

Continuous Production of Copper Oxide Nanoparticles Using Picosecond Laser Fragmentation: Effect of Irradiation Time

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Abstract

Metal oxide powders at the macro-scale level exhibit low properties as compared to nanoscale powder despite their wide-availability, low-cost processing, and bulk quantities production. The present study introduced a two-step synthesis method for the continuous and high yield production of copper oxide nanoparticles. The first step comprises a chemical reduction process to synthesis copper tartrate micro-flakes of larger than 1µm. In the subsequent step, these micro flakes are physically fragmented to nanoparticles in water medium using picosecond laser pulses (532 nm, 10Hz, 30 ps.). Besides, a time-based study showed that the particle size increases as the laser exposure time increases. The obtained copper tartrate nanoparticles from laser fragmentation are calcinated at 250 °C to remove tartrate, and then copper oxide nanoparticles are produced at the end of the experiments. The acquired particles at different stages are characterized by XRD, TEM, and FESEM to study their morphology and structure changes due to shape reduction. The results showed nanoparticle in the range of 5-15 nm in size, while the design setup is suitable for the cost-effective and continuous production of nanoparticles.

Keywords: Picosecond laser; Nanoparticles; copper oxide; Fragmentation; Copper tartrate

الإنتاج المستمر لحبيبات أكسيد النحاس النانوية باستخدام التفسير بالليزر الدقيق: تأثير زمن الإشعاع الليزري

الملخص

مساحيق أكاسيد المعادن ذات الحبيبات الكبيرة الحجم بالرغم من كثرة تواجدها وسهولة تحضيرها إلا أنها تمتلك خصائص أقل عند مقارنتها بالمساحيق النانوية. الدراسة الحالية تقدم طريقة تحضير مستدامة وإنتاج عالي على مرحلتين لإنتاج جزيئات أكسيد النحاس النانوية. المرحلة الأولى من التحضير تتضمن عملية تحضير كيميائية لإنتاج شرائح تارتريت النحاس ذات الحجم أكبر من 1 مايكرومتر. في المرحلة الثانية، هذه الشرائح الكبيرة يتم تعريضها للتفسير الفيزيائي باستخدام اشعة الليزر الدقيقة في وسط مائي (532 nm, 10Hz, 30 ps.). علاوة على ذلك، فإن دراسة تأثير زمن الإشعاع الليزري على حجم وتركيب الحبيبات النانوية أوضح أن حجم الحبيبات يزيد مع زيادة زمن الإشعاع. الحبيبات النانوية لتارتريت النحاس الناتجة من تفسير الليزر تم تسخينها عند 250 درجة مئوية بغرض إزالة التارتريت من النحاس وينتج في النهاية حبيبات نانوية من أكسيد النحاس. هذه الحبيبات النانوية تم دراسة خصائصها باستخدام تقنيات حديثة مثل الميكروسكوبات الالكترونية والتي أوضحت أن حجم الحبيبات من 5 - 15 نانومتر، بينما هذه الطريقة ملائمة أيضاً لتحضير كميات كبيرة واقتصادية ومستدامة من حبيبات أكاسيد المعادن الأخرى

1. Introduction:

Reducing the size of matters to the nanoscale is a crucial topic in the engineering and science fields. That is due to the enhancement of materials properties at the nanoscale, which increases their potentials for unique applications . (Okada-2007),(Yang-2007) (Amendola-2009) . Copper is a noble metal that exhibits extraordinary physicochemical properties (Ingle-2014). Copper nanoparticles (Cu NPs) and its oxides show an extremely high electrical and thermal conductivity, high melting point, excellent malleability, low electrochemical migration behavior, relatively easy preparation methods, and low-cost processing (Ingle-2014) (Ananth-2015) . These unique properties drive research groups to predict numerous synthetic technologies at the micro and nano level. In other words, a large number of physical, biological, and chemical methodologies are employed to reduce the size of bulk copper particles to the nanometer scale (Ananth-2015). However, most of these technologies face uncertainty in the control of their sizes, shapes, surface properties, and mass production.

Continuous production of Cu NPs using bottom-up approaches is a challenging duty owing to their time-consuming and low-yield synthesis. In this regard, the size reduction of materials by using top-down approaches has the potential for clean and large scale production. In fact, ball milling, ultrasonic, piezoelectric, electromagnetic, electrohydraulic, pneumatic technologies are among the top-down approaches for the fabrication of nano-sized structures from micron size (Ayoman-2016) (Murty-1998) (Yadav-2012) (Wei-2020) . Many of these methods are useful for specified applications, and in general, they are facing many drawbacks such as aggregation, contamination, time-consuming approaches, and high energy consumption (Amendola-2009) (Ingle-2014) (Ananth-2015) (Ayoman-2016) (Murty-1998) .

Laser ablation offers one of the most effective top-down approaches to generate and fragment

large varieties of metals, oxides, composites, and alloys, which are free from contamination and aggregation (Okada-2007),(Yang-2007) (Amendola-2009) .Furthermore, laser ablation can be regularly achieved in a short time, low-cost, and produce high yield (Ancona-2009) (Al-Antaki-2019) (Fernandez-Arias-2020) . Moreover, studies of short-pulsed laser ablation have shown that Picosecond and Femtosecond laser pulses of suitable wavelength can effectively ionize the materials in the focused spot region, resulting in fine nanoparticles (Sasaki-2006) . Another exciting direction of laser ablation goes towards the laser fragmentation of coarse particles to nanoparticles in a solution (Ancona-2009) (Kochemirovsky-2015) (Ali-2015) .That is because micron-size particles are widely available and easily synthesized in bulk quantities. Of course, laser fragmentation shortens the irradiation time and saves the energy readily (Ali-2015) (Schwenke-2011) (Ma-2009).

Sodium potassium tartrate tetrahydrate (Rochelle salt) is a mild reducing agent often used to reduce copper ions to copper tartrate (Ma-2009). In this work, we have synthesized copper tartrate micro-flakes using Rochelle salt to reduce copper ions to coarser particles of copper tartrate. In the second step, micro-flakes of copper tartrate was reduced to nanoparticles using picosecond laser pulses (532 nm, 10Hz, 30 Ps.). Of note, this process could expand for the reduction of other metals (Brikas-2007).

2. Materials and Experiments

The experimental procedure summarizes into two steps. The first step is the reduction of copper ions to coarser particles by using a chemical method, and the second step is fragmenting these coarser particles to nanoparticles either by Ps laser fragmentation.

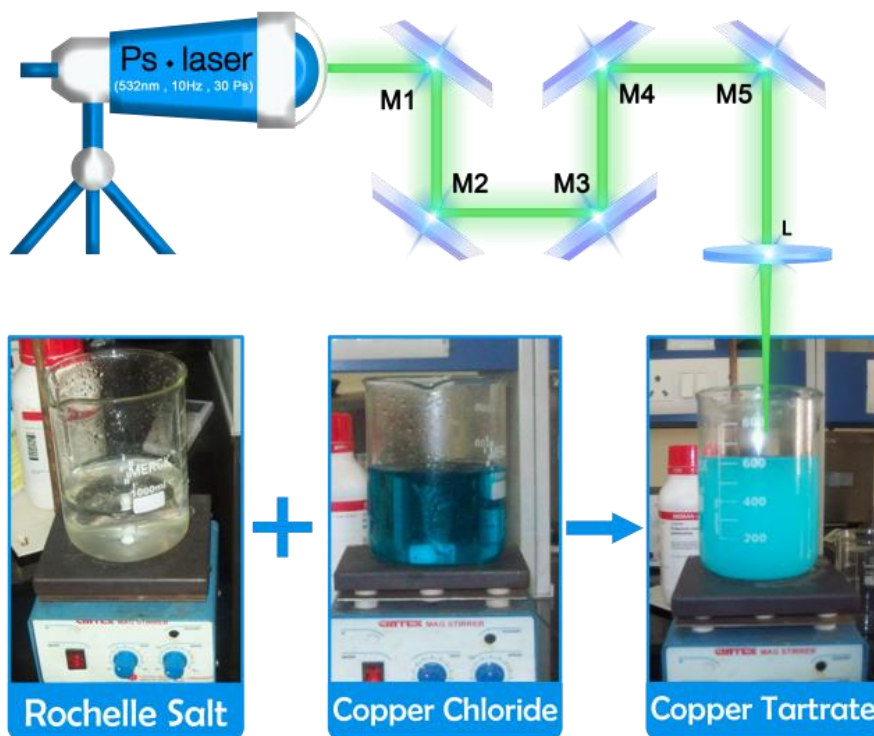


Figure 1. a schematic illustrating diagram for the experimental setup of the continuous production of copper oxide nanoparticles.

2.1 Synthesis of micron-size copper tartrate

The present study illustrates a simple, convenient, room temperature, and two-step reduction method for the synthesis of CuO NPs. In the first step, the stoichiometric amount of Copper Chloride (II) Dehydrate and Sodium-Potassium Tartrate Tetrahydrate were independently dissolved properly under vigorous mixing in distilled water. In the next step, Copper Chloride (II) Dehydrate aqueous solution was added drop-wise to the Sodium-Potassium Tartrate Tetrahydrate aqueous solution under vigorous stirring. Of note, no reaction was observed until the addition process is completed. The obtained solution is kept with stirring for one hour for achieving a complete reaction. The obtained solution had a light blue color as a first indication for the synthesis of copper tartrate (Qin -

2003) (Aripnammal-2019). In the subsequent step, the obtained powder was filtered using a vacuum pump-paper filter system, properly washed using ethanol. Finally, the obtained precipitate was then dried in a vacuum oven at 100 °C for about 1 hour.

2.2 Picosecond fragmentation experiment

Picoseconds laser (532nm, 30ps, 10Hz) was implemented to fragment and reduce coarser particles into nano-sized particles at different irradiation times by dispersing a preset amount of copper tartrate powder in the water solution with stirring and exposing it to a focused beam as shown in **Fig. 1**. In brief, 50 mg of copper tartrate powder, which was prepared by chemical method, is dispersed well in 100 ml de-ionized water and exposed it to high energy laser pulses for 20 min. Similarly, the above procedure was repeated with 40 minutes of irradiation time while the other parameters kept unchanged. **Fig. 1** shows a simplified schematic diagram of the picosecond laser technology used to fragment copper tartrate particles.

3. Results and Discussion

3.1 Copper tartrate analysis

The obtained solution with a light blue color (**Fig. 1**) is the first indication of the synthesis of copper tartrate particles (Ma-2009). (Qin -2003) (Aripnammal-2019). **Figure 2** depicts the X-ray diffraction pattern of the obtained powder. The diffraction peaks are indexed well to the copper tartrate phase (Aripnammal-2019). The peaks' low broadness is an indication of the large crystals.

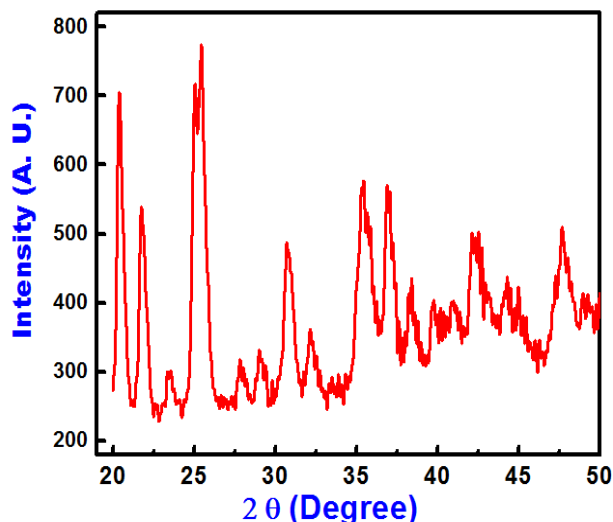
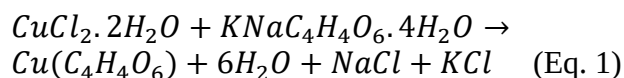


Figure 2, XRD pattern of copper tartrate ($C_4H_4CuO_6 \cdot 3H_2O$) particles

The plausible reaction progresses as soon as the two chemical reactant solutions mixed, as stated by the following equations:



The above equation confirms the production of copper tartrate as the main product in the

reaction. Water and other salts are eliminated by proper washing of the obtained powder. Copper tartrate powder is quite stable in almost all environments, allowing it to handle, transport, and store easily. Calcination of copper tartrate at $\sim 350^\circ\text{C}$ in the atmospheric air produces copper oxide. Of course, pure copper nanoparticles could also be achieved if the calcination process is executed in an air-free environment.

The morphology of the obtained powder is characterized using a transmission electron microscope and scanning electron microscope, as shown in **Fig. 3**. The results show micro flakes of copper tartrate with irregular morphologies, which are aggregated together during the reaction, leading to a reduction of their surface area. Also, the flakes had no regular shape and thickness.

3.2 Laser fragmentation

The obtained micron-size flakes are dispersed in water solution and exposed to Ps laser irradiation beam for different irradiation time. In other words, a modified laser ablation reduction process is investigated to fragment the large flakes to obtain fine nanoparticles instead of bulk targets. This

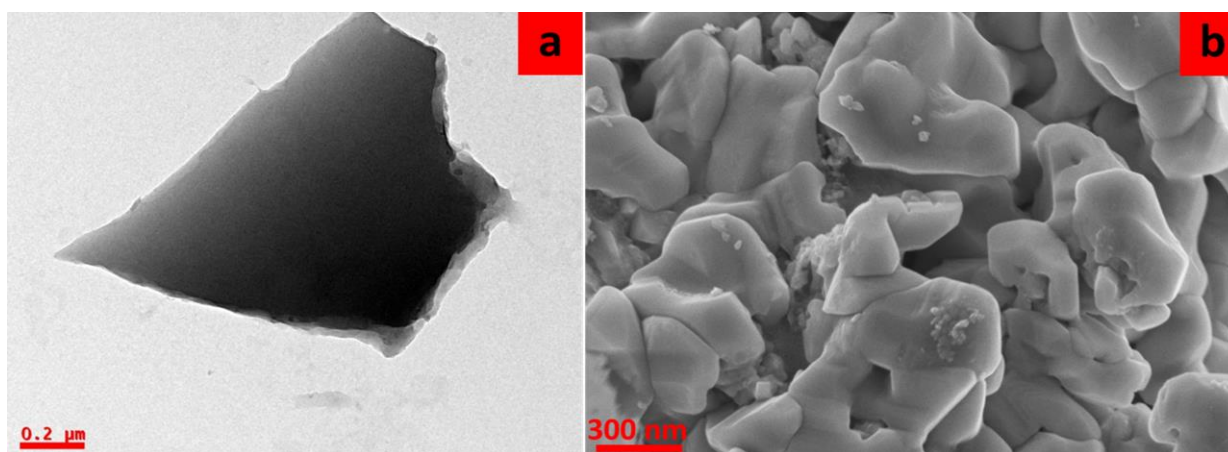


Figure 3. (a) TEM and (b) FESEM images of the obtained copper tartrate flakes, water is the solvent, and Rochelle salt is the reducing agent

method has advantages over the traditional laser ablation method in the simplicity of preparation since it does not need any nano-stage 3-D displacement system. That is to allow the target to move in a stepwise manner. However, it is disadvantageous in the random fragments, which results in wide broadening particle size. Of note, the dispersed particles in water solution vigorously

method despite its high energy consumption can provide a framework for the continuous production of nanoparticles. Surfactant addition could embed the agglomeration process (Wen-2011) (Tilaki-2007). Furthermore, vigorous and constant agitating of the solution containing the particles could eventually minimize the size distribution broadening of the particles and the required irradiation time (Zhang-

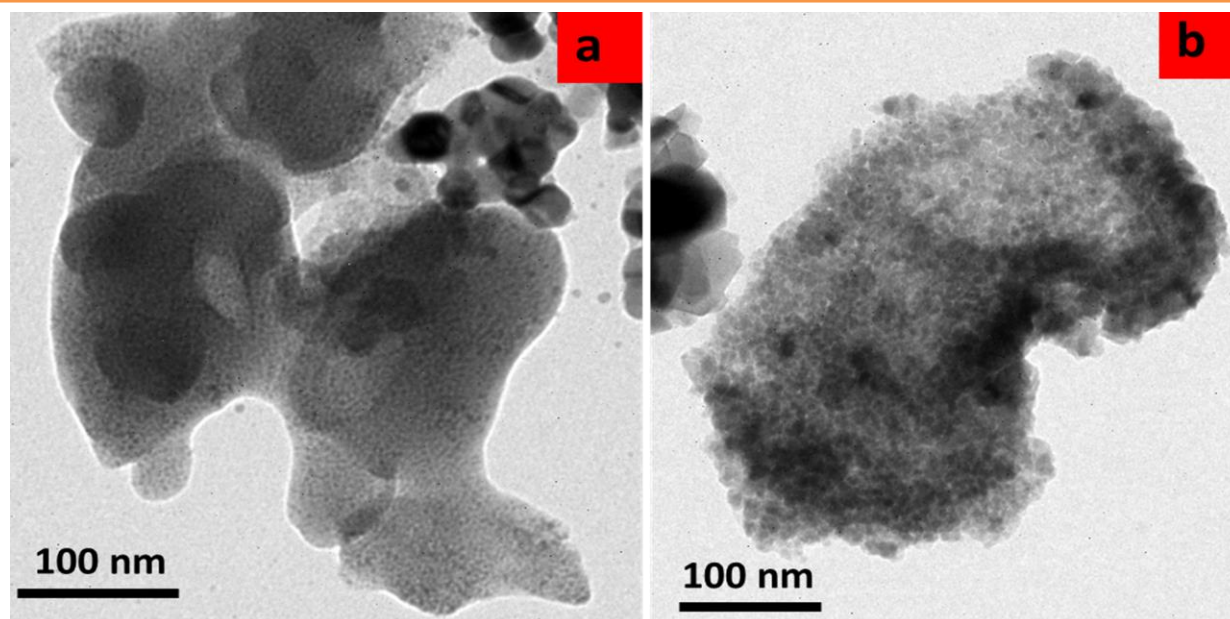


Figure 4. TEM images of copper tartrate nanoparticles were reduced by Ps laser (532nm, 30ps, 10Hz) fragmentation in water solution for (a) 20 min., and (b) 40 min irradiation periods.

move during the laser irradiation due to the magnetic stirrer effect.

The effect of irradiation time was investigated in two time periods separately; 20 minutes and 40 minutes. Besides, the obtained particles are studied using TEM microscopy as shown in **Fig. 4**. Interestingly, the results showed smaller particles in the case of 20 min as compared to 40 min irradiation time. The images showed regular nanoparticles with an average size of ~ 3 nm and ~ 7 nm in the case of 20 min and 40 min irradiation time, respectively. This finding elucidated that the ablated particles get aggregated in the water solution as the irradiation time increases. This

2017)..

3.2 Copper oxide analysis

In a separate step, copper tartrate powder dissociates under heating at ~ 250 °C in the air environment to copper oxide based on this equation:

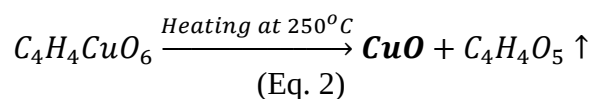


Figure 5(a) shows the XRD pattern of copper oxide powder after the calcination step. The obtained peaks are indexed to the copper oxide

phase. The broadening of the peaks is an indication

could be calcinated at 350 °C to attain stable and

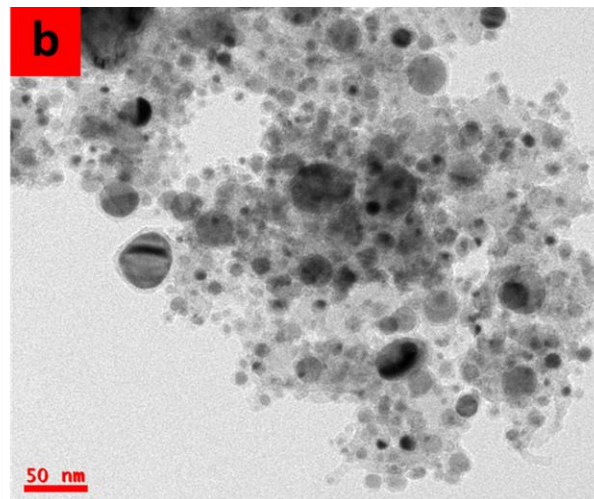
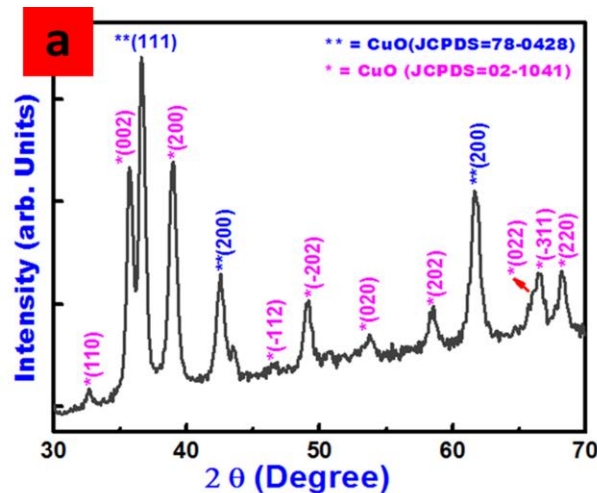


Figure 5. (a) XRD pattern and (b) TEM image of the obtained CuO nanoparticles after the calcination of copper tartrate flakes at 350 °C in the air environment

of the small features of the particles. The size, shape, and size distribution of the particles rely mainly on the calcination temperature. **Figure 5(b)** exhibits the TEM image of CuO nanoparticles calcinated at 350 °C. The results show fine nanoparticles with a size range of 10 - 40 nm, with high concentration to smaller particles.

4. Conclusions

The present study introduced a two-step approach for the synthesis of CuO NPs. Copper tartrate synthesized using a chemical route in bulk quantities, and the obtained powder is dispersed in distilled water and subjected to Ps laser fragmentation to get copper tartrate nanoparticles. The structure, shape, and size of the obtained copper tartrate were confirmed using XRD and electron microscopy before and after the laser fragmentation process. Attracting results showed a slight increase to the particle size as the irradiation time increases. The mechanism of particle growth undergoes an aggregation phenomenon during the irradiation process. Furthermore, the obtained results showed that copper tartrate nanoparticles

well-dispersed CuO nanoparticles. This method stands for the continuous production of copper oxide nanoparticles with a time- and energy-saving procedure.

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