles with variable color as a demonstration of size-dependent optical properties of semiconductors for high school students. The synthesis of Cu_2O particles is performed by reducing alkaline copper(II)−citrate complex (Benedict's reagent) with glucose. Significant color and size changes of Cu_2O particles at various reaction conditions are observed and discussed. Proposed demonstration is very useful for introducing students (including undergraduate students) to size-dependent optical properties of semiconductors and principles of synthesis of nanosized objects.



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INTRODUCTION

Nowadays nanoscience and nanotechnology play a very important role in everyday life: processors of personal computers and mobile phones, light emitting diodes and USB flash drives, medical equipment, drugs and many other things consist of nanosized parts with unique properties. In addition, part of the above-mentioned products (electronics) are mainly based on semiconductor materials such as silicon and gallium arsenide whose unusual properties depend not only on their composition, but also on size and shape as well, especially when their size is approximate to hundreds of nanometers and less.

Unfortunately, the nature and features of the "nanoworld" are not discussed during chemistry lessons in high school (a common situation for most schools in Russia). Despite the fact that specific properties of nanoobjects (e.g., gold and silver nanoparticles) have been well-known since the end of the 19th century (e.g., Faraday's gold[1]), their application in demonstration experiments for school and undergraduate students has been reported only recently. However, in most cases these demonstrations require sophisticated laboratory equipment and undergraduate level knowledge,[2−4] expensive noble metal compounds[3−7] or quite toxic materials.[8,9] Thus, this article is specifically designed for overcoming this lack of demonstration experiments and has been successfully tested at after-school classes with high school students (9th−11th grade in Russia, 14−17 years old).

The proposed demonstration has been used as a supplement to lecture titled "Introduction to Nanoscience and Nanotechnology" aimed at providing an explanation of size-dependent optical properties of semiconductor compounds. The demonstration is based on synthesis of Cu_2O particles by reduction of copper(II) ions with glucose. The size of synthesized Cu_2O particles varies from hundreds of nanometers to micrometers depending on concentrations of initial reagents and their color varies from yellow to dark red, accordingly. The simplicity of the experimental procedure, as well as availability of harmless and cheap reagents, enables us to perform this demonstration at any school and familiarize students with basics principles of nanomaterials synthesis.

PRELAB ACTIVITY: INTRODUCTION AND BACKGROUND

Synthesis of Cu_2O

The synthesis basics are discussed for the first step in order to introduce students to the involved reactions. The demonstration is based on the synthesis of Cu_2O particles via redox reactions between dextrose (or another reducing sugar) and alkaline solution of copper(II) complex with citrate anions (Benedict's reagent). Initially, Benedict's reagent was proposed for detecting dextrose in urine,[10] and currently, it is used in analytical and organic chemistry for colorimetric detection and quantification of reducing sugars,[11,12] in an open-chain form, containing formyl (e.g., glucose) or α-hydroxy-ketone functional group (e.g., fructose). Heating (reaction is endothermic) those sugars with Benedict's reagent in alkali medium leads to their oxidation to

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corresponding carboxylic acid salts (reaction a) or diketones (SI.1, reaction **a** and **c**) and conversion of blue colored copper(II) ions to Cu_2O with other color (mainly red) (reaction b):

Oxidation:

$$\mathrm{RCHO} + 3\mathrm{OH}^- = \mathrm{RCOO}^- + 2\mathrm{H_2O} + 2e^- \qquad \text{(a)}$$

Reduction:

$$2\mathrm{Cu}^{2+}_{\text{(in complex)}} + 2\mathrm{OH}^- + 2e^- = \mathrm{Cu_2O} + \mathrm{H_2O} \qquad \text{(b)}$$

Summary:

$$\begin{aligned}&\mathrm{RCHO} + 2\mathrm{Cu}^{2+}_{\text{(in complex)}} + 5\mathrm{OH}^- \\ &\quad = \mathrm{RCOO}^- + \mathrm{Cu_2O} + 3\mathrm{H_2O}\end{aligned}$$

The reactions above show the important role of the pH of reaction medium for reaction rate and that pH value must be taken into account for correct result interpretations. Moreover, alkali media activate conversion of sugars to enediols[12] that have high reducing properties, thus speeding up the reaction as well (conversion reaction is shown in SI.1, reaction **d**).

Semiconducting and Optical Properties of Cu_2O

It is interesting to note that Cu_2O is one of the most investigated materials in the history of semiconductor physics and it was used to make many experimental observations in that field for the first time. Currently, Cu_2O as semiconductor is entirely supplanted with more efficient materials based on silicon, germanium, gallium arsenide, and so forth. However, feasibility of its preparation in school laboratories makes Cu_2O an attractive compound for educational purposes, e.g., for fabrication of a simple photovoltaic solar cell that converts solar energy to electricity.[13]

Before further discussion of Cu_2O optical properties, students should first be familiarized with several theoretical principles. The color of light reflected, absorbed, transmitted or emitted by a semiconductor strongly depends on the bandgap energy value and this fact must be highlighted together with the concepts of energy quantization and wave-particle dualism of light. For example, Cheek[14] reported perfect hands-on experiments for introducing students to bandgap concept. At the same time, the energy bandgap value depends upon chemical composition, structure, size and shape of an object. For example, quantum dots (e.g., CdSe based dots)[8,9,15] are a famous example of semiconducting objects with size-dependant properties. If quantum dots receive energy from external sources (light, heat, current, etc.) they start emitting light with a certain color depending on their size (Figure 1). However, interaction between light and matter can be observed not just for visible light; for example, Reid et al.[2] described an experiment where ZnO (another semiconductor) nanoparticles absorb light in ultraviolet range and their absorption characteristics depend on particles size as well.

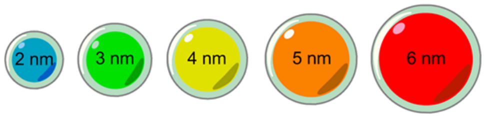

Figure 1. Dependence of luminescence color of CdSe quantum dots on their size.

Usually, Cu_2O absorbs light in wavelength range from UV to orange[16−18] and its most common color is red. However, as Cu_2O is a semiconductor, its bandgap depends on size, shape, and crystalline structure[18] of the sample, and below certain limit (less than micrometer), it changes subsequently changing the color of Cu_2O as well. That change will be shown further in Lab and Postlab sections.

Completing the theoretical introduction, a teacher should mention that not only in semiconductor nanoparticles does the color depend on size (shape, composition, etc.), but also metal nanoparticles can show almost similar dependences of light interaction with matter,[3−5] but in this case, plasmon concept is used instead of bandgap theory.

■ LAB ACTIVITY: SYNTHESIS OF COPPER(I) OXIDE

List of applied reagents, description of methods used for samples characterization, description of Cu_2O particle synthesis and potential hazards are provided in Supporting Information (SI.2−SI.5).

■ POSTLAB ACTIVITY: SYNTHESIS, SIZE, AND OPTICAL PROPERTIES OF COPPER(I) OXIDE

Synthesis of Cu_2O

Students should be informed that the synthesis of Cu_2O can be performed in several ways by changing the various conditions (e.g., reagent concentrations and ratios, pH of the medium, etc.) with almost the same product yield. Variation of these conditions allows us to produce particles with required size or shape. Here, we have described only one series of experiments where pH is variable (Table S1, SI.4) that allows teachers to show the high influence of pH on the product properties. Level of pH was varied by adding NaOH; total concentration of NaOH was varied from 10^{-4} to 1 M; the ratio of reducing agent to oxidizing agent content was fixed at 8.67:1 (by moles); temperature treatment was the same for all samples (Table S1, SI.4). First color changes of reaction mixtures can be observed almost immediately after test tubes with reaction mixture were dipped into the boiling water. After 5 min, the reaction was artificially stopped by transferring test tubes to cold water; finished samples (transferred to plastic cuvettes) are shown in Figure 2a.

As we can see the sample without NaOH (sample 1, Figure 2a) is almost transparent because of the low reaction rate caused by small internal amount of an alkali in Benedict's reagent compared to other samples of the series.

The synthesis can be performed in another way, e.g., by varying the reagents ratio. Changing the volume of Benedict's reagent while keeping concentration of reducing agent constant leads to formation of Cu_2O particles with different size and color as well (Table S2, Figure S2, SI.4). Students can be separated into two groups and this series of experiments can be performed in parallel to the previously described one; matching the results will help students to deeply understand the synthesis process and influence of various parameters on the final products.

Size of Cu_2O

Besides the color changes of synthesized Cu_2O particles (Figure 2a), their size changes as well and can vary from hundreds of nanometers to micrometers (Figure 2b). Cu_2O size, or, more precisely, its hydrodynamic diameter (details are provided in SI.3), changes in accordance with changes in NaOH content that can be explained by different reactivity of reducing sugars at various pH as it is discussed above (Prelab Activity section): increasing reactivity at higher pH leads to formation of bigger Cu_2O particles.

If a sample is left unstirred for several minutes, sedimentation of Cu_2O is observed with sedimentation period depending on two factors: (i) size and (ii) aggregation. Smallest Cu_2O particles

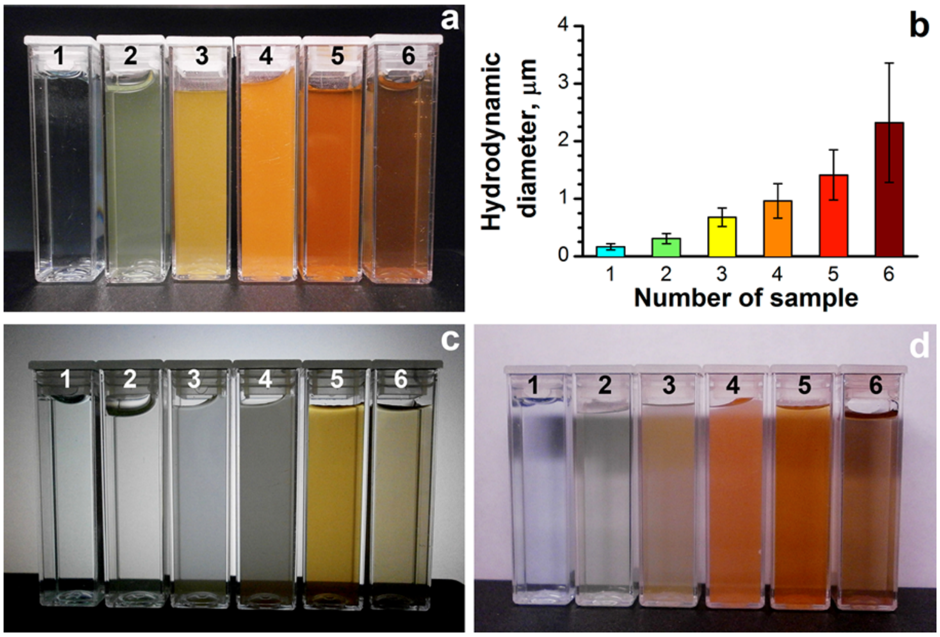

Figure 2. (a) Registration of backscattered light of Cu_2O samples synthesized at various NaOH concentration; NaOH concentration increased from sample 1 to 6 as follow: 0, 10^{-4}, 10^{-3}, 10^{-2}, 0.1, and 1 M (more details are provided in Supporting Information, SI.4, Table S1); (b) hydrodynamic diameter of Cu_2O particles in synthesized samples (description of size measurement is provided in SI.3; optical microphotographs of the samples 3 to 6 are shown in Figure S1); (c) registration of light transmitted through Cu_2O samples; laptop with white screen background was used as a uniform illumination source for transmitted light registration; (d) registration of mixed (backscattered and transmitted) light obtained by photographing the samples on white background (a white paper sheet).

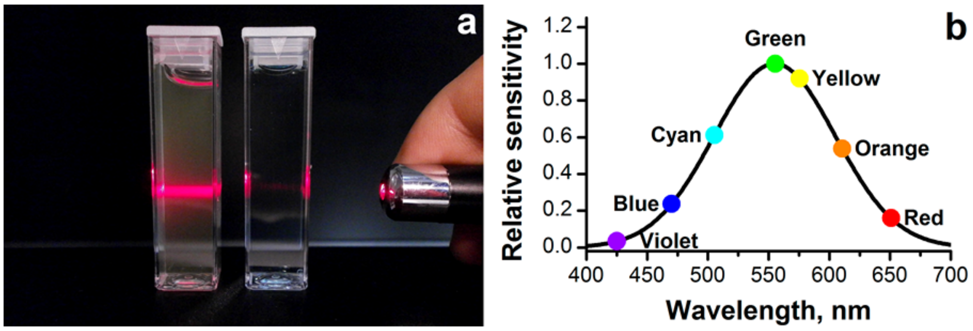

Figure 3. (a) Demonstration of Tyndall effect using sample 2 (left cuvette; sample description is provided in Table S1) with comparison to diluted Benedict's reagent (water to reagent ratio, 200:1); (b) relative spectral sensitivity of human eye; the colored dots show the color of the corresponding wavelength.

(Figure 2a, sample 2) need a longer sedimentation period (around 12 h), while bigger particles sediment completely within 30−45 min (sample 6). An example of aggregates is shown in Figure S1b.

Aggregation is the key factor for sedimentation of small particles (0.5 μm and less) and can be prevented by deposition of stabilizer molecules to the particles surface, e.g., poly(vinylpyrrolidone) is a well-known stabilizer for Cu_2O nanoparticles.[17]

Optical Properties of Cu_2O

Figure 2a shows variations of light color that is backscattered for samples; increase in Cu_2O size (Figure 2b) leads to backscattering of light with longer wavelength from yellow (sample 3) to dark red (sample 6). The color of the same samples is changed in the case of transmitted (Figure 2c) and mixed (transmitted and backscattered) light (Figure 2d). For example, colorless sample 1 in Figure 2a turns blue in Figure 2d which indicates of an excess of unreacted Benedict's reagent. This example shows students that application of inappropriate concentration of reagents can lead to mistakes in interpretation of the results and should be identified with suitable approach (transmitted light instead scattered).

The Cu_2O samples with smallest particles (samples 1 and 2, Figure 2a) can be used for demonstration of Tyndall effect by illumination with laser beam (Figure 3a). This small experiment is suitable for introducing students to methods of nanoparticles investigation by analyzing the light scattered on them; e.g., dynamic light scattering method[19] was used in this work for determining hydrodynamic diameter. Application of laser pointer can be successfully applied for monitoring particle growth as it was done by Ahn and Whitten for colloidal sulfur particles.[20]

Samples 3 and 4 are more complicated cases: their color changes from yellow (backscattered light, Figure 2a) to gray-blue (transmitted light, Figure 2c) and reddish (mixed light, Figure 2d). For correct interpretation of those changes, it is not enough to know function of light absorption by an object but familiarity with Mie theory is strongly required.

At the end of demonstration, it is good to superficially familiarize students with limitations of instruments that we have used for color registration during the demonstration, e.g., the human eye has different sensitivity to different colors with maxima at ~550 nm (green color; Figure 3b) while any digital cameras have restrictions caused by registration of only three colors (blue, green, and red) with further mathematical reconstruction. Therefore, for sophisticated studies we need to use special instruments that can analyze full visible spectrum and maybe using both scattered and transmitted light for registration.

■ SUMMARY AND PERSPECTIVES

The main goal of this report is helping school teachers to familiarize students with size-dependent optical properties of semiconductors by taking copper(I) oxide as an example. Performing and explaining the proposed synthesis procedure may help students to understand the basics of micro- and nanostructured materials' synthesis and the influence of reagent concentrations and other parameters (pH, reagents ratio, etc.) on particles' size and their optical properties. The described synthesis can also be used for laboratory experiments and individual student projects with the following directions: (1) optimization of synthesis procedure, e.g., optimization of reactants concentrations and ratios, etc.; (2) application of different reducing agent (e.g., ascorbic acid) or another complex with copper(II) ions (e.g., Fehling's solution); and (3) synthesis of Cu_2O particles in the presence of natural (gelatin, starch, heparin) or synthetic (soap, poly(vinylpyrrolidone)) stabilizers, etc. Therefore, simplicity and low cost of applied reagents are the main advantages of the synthesis allowing it to be carried out as a demonstration at any school, while variability of synthesis characteristics and resulting numerous optical phenomena provide high education potential.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00563.

> Additional reaction schemes, list of reagents, description of Cu_2O synthesis, methods used for samples characterization and potential hazards (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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