

Article

Application of Sonication and Microwave Irradiation to Boost Continuous Fabrication of the Copper(II) Oxide Sub-Micron Particles

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Abstract: Viability of the continuous-flow synthesis of rhomboidal copper(II) oxide (CuO) micro- and nanoparticles was demonstrated. It has been shown that ultrasonic mixing of reactants, in the stage of Cu(OH)₂ synthesis, followed by microwave irradiation of the resulting suspension, gives very fine particles of CuO at high yield and within minutes. Near optimal parameters for the synthesis of fine particles in the continuous reactor were determined.

Keywords: copper oxide; microwave irradiation; sonication

1. Introduction

The unique properties and most attractive application prospects of sub-micro and nanomaterials stimulate a booming interest in the development of effective synthesis procedures and drive the research for large scale and cost effective production technologies.

Among many substances a significant attention attract micro- and nanoparticles of CuO, applied in fabrication of hydrogen cyanide [1], and moisture sensors [2], parts of batteries [3], carbon monoxide oxidation catalysts [4–6], chemical warfare decomposition [7], nanofluids for intensive heat transfer [8], fungicides and germicides [9].

Copper(II) oxide can be prepared by various methods: hydrothermal or alkothermal processes [10,11], a direct thermal decomposition of copper compounds [12,13], metallic copper evaporation in oxidizing system during electric discharge [14], or by laser vaporization controlled condensation method [15]. CuO nanoparticles can be prepared quite efficiently by precipitation from Cu(II) solution using sodium hydroxide. At elevated temperature (80–100 °C), the already formed Cu(OH)₂ precipitate decomposes to CuO according to Equations (1) and (2) [16]:



Promising results were achieved when these reactions were carried out in ethylene glycol in a batch process. More recently, it has been also shown that the second reaction can be boosted by sonication and microwave irradiation [17], which is not surprising as a positive impact of electromagnetic irradiation was reported already before [18–20]. However, a further significant reduction in manufacturing costs can be achieved when the conventional batch technologies are replaced by continuous [21,22] or semi-continuous [23] operations. In addition to the facilitated scale-up the continuous-flow technologies ensure same quality of the product. For this reason we deemed it important to focus our studies on the production of CuO micro and nanoparticles in the continuous-flow process boosted by both ultrasonic and microwave irradiation.

2. Experimental Section

2.1. Chemicals

Copper(II) acetate monohydrate (Cu(OAc)₂·H₂O) with A.C.S. purity was obtained from Alfa Aesar Co. Copper(II) chloride (CuCl₂), sodium hydroxide (NaOH) and potassium hydroxide (KOH) with analytical purity were obtained from POCH Co. All chemicals were used as received without further purification.

2.2. Experimental Set-Up and Procedure

A continuous synthesis of CuO particles was achieved in two consecutive steps. In the first a homogeneous suspension of copper(II) hydroxide was synthesized and then it was charged into a helical-tubular glass microwave-irradiated reactor. Aqueous 0.05–0.2 M solutions of Cu(OAc)₂ or CuCl₂ were used as copper precursors and 0.1–0.4 M aqueous solutions of NaOH or KOH were added to induce precipitate formation.

The investigations were carried out using the experimental set-up presented in Figure 1. Solutions of copper oxide precursor and NaOH or KOH were pumped from storage tanks (1,2) by means of metering pump (3) to the continuous flow cell (4) of 37 mm i.d., 90 mm height (CFC500-750, Sonics), with ultrasonic mixer of 13 mm in diameter and maximum amplitude of 114 μm mounted inside (5). The

latter was powered by ultrasonic generator Sonics (VCX 750, Sonics) (6), with operating frequency 20 kHz. Sonication intensity was varied by changing ultrasonic mixer amplitude. Volumetric flow rates for both solutions were 1.5 dm³/h (unless otherwise stated), in accord with reaction (1) stoichiometry. In effect, a uniform suspension of Cu(OH)₂ was obtained. Then, it was passed into a helical continuous reactor (7), glass tube: 8 mm i.d. and *ca.* 2.85 m length, embedded in an adapted domestic microwave oven (8), to dehydrate Cu(OH)₂ to CuO.

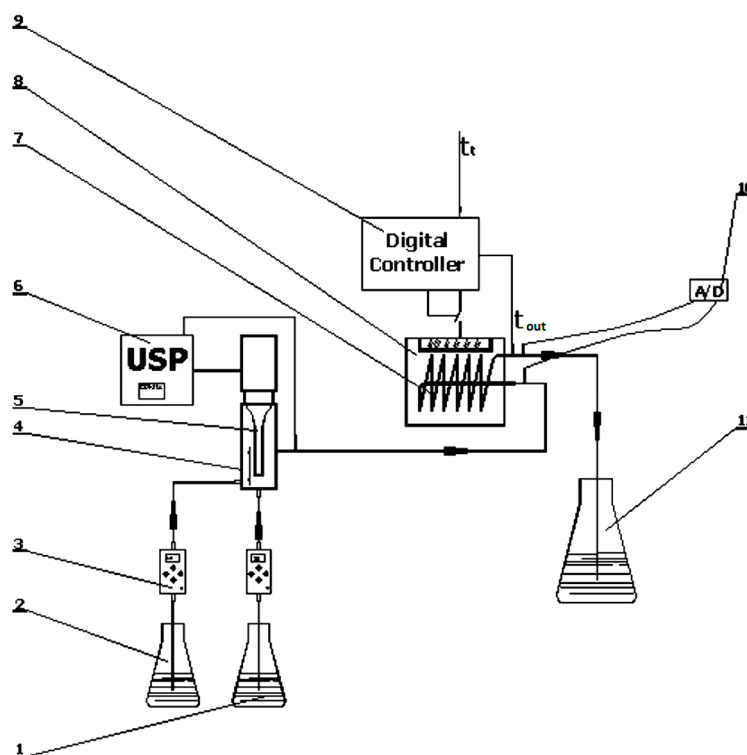


Figure 1. Scheme of a continuous flow laboratory set-up for CuO preparation. 1,2-storage tanks; 3-metering pump; 4-continuous flow cell; 5-ultrasonic mixer; 6-ultrasonic generator; 7-tubular reactor; 8-microwave oven; 9-digital controller; 10-A/D transducer; 11-product vessel.

Output power of the oven (800 W) was controlled by PID controller (9), Shimaden SR-91, connected to a magnetron power system to ensure that target temperature t_i at the reactor outlet was maintained within the range of 80–89 °C. The preliminary experiments performed showed that it was optimal to ensure a smooth decomposition of copper hydroxide, while avoiding overheating of the reactants at their exit. Additionally, two thermocouples were placed at the inlet and outlet of the reactor, for data measurement and recording by an Advantech A/D transducer (10). A plot of the outlet temperature t_{out} variation in time is shown in Figure 2. An image of the reactor with clearly appreciable zone of Cu(OH)₂ decomposition, is shown in Figure 3. The product was collected in the vessel (11). CuO particles were separated by a triple centrifugation and dispersion in deionized water and the suspensions thus obtained were analyzed.

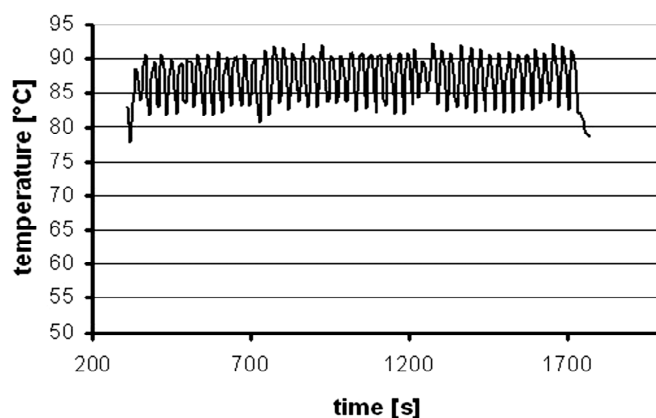


Figure 2. Variation of the temperature at the reactor outlet t_{out} at $t_i = 86$ °C.



Figure 3. The view of microwave reactor interior.

2.3. Analytical Methods

Particle size distribution (PSD) by volume fraction was determined by DLS (Dynamic Light Scattering) technique using Malvern, Zetasizer S90. Mean hydrodynamic diameter (z-average diameter) was also determined from the intensity of scattered laser radiation by grains fractions and averaged from five measurements. X-ray diffraction (XRD) patterns were recorded using Phillips X'pert Pro apparatus with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm). For the selected samples absorbance measurements with respect to wavelength were performed on a UV-vis spectrophotometer (Hitachi, U2800A) with quartz quvette. A qualitative analysis of the colloidal system was also carried out using micrographs taken by a JEOL 3010 microscope working with accelerating voltage of 300 kV. A drop of CuO containing suspension was placed on a holey carbon film covering copper grid and allowed to evaporate at room temperature. The results are listed in Table 1.

Table 1. Results of the CuO nanoparticles preparation tests.

Sample	$C_{Cu(OAc)_2}$ (mol/dm ³)	C_{NaOH} (mol/dm ³)	t_t (°C)	Amplitude ^a (%)	z-Average (nm)
1	0.1	0.2	-	100	405.5
2	0.1	0.2	86	-	238.7
3	0.1	0.2	86	80	273.5
4	0.1	0.2	86	40	379.2
5 ^b	0.1	0.2	86	60	-
6	0.1 ^c	0.2	86	60	385.5
7	0.2	0.4 ^d	89	60	830.5
8	0.1	0.2	86	60	194.5
9	0.05	0.1	86	60	206.6
10	0.2	0.4	89	60	211.7
11 ^e	0.1	0.2	86	-	496.6

Notes: ^a determined with respect to maximum amplitude of ultrasonic horn 114 μ m; ^b volumetric flow rate of NaOH solution—1.8 dm³/h; ^c CuCl₂ solution; ^d KOH solution; ^e batch mode.

3. Results and Discussion

To study the process of CuO particle fabrication the preliminary experiments were focused on:

- sonication of the reaction system with maximum (100%) amplitude to boost first reaction, with no microwave stimulation of the second reaction (Table 1, sample 1),
- microwave irradiation of the second reaction, with no sonication of the (Table 1, sample 2).

In the case of intensive sonication, both CuO and Cu(OH)₂ were observed in the outlet stream and a partial decomposition of Cu(OH)₂ was ascribed to thermal effects of sonication. The mean diameter of CuO particles thus was ca. 405 nm. On the other hand, the lack of sonication (sample 2) led to the formation of nonuniform Cu(OH)₂ suspension, and therefore also of CuO particles, as well as resulted in overheating and overall instability in the second reaction, again detrimentally affecting quality of the end product.

These experiments clearly showed that a successive application of ultrasonic and microwave irradiations, in the first and second step, respectively, facilitates the synthesis of smaller particles with no compromise on the quality. Then the performed experiments showed that a minor decrease in the intensity of sonication, had a very positive effect on decrease in the particle size (Table 1, sample 3 and 8) but further decrease had an opposite effect (Table 1, sample 4), as could be expected from the observations with sample 2. This clearly indicates that there is an optimal intensity of sonication for each reaction system.

An excess of NaOH with respect to reaction (1) stoichiometry (Table 1, sample 5) led to large agglomerates of CuO, which despite repeated washing and dispersion failed to form stable suspension. The use of CuCl₂ (Table 1, sample 6) and KOH (Table 1, sample 7) solutions as alternatives for Cu(OAc)₂ and NaOH, respectively, also failed to satisfy as regards to the final dimensions of particles and suspension stability. The experiments performed with different initial concentrations of NaOH and Cu(OAc)₂ showed their minor impact on the particle size (Table 1, samples 8–10).

Thus, the performed experiments tend to indicate that for CuO particles' synthesis the optimal process parameters are around of:

- working amplitude of about 60% of maximum mixer amplitude; it appears to ensure good homogeneity of the $\text{Cu}(\text{OH})_2$ suspension discharged from the mixer while preventing uncontrolled formation of the CuO particles,
- second stage temperature (t_i) of about 86–89 °C, which enables smooth transformation of the uniform suspension $\text{Cu}(\text{OH})_2$ and a stable synthesis of sub-micrometric CuO,
- supply of substrates in amounts (streams, concentrations) meeting the stoichiometry of reaction (1).

The particle size distribution (by DLS) of the CuO particles obtained under near optimal conditions (Table 1, sample 8) is shown in Figure 4. As can be seen from TEM micrograph the particles obtained were rhomboidal (Figure 5).

The powder X-ray diffraction pattern recorded for sample 8 (Figure 6) reveals that it represents a crystalline structure of CuO [24], and no peaks originating from either substrates or byproducts were detected. Broadening of the peaks indicates the presence of the nanosized copper oxide grains.

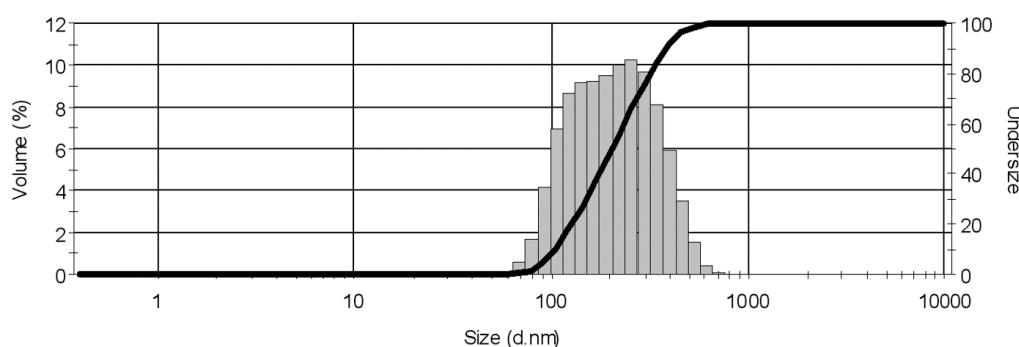


Figure 4. PSD of CuO particles (Table 1, sample 8).

Maximum of the UV-Vis absorbance spectrum at the wavelength of 295 nm (Figure 7) indicates the presence of CuO nanoparticles (Table, sample 9), *i.e.*, those with at least one dimension <100 nm. Its diffused shape in the region of longer wavelengths may also indicate the presence of larger particles.

In order to compare the products of the continuous process, CuO particles were also prepared in batch mode. Solutions of NaOH and $\text{Cu}(\text{OAc})_2$ were mixed and then heated to 86 °C with simultaneous intensive mechanical mixing for ca. 530 s (Table 1, sample 11). Mean diameter of the particles was of 496.6 nm and fractions of the respective classes were shifted towards larger mean values (Figure 8) in comparison to optimal process parameters. This observation can be explained by a fairly low intensity of mixing during $\text{Cu}(\text{OH})_2$ formation, affecting its homogeneity and hence subsequent decomposition to CuO and resulting in the synthesis of larger CuO crystals. Additionally, for batch synthesis the estimated ramp of temperature increase from 25 to 86 °C was ca. 0.12 K/s. In the case of microwave system that rate, determined for temperature increase from 40 to 86 °C and within 172 s, was ca. 0.27 K/s. This accelerated heating also boosted the $\text{Cu}(\text{OH})_2$ decomposition to give much smaller CuO crystals.

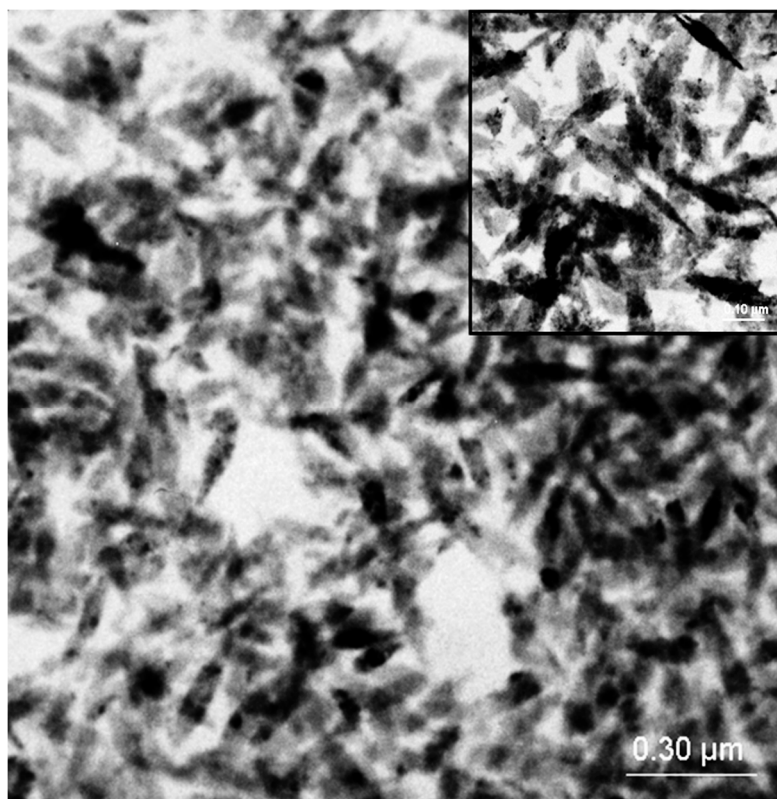


Figure 5. TEM image of CuO prepared at optimized conditions (Table 1, sample 8).

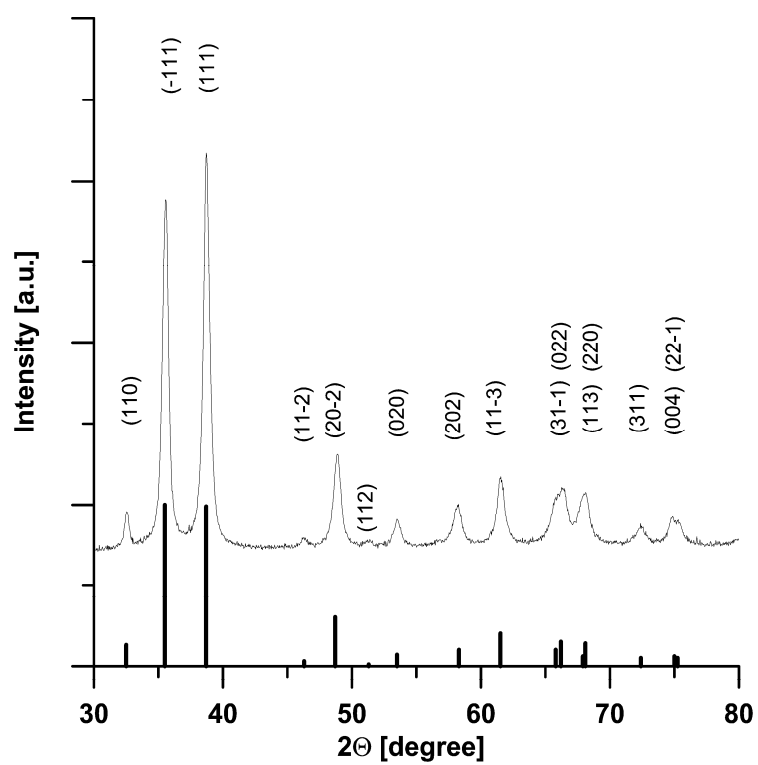


Figure 6. XRD pattern of the CuO sample (Table 1, sample 8).

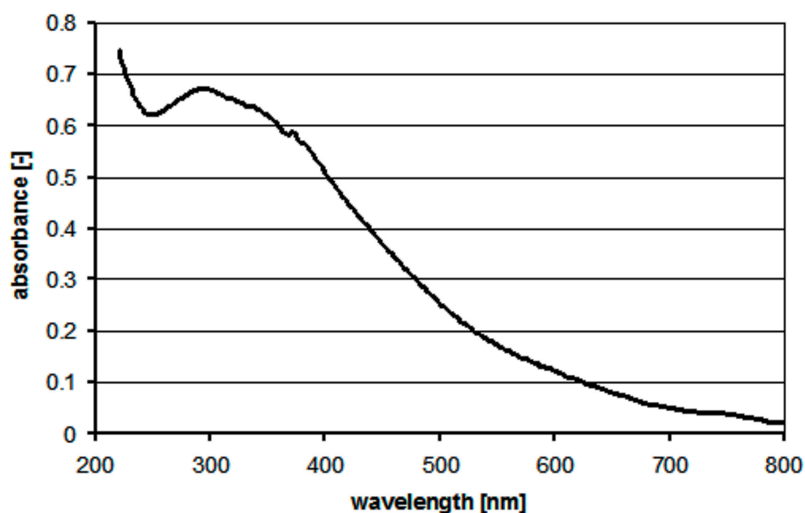


Figure 7. UV-Vis absorption spectrum of CuO suspension (Table 1, sample 9).

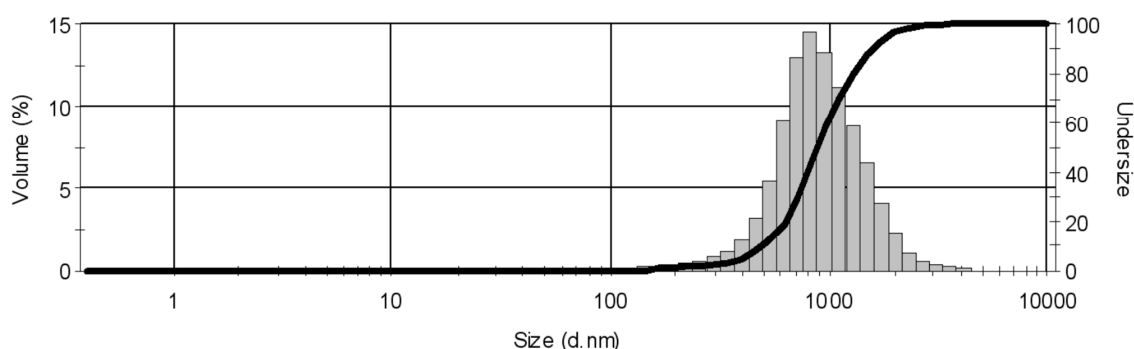


Figure 8. PSD of CuO particles prepared in batch process (Table 1, sample 11).

4. Conclusions

The presented method paves the way to the fabrication of copper oxide sub-micron particles and nanoparticles suspensions in a rapid, continuous and cost-effective way.

It has been shown that by a judicious choice of intensities of sonication and microwave irradiation the size of particles can be varied according to demand. For the proposed set-up of critical importance appear to be temperature of the process, sonication intensity (amplitude), flow rate and composition of substrates. The regions of process variables which afford the smallest CuO particles were identified.

Acknowledgments

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Author Contributions

Grzegorz Dzido: construction of set-up for continuous fabrication of copper oxide. Michał Drzazga: drafting of manuscript. Piotr Markowski: acquisition of data. Andrzej B. Jarzębski: critical revision.

Conflicts of Interest

The authors declare no conflict of interest.

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