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Laboratory Experiment

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Microwave Synthesis of Zinc Hydroxy Sulfate Nanoplates and Zinc Oxide Nanorods in the Classroom

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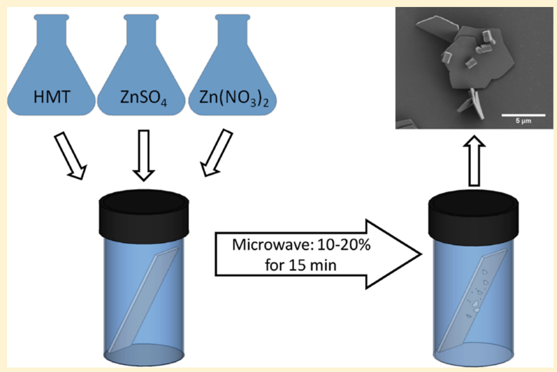
Supporting Information

ABSTRACT: In this hands-on, inquiry-based lab, high school and undergraduate students learn about nanotechnology by synthesizing their own nanoparticles in a single class period. This simple synthesis of zinc oxide nanorods and zinc hydroxy sulfate nanoplates can be done in 15 min using a household microwave oven. Reagent concentration, reaction temperature, and time all affect the size and shape of the particles synthesized, allowing students to explore how materials scientists control reaction conditions to achieve desired results.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Laboratory Instruction, Inquiry-Based/Discovery Learning, Hands-On Learning/Manipulatives, Nanotechnology, Synthesis, Materials Science, Interdisciplinary/Multidisciplinary, Inorganic Chemistry*

INTRODUCTION

Nanomaterials are being studied extensively because they show potential uses in a broad range of areas including energy conversion, medicine, electronics, optoelectronics, and catalysis.[1−3] Many of the unique properties of nanomaterials are strongly dependent on their size and shape. Thus, much of the time spent on nanomaterial synthesis is devoted to trying to obtain the desired morphology while decreasing defects. Despite its importance, nanotechnology is often absent in high school curricula due, in part, to a lack of practical nanotechnology inquiry activities. Synthesis of nanomaterials is not readily performed in a classroom setting due to the expensive instrumentation and complex procedures that are often required.

In this article, we present a simple synthesis of two types of nanoparticles: zinc oxide (ZnO) nanorods and zinc hydroxy sulfate, $3Zn(OH)_2{\cdot}ZnSO_4{\cdot}0.5H_2O$, (ZHS) nanoplates in 15 min using a household microwave oven. This protocol is based upon work done by Morin et al.[4] in which ZHS nanoplates were synthesized using a low temperature aqueous method and characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Since the nanoplates are typically several micrometers wide and 100−200 nm thick, they can be viewed with an optical microscope. Likewise, ZnO nanorods have been synthesized using a low temperature aqueous method in which no sulfate is present and phase purity was confirmed using X-ray diffraction.[5−7] Various other methods of nanoparticle synthesis (e.g., chemical vapor deposition, hydrothermal growth, and seeded-solution synthesis) have been reported to produce high quality nanomaterials but require synthesis times of several hours.[5−11] These long synthesis times are generally not practical for classroom experiments at the high school or undergraduate level. Solution synthesis of spherical ZnO nanoparticles was previously reported that allows students to measure the change in UV−visible light absorption with changing particle size.[12] The simple synthesis described here allows for hands-on nanotechnology to be introduced in a single class period.

EXPERIMENTAL PROCEDURES

A glass coverslip and reaction vial (VWR vials, borosilicate glass, with phenolic screw cap, Catalog No. 66011-121) were cleaned with deionized water, rinsed with ethanol, and then dried with nitrogen gas or air from a canned air duster (Staples item 326197). A glass substrate was used rather than silicon because glass is nonconductive and can be used in a microwave oven. In order to obtain uniform growth it is critical to thoroughly clean the coverslip and reaction vial to minimize

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contamination that might cause unwanted nucleation. Two different types of nanoparticles can be synthesized using the solutions listed in Table 1. To synthesize ZnO nanorods a 12 mL solution containing 2.0 mM zinc nitrate and 2.0 mM hexamethylenetetramine (HMT) was prepared. To synthesize ZHS nanoplates a 12 mL solution containing 2.0 mM zinc sulfate and 2.0 mM hexamethylenetetramine (HMT) was prepared. To synthesize a mixture of ZHS nanoplates and ZnO nanorods a 12 mL solution containing 1.0 mM zinc nitrate, 1.0 mM zinc sulfate, and 2.0 mM hexamethylenetetramine (HMT) was prepared.

Table 1. Reagent Concentrations Used To Obtain ZnO Nanorods and ZHS Nanoplates

Reagents	ZnO Nanorods	ZHS Nanoplates	ZnO/ZHS Mixed Product
HMT	2.0 mM	2.0 mM	2.0 mM
$Zn(NO_3)_2$	2.0 mM		1.0 mM
$ZnSO_4$		2.0 mM	1.0 mM

The vial was capped and briefly shaken to mix the reagents, and then the glass coverslip was inserted into the reaction vial so that it stood diagonally (Figure 1). The cap was tightly screwed onto the reaction vial to prevent evaporation, and then the capped vial was placed in a 700 W microwave oven for 15 min at 10−20% power. Depending upon the microwave oven used, the time and power level may vary. This should be determined empirically and can be an inquiry step for students in this experiment. We recommend groups of 2−4 students to conduct this experiment.

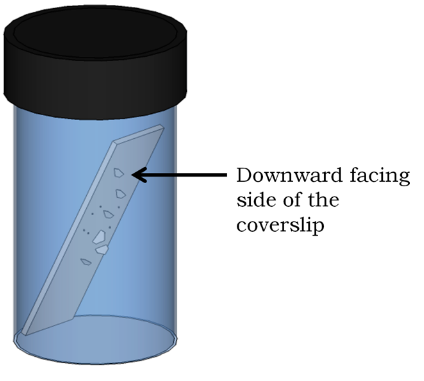

Figure 1. Vial showing the growing of nanoparticles on the glass coverslip. Note: Mark the downward facing side of the glass coverslip (arrow) because, although nanoparticles will grow on both sides of the slide, the downward facing side will accumulate less debris than the upward facing side of the slide.

After the heating cycle, the vials were allowed to cool until they were warm to the touch, at which point there is some pressure built up, but the vials will not steam when opened. The vials were then opened slowly to relieve any built-up pressure, and the glass coverslip was removed using tweezers. The coverslip was gently rinsed with ethanol and dried with a stream of nitrogen gas or canned air. Nanoparticles will grow on both sides of the slide, however, since the downward facing side will accumulate less debris (Figure 1), the particles on that side are analyzed. The ZHS and ZnO nanoparticles were observed directly on the glass coverslip with a low power optical microscope, a high power optical microscope, and a tabletop scanning electron microscope (SEM).

To observe the particles with a SEM Zeiss Leo Supra, Figure 2, the samples were sputtered with gold for 30−60 s to prevent the substrate from charging in the SEM. Alternatively, the particles can be collected directly from the growth solution with a pipet and dropped onto a glass or silicon slide and imaged once the water evaporates. Nanoparticles from the growth solution can also be imaged by UV/vis spectrophotometry to determine particle type.

HAZARDS

Hexamethylenetetramine (HMT), zinc nitrate hexahydrate, and zinc sulfate monohydrate in their powder form may cause irritation to the skin and eyes on contact. An adult should carefully handle the powders inside a chemical fume hood or in a well-ventilated area. Students should wear goggles and gloves at all times during this experiment. The reaction vials should be handled carefully with heat resistant gloves after heating in the microwave oven to avoid burns. Compressed air contains difluoroethane (CAS 73-37-6), which is flammable and can be harmful if high concentrations of gas are inhaled. In order to ensure that the vials used in the experiment are safe when heated in the microwave, only the Borosilicate Glass with Phenolic Screw Cap Vials from VWR should be used (VWR Catalog No. 66011-121). Other types of vials have not been tested and may melt or break during the procedure. In addition, an adult should supervise students during the microwave heating. Multiple reactions can be done in a single microwave oven (see Supporting Information for adjustments to heating time and power), and the authors recommend that an adult be in charge of the heating.

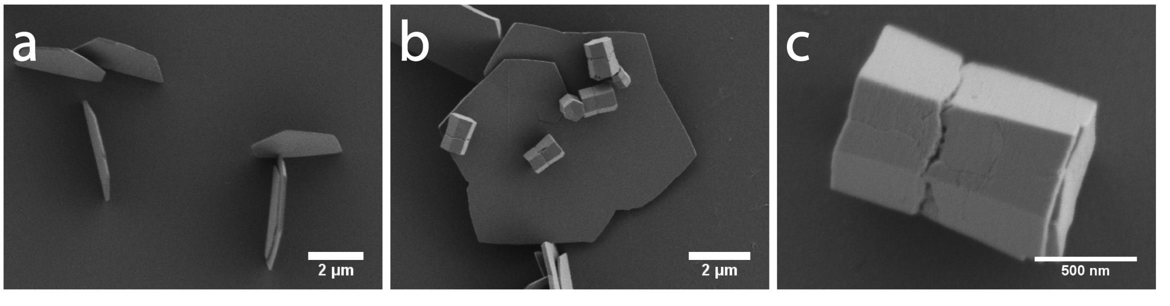

Figure 2. (a) SEM image of ZHS nanoplates; (b) SEM image of a mixture of ZHS nanoplates and ZnO nanorods; (c) SEM image of a ZnO nanorod taken using a Zeiss Leo Supra 55 VP.

■ RESULTS

Chemistry

The microwave radiation rapidly heats the water in the reaction mixture, causing HMT to degrade into formaldehyde and ammonia, creating a basic environment (Figure 3, reactions 1 and 2)[11] which precipitates Zn^{2+} as $Zn(OH)_2$ (Figure 3, reaction 3). In the high temperature environment, the $Zn(OH)_2$ dehydrates to ZnO + H_2O, resulting in ZnO nanorod formation (Figure 3, reaction 4). If SO_4^{2-} is present, the hydrated layer structure of $3Zn(OH)_2{\cdot}ZnSO_4{\cdot}xH_2O$ (Figure 3, reaction 5) may form faster than the precipitation and dehydration of $Zn(OH)_2$ to ZnO (Figure 3, reaction 4), making ZHS nanoplates the dominant crystal in the reaction solution.

$$(CH_2)_6N_{4(aq)} + 6\,H_2O_{(l)} \longrightarrow 6\,H_2CO_{(aq)} + 4\,NH_{3(aq)} \quad (1)$$
$$NH_{3(aq)} + H_2O_{(l)} \longrightarrow NH^{+}_{4(aq)} + OH^{-}_{(aq)} \quad (2)$$
$$Zn^{2+}_{(aq)} + 2\,OH^{-}_{(aq)} \longrightarrow Zn(OH)_{2(s)} \quad (3)$$
$$Zn(OH)_{2(s)} \xrightarrow{\Delta} ZnO_{(s)} + H_2O_{(l)} \quad (4)$$
$$3\,Zn(OH)_{2(s)} + Zn^{2+}_{(aq)} + SO^{2-}_{4(aq)} + x\,H_2O_{(l)} \longrightarrow 3\,Zn(OH)_2{\cdot}ZnSO_4{\cdot}x\,H_2O_{(s)} \quad (5)$$

Figure 3. Proposed chemical reaction mechanism for ZnO nanorod and ZHS nanoplate formation.

Nanoparticle Visualization

Nanoplates grown in the microwave oven tend to align almost vertically with the glass substrate and appear as dark lines (Figure 4A–C). This vertical orientation allows the plates to be observed along their edge, which has a higher contrast than a nanoplate that is lying flat. When low concentrations of SO_4^{2-} were present in the reaction solution, short ZnO nanorods formed, ~200–400 nm wide and ~400–600 nm long (Figure 4E,F). These nanorods appear as small particles or dots when observed with an optical microscope. SEM images show that these are well-faceted nanorods (Figure 2c).

ZHS nanoplates are defined as a 2-D nanomaterial because while they are several micrometers in diameter they are only 100–200 nm thick and thus resemble a two-dimensional plane. ZnO nanorods are considered a 1-D nanomaterial because the length of the nanorods can reach several micrometers long, resembling a one-dimensional line. Although nanoparticles are difficult to see with an optical microscope, 2D ZHS nanoplates are more easily resolved due to their unique shape and vertical orientation (Figure 4A compared to Figure 4D).

A light microscope with 500× magnification (10× and a 50× objective) allows students to clearly distinguish between nanoplates and nanorods (Figure 4A and Figure 4D). Using a light microscope with 1000× magnification students can see the edges of the hexagonal nanoplates, while use of a scanning electron microscope (SEM) allows students to see the crystal facets (Figure 4B,C and Figure 2a–c). Although access to SEMs is often limited to university courses, students can determine whether they have synthesized nanoplates or nanorods using a light microscope and compare their particles to representative SEM images of ZnO nanorods and ZHS nanoplates provided in the Supporting Information.

Nanoparticle Morphology

The shape of a crystal is determined by the relative growth rates of its different facets. In the case of ZnO and ZHS the crystals can be generalized as having different growth rates of the normal face and the lateral face (Figure 5). If a crystal's normal face (V_N) grows faster than its lateral face (V_L) as is the case with ZnO, it will resemble a rod. Conversely, if the crystal's lateral face (V_L) grows faster than its normal face (V_N), it will resemble a plate such as the ZHS nanoplates. For a more detailed discussion of crystal growth see ref 4.

Different morphologies can be obtained by changing the reagent concentrations and ratios. A 1:1 ratio of $Zn(NO_3)_2$ to

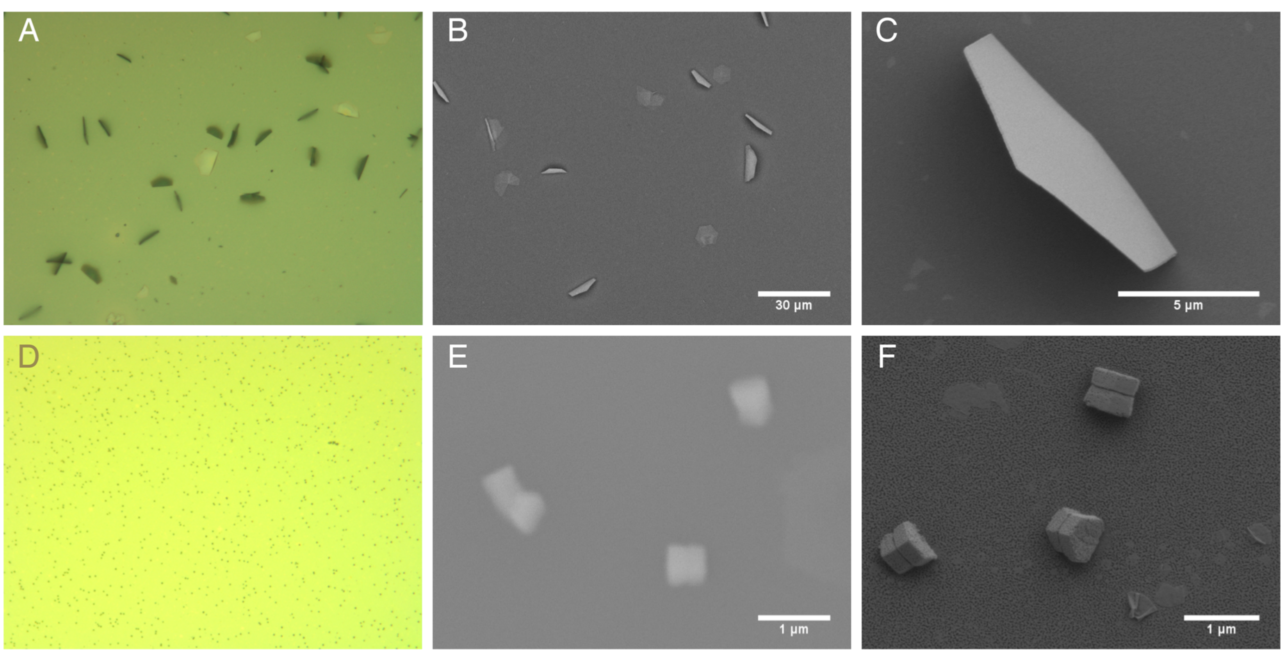

Figure 4. ZHS nanoplates observed using a (A) light microscope, 500× magnification; (B) Hitachi TM3000 Tabletop SEM, 600× magnification; (C) Zeiss Leo Supra 55 VP SEM, 15000× magnification. Short ZnO nanorods observed using a (D) light microscope, 500× magnification; (D) Hitachi TM3000 Tabletop SEM, 18000× magnification; (F) Zeiss Leo Supra 55 VP SEM, 40000× magnification.

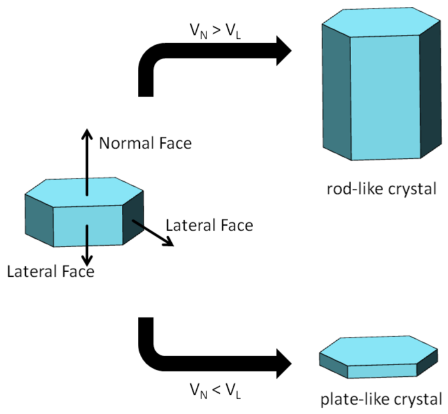

Figure 5. Schematic showing how crystal facet growth rates determine ZnO and ZHS morphology. V_N and V_L correspond to the growth rates of the normal and lateral faces, respectively.

HMT yields only ZnO nanorods (Figures 4C and 2c) while replacing the $Zn(NO_3)_2$ with $ZnSO_4$ results in only ZHS nanoplates (Figures 4A–C and 2a). Adding both $Zn(NO_3)_2$ and $ZnSO_4$ to HMT results in both ZnO nanorods and ZHS nanoplates (Figure 2b). This transition from an exclusively nanorod synthesis to an exclusively nanoplate synthesis allows students to easily explore different reaction conditions by preparing multiple samples. A microwave power of approximately 15% results in a combination of nanoplates and nanorods that form "twin-plates": two parallel nanoplates connected at the center (see Figure S1.2.B in the Supporting Information). A power of 15% can be manually applied by heating the reaction solution for 2–3 s at 100% power every 30 s for 15 min. Alternate reaction conditions are provided in the Supporting Information.

Additional Characterization Methods

Although ZHS nanoplates can be easily characterized by optical microscopy because of the plates' large size, vertical orientation, and thin film interference when drop cast on silicon/silicon oxide, the ZnO nanorods are not as easily distinguished. However, the ZnO nanorods suspended in the growth solution can be easily identified by their unique, well-documented UV–vis absorption peak. ZnO is a semiconductor with a band gap between 3.1 and 3.3 eV.[13] The absorption peak at 387 nm (3.2 eV) corresponds to the absorption of a photon to excite an electron from the valence band to the conduction band across a band gap of ~3.2 eV.[14−16] The presence of an absorption peak at ~380 nm indicates that ZnO is present in the growth solution.

Figure 6 shows the UV–vis absorption spectra of three samples and their corresponding optical images; samples 1 and 2 contain ZHS nanoplates (Figure 6B and Figure 6C), and sample 3 contains ZnO nanorods (Figure 6D,E). Samples 1, 2, and 3 were prepared according to Table 1 and were heated at 10% power for 15 min in a 1350 W microwave oven. The UV–vis spectrum of the ZnO nanorod suspension, sample 3, shows an absorption peak at 387 nm, which is characteristic of the ~3.2 eV ZnO band gap. However, ZHS does not have a narrow enough band gap to exhibit an absorption peak in the UV–vis spectra.

■ CLASSROOM TESTING

This activity was conducted with a group of high school teachers in a 50 min period. We were able to successfully complete the procedure of microwave synthesis, but some of the participants had difficulties locating the nanoplates on the glass substrate using the optical microscopes. The difficulty that participants faced with the microscopes could be overcome by familiarizing students with the microscopes prior to the experiment. The activity was also done with a group of middle school students, who synthesized ZHS nanoplates, changed variables such as concentration and heating time, and examined their samples using optical microscopes and the tabletop SEM described above. The students were familiar with the operation of the microscopes and were able to complete the entire procedure including observation in 1 h.

■ CONCLUSIONS

In summary, ZHS and ZnO nanoparticles were synthesized in 15 min using a conventional microwave oven, which significantly reduced the reaction time in comparison to previously report syntheses.[7−11] Both types of particles are visible by optical microscopy although the ZHS nanoplates are more distinctive due to their width, which is on the microscale rather than the nanoscale. The particles are easily visualized

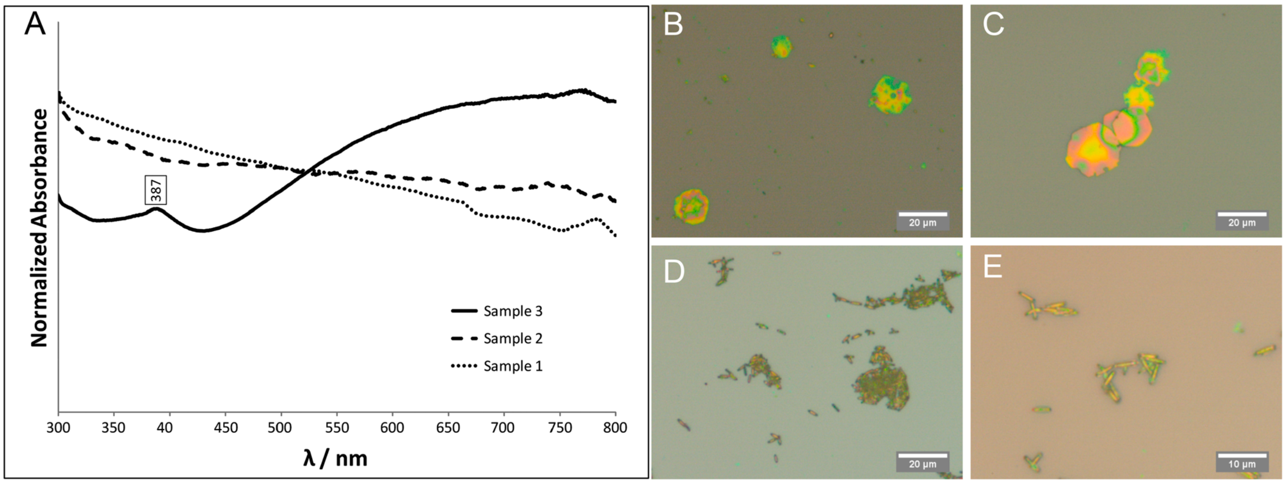

Figure 6. (A) UV–vis absorption of ZHS nanoplates, samples 1 and 2; and ZnO nanorods, sample 3. (B–D) Optical images of samples 1, 2, and 3, respectively, taken at 500× magnification, 20 μm scale bar. (E) Optical image of sample 3 taken at 1000× magnification, 10 μm scale bar.

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with a tabletop SEM although a research grade instrument gave the most detailed results (Figure 4 and Figures S1, S2, and S3 in the Supporting Information). This hand-on synthesis of nanomaterials is straightforward enough to be successfully completed by students as young as sixth grade (11−12 years old) in a 1 h class period. An inquiry component can be added to the laboratory by allowing the students to explore the effects of microwave power and length of heating time, or reagent ratio. Details on these changes to the procedure are in the Supporting Information (Figures S2.3−7 in the Supporting Information). Synthesis of these particles is an excellent introduction to nanotechnology and the challenges faced by scientists in obtaining particles of a particular size and shape. In addition, the use of multiple types of microscopes gives students an opportunity to learn about size and scale with materials they have synthesized themselves.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Alternate reaction conditions; complete detailed description of solution preparation; experimental details; SEM images; description of the chemicals used; hazard information. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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