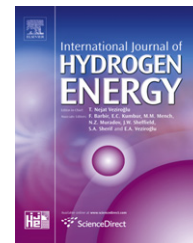


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# Copper oxide nanoparticle made by flame spray pyrolysis for photoelectrochemical water splitting – Part I. CuO nanoparticle preparation<sup>☆</sup>

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## ABSTRACT

Copper oxide (CuO) semiconductor nanoparticles are of interest because of their promising use for electronic and optoelectronic devices, and the size of the CuO particles for these applications is important. In this work, near spherical CuO nanoparticles with aspect ratio of 1.2–1.3 were made by a flame spray pyrolysis (FSP) method. In FSP, flame temperature, residence time, precursor concentration can be used to control particle size. As the precursor concentration increased from 0.5% to 35% w/w, primary particle diameter increased from  $7 \pm 2$  to  $20 \pm 11$  nm. Larger primary particle diameters were observed in the low gas flow system (set B) due to the long residence time in the high temperature zone. For the dependence of temperature on particle diameter, particles grew to similar diameter, i.e.  $\sim 11$  nm, in both flame conditions within the hot temperature zone (80% of melting point of CuO) but for particles having longer residence time, i.e. 550 ms in set B, the standard deviation of particle diameter is 45% larger than for particles with 66 ms as residence time in set A. Modeling gave a result for CuO final particle diameter, based on collision/sintering theory with sintering by solid state diffusion, of 6.7 and 9.0 nm for set A and set B, respectively, with surface tension assumed to be  $0.5 \text{ J/m}^2$ . Comparison with the experiment results,  $11 \pm 4$  nm diameter for both flame conditions, indicates the simulations were reasonable.

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## 1. Introduction

Copper oxide (CuO) semiconductor materials have been particularly interesting because of their promising use for electronic and optoelectronic devices, such as electrochemical cells [1,2], gas sensors [3–5], magnetic storage media [6], solar cells [7–9], field emitters [10,11], high-Tc superconductors [12,13], nanofluid [14], and catalysts [15–19]. However, for these applications, the size, morphology, and specific surface

area of the CuO particles are very important, and sometimes are strongly dependant on the preparation methods.

Nanoparticles are distinguished from bulk materials due to their high surface area to volume ratio which causes the structural and electronic changes. A decrease in size invariably leads to sharpening of the energy bands and also leads to discretization of electron energy levels, concentration of oscillator strength, highly polarizable excited states, increased electron–electron correlation etc. Investigations have revealed that CuO

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nanocrystals show distinct structural, chemical bonding [20] and electronic characteristics [21] due to quantum size effects.

For a number of applications, the characteristics of inorganic particles must be tailored through control during preparation. Many methods are available to prepare micron size CuO particles, such as metal-organic chemical vapor deposition (MOCVD) for producing CuO with grain diameters from 0.05 to 0.8  $\mu\text{m}$  [22] and sonochemical synthesis for producing CuO of grain size varying from 10 nm to several microns [23]. For preparing nanosized CuO, some results have been published such as crystallites in the size range of 7–9 nm [24] and 1–10 nm diameter particles [25] by sol-gel techniques, average diameter of 15–20 nm CuO nanoparticles by solid state reaction [26,27], CuO with diameter as small as 4 nm by electrochemical method [20], controllable diameters of 3–9 nm by alcohothermal decomposition of copper acetate [28], diameters between 3 and 5 nm by colloid-thermal synthesis processing [29], primary particles of copper oxide about 20–30 nm by spinning disk reactor [14].

Although there are many methods available for producing small CuO particles, many are time consuming [22,30], energy intensive [23,26,27], and require expensive raw materials [20,23,30] which make them difficult to be scaled up. Economic concerns dictate that a relatively low cost, easy to operate, and scalable process would be needed. Flame-based aerosol methods have been developed for the synthesis of a wide variety of metal oxide particles [31–33]. Compared to the various post-treatment steps needed in wet-chemical routes, gas-phase processes allow the preparation of the desired material often without any further post-processing [34–36]. Furthermore, flame-based aerosol methods also have potential commercial importance because they can be conducted continuously with a high production rate at a relatively low cost [37–39].

Flame synthesis is a novel technique for producing fine and pure particles in the as-prepared state in just few milliseconds. However, the produced particles are generally hard agglomerates and the size distribution is somewhat broad, making them undesirable for many applications [37,39]. The preparation of nonaggregated particles by methods using flames with liquid precursor sources, i.e. flame spray pyrolysis, has been reported [40,41]. Flame spray pyrolysis (FSP) is a flame-assisted liquid droplet-vapor-to-particle conversion process used to produce single and multi-component nanoparticles [31–33,42–46]. In addition, the FSP setup allows the adjustment of precursor compositions, flame temperature, production rate, and residence time of particles in the flame and hence particle growth and morphology can be controlled, leading to tailor-made single or multi-component nanocomposite particles.

In this study, several ways to control and vary the size of nano CuO particles are explored and evaluated. Particle size was changed by varying the precursor concentration. With lower precursor concentration, loading of aerosol decreases and the collision rate is slower. Also, the effect of quenching rate on crystalline size was studied by introducing liquid nitrogen into the post flame zone. Furthermore, the temperature of flame and the residence time of particle in high temperature zone were considered and modeling based on sintering/collision theory was compared with the experimental results.

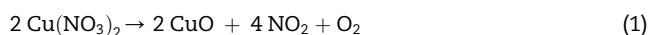
## 2. Material and methods

### 2.1. Aerosol generator and flame conditions

In an FSP reactor, an aqueous solution of copper (II) nitrate,  $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ , (Strem Chemicals, Inc. USA) was atomized by a nebulizer (Gemini Scientific Corp., USA) and passed through a premixed methane flame where vaporized precursor reacted to oxide and formed nanosized CuO particles through gas to particle conversion. Particles then were collected on a polytetrafluoroethylene (PTFE) fabric filter (W. L. Gore & Associates Inc., USA) within a filter funnel (Whatman, Japan) using a vacuum pump (United Vacuum, USA). A schematic of the experimental apparatus for producing copper oxide aerosol from metal salt precursor is shown in Fig. 1. The liquid nitrogen was introduced to the system at varying distances from the flame by changing the height and angle of the liquid nitrogen bottle also as shown in Fig. 1.

The filtered laboratory air at 3.6 L/min flowed through a nebulizer atomizing precursor solution. Gas flow rates were controlled by rotometers (Cole-Palmer, USA). Both gas flow rates and flame conditions are tabulated in Table 1. The flame was made from methane (99.0%, Airgas) and oxygen (99.8%, Airgas) at an equivalence ratio of 1.0. To stabilize the flame, nitrogen (99.998%, Airgas) was introduced. The methane, oxygen and nitrogen were combined at the bottom of the burner then the mixture flowed upward through holes on the aluminum foil while the stream with air/droplets was introduced into the upper part of burner and mixed. The flat flame was stabilized on two parallel stainless steel plates. The temperature profile was measured at the middle of flame with an S-type thermocouple and corrected for radiation losses [47]. Two different flame compositions and temperature profiles were chosen (Fig. 2) based upon the limits of our system. For set A, the maximum measured temperature was 1748 K with a cooling rate of approximately 209 K per centimeter over the first 6 cm downstream, 54 K per centimeter from 6 to 10 cm, and 14 K per centimeter from 10 cm to the collector. For set B, the maximum measured temperature was 1432 K with a cooling rate of approximately 168 K per centimeter over the first 4 cm downstream, 109 K per centimeter from 4 to 8 cm, and 9 K per centimeter from 8 cm to the collector. The adiabatic flame temperatures calculated for the flame were 2185 K and 2383 K, respectively. The difference between the maximum measured temperature and the adiabatic flame temperature could be attributed to heat losses to the stainless steel cover and the evaporation of water.

The copper (II) nitrate (Strem Chemicals, Inc. USA) precursor solutions were prepared in the concentrations of 0.5%, 5%, 17%, 25%, and 35% w/w copper nitrate/solution with DI water as solvent. Decomposition of copper nitrate in the flame is expected to follow the mechanism given in Eq. (1).



### 2.2. Particle sampling and characterization

For phase determination, X-ray diffraction (XRD) measurements were performed using a Philips PW 1800 diffractometer

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