

Synthesis of submicrometre Cu particles via a reduction in triethanolamine solvent

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With the aim of preparing a low-cost filler material to enhance the bondability of a sinter-bonding paste, submicrometre Cu particles with little agglomeration were successfully synthesised by a simple solvothermal recipe using CuO as a precursor and triethanolamine as a solvent. The required synthesis time and the average size (216–821 nm) of the synthesised Cu particles decreased proportionally with the increasing synthesis temperature. The required synthesis times were found to be 30 and 60 min and the particle sizes of 410 and 821 nm were achieved at synthesis temperatures of 200 and 180°C, respectively. The CuO particles were transformed into Cu₂O nanoparticles by accepting the hydrogen ions and electrons released during the conversion of the triethanolamine to the aldehyde by the oxidation of its three hydroxyl groups. Submicrometre pure Cu particles could be subsequently formed from aggregates of the Cu₂O nanoparticles by removing O ions from Cu₂O during the continuous conversion of the aldehyde to nitrilotriacetic acid.

1. Introduction: Cu powder has been used as an important conductive material for electronic packaging because of its excellent electrical conductivity and low electrochemical migration [1–5]. In particular, even though Cu is only 6% less conductive than Ag, its overwhelmingly lower cost has recently encouraged more interest in Cu powder. For example, Cu powder can be used as a low-cost alternative to Ag filler in the sinter-bonding paste for the die-attachment of wide bandgap (WBG) semiconductors such as GaN or SiC, which are important materials for next-generation high-power devices [6–9]. Although sinter-bondability strongly depends on particle size (the smaller the particle size, the higher the sinter-bondability), the usage of nanoparticles as a filler material in pastes is difficult due to both the mixing process and the need to attain a low cost [10, 11]. Hence, submicrometre Cu particles are required as an additive to increase sinter-bondability by enhancing the packaging density [9]. Also, the formation of Ag shells on the surfaces of submicrometre Cu particles allows for low temperature and high-speed bonding characteristics in identical applications [12]. Therefore, an effective method for synthesising submicrometre Cu particles may be a crucial technology in the die-attachment material industry for WBG semiconductors and high heat-generating devices.

Wet chemical synthesis is an effective process for the formation of small metal particles that cannot be fabricated by the atomisation of molten metal. However, the wet chemical processes used for the synthesis of Cu particles are complex and usually require the usage of a reducing agent, a protective agent, and other chemicals [13–26]. Furthermore, some reducing agents are toxic to humans, and the capping agent might be an obstacle in subsequent processes such as Ag coating [20–26]. Thus, removal of the reducing and protective agents is a significant factor in the establishment of a more competitive wet chemical synthesis method for submicrometre Cu particles.

In this Letter, therefore, we report a simple solvothermal process for synthesising submicrometre Cu particles with little agglomeration. In addition, the reactions occurring during the synthesis are discussed based on the microstructural and compositional analysis of samples obtained at different reaction times.

2. Experimental study: CuO powder was selected as a precursor for synthesising submicrometre Cu particles, and triethanolamine (HOCH₂CH₂)₃N₂, 99% (Samchun Pure Chemical Co.) was used as a solvent for the synthesis. A 2 mol CuO particles were

added to 300 ml of triethanolamine, and then the resulting mixture was heated to different reaction temperatures (235, 200, and 180°C) with continuous stirring in a mantle heater under an air atmosphere. The particles dispersed in the solution were washed using ethanol after centrifugation at 7000 rpm for 3 min and decantation. The centrifugation–decantation–washing process was repeated three times. The washed particles were dried in a low-vacuum chamber at room temperature. The size and morphology of the CuO and synthesised particles were analysed using a field emission scanning electron microscope (FE-SEM, JSM-7500F, JEOL Ltd.). The composition of the synthesised particles was confirmed using X-ray diffraction (XRD, DE/D8 Advance, Bruker). The temperature variation of the solution was also measured by inserting a thermocouple into the solution during the synthesis.

3. Results and discussion: Fig. 1 shows the SEM images of Cu particles synthesised by a reduction in triethanolamine solvent under different conditions. As shown in Fig. 2, XRD analyses were used to determine whether the finally synthesised particles were pure Cu or not. When the synthesis was carried out at 235°C, pure Cu particles could be obtained after a reaction time of just 20 min, as shown in Fig. 1a. When the synthesis temperature was decreased to 200°C, the time required to obtain pure Cu particles increased to 30 min (Fig. 1b). Eventually, the time increased to 60 min at the lowest synthesis temperature of 180°C (Fig. 1c). The average particle size was 216 (±33), 410 (±65), and 821 (±150) nm, respectively, at synthesis temperatures of 235, 200, and 180°C, respectively, which indicates that decreasing the temperature increases the particle size. With the increase in particle size, the smooth surface morphology changed, with the surfaces taking on a more polygonal shape. A higher synthesis temperature will lead to the formation of considerably more nuclei during a single nucleation period thanks to an enhanced reduction reaction rate, thus resulting in smaller average particle size [23, 27, 28]. On the contrary, a low synthesis temperature may induce a reduction in the number of nuclei due to the decreased reaction rate and the reinforcement of the growth step in which the size of each nucleus increases [23, 27, 28]. The particles grown during the growth step might be transformed into a polygonal shape by the oriented attachment of atoms. However, the synthesis at 235°C was not considered hereafter because the gas pressure in the flask increased to a dangerous level.

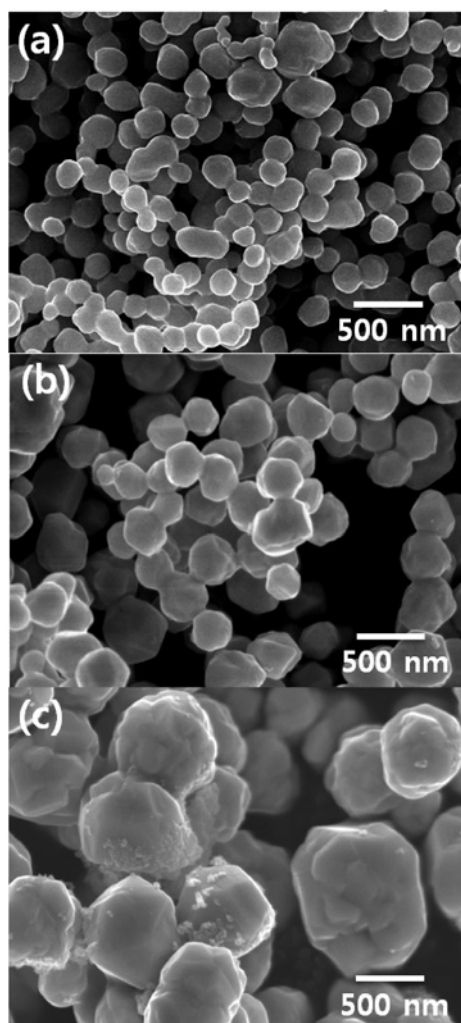


Fig. 1 SEM images of Cu particles synthesised by reduction in triethanolamine solvent with different conditions

a At 235°C for 20 min
b At 200°C for 30 min
c At 180°C for 60 min

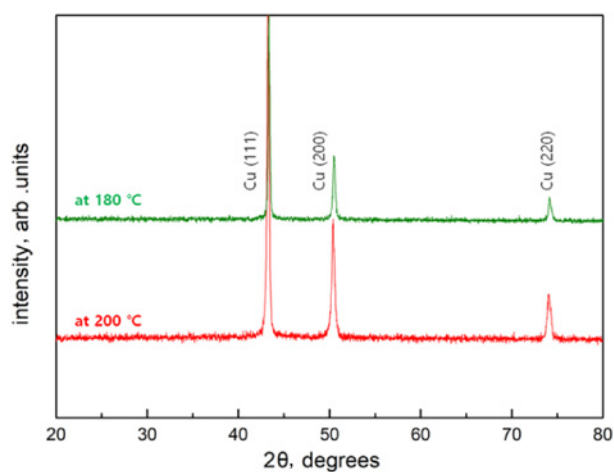


Fig. 2 XRD patterns of particles synthesised in triethanolamine solvent at different temperatures

The XRD results shown in Fig. 2 verify that the particles synthesised both at 200°C for 30 min and at 180°C for 60 min are pure Cu.

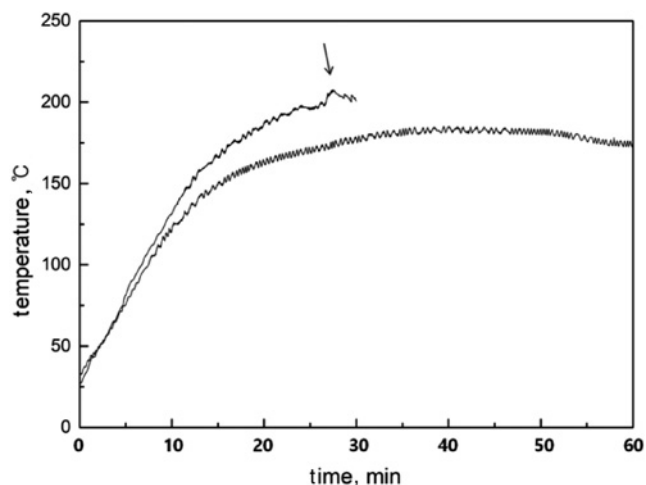


Fig. 3 Temperature profiles of triethanolamine solution during synthesis at different temperatures

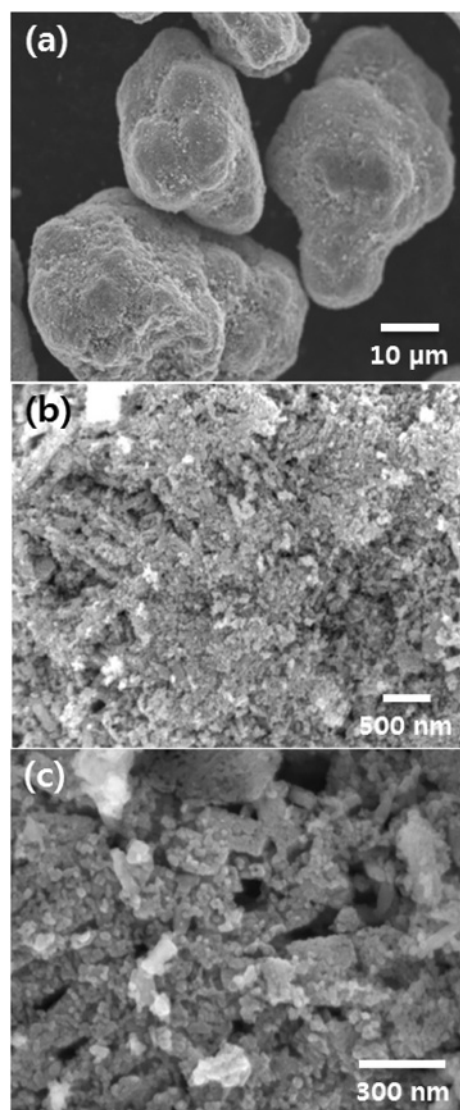


Fig. 4 SEM images of used CuO powder

a At low magnification
b At middle magnification, and
c At high magnification

To investigate the cause of the more rapid synthesis at 200°C in comparison to that at 180°C, the temperature of the triethanolamine solution was measured during the synthesis process. The temperature profiles in the synthesis experiments with 180 and 200°C as the final temperature are displayed in Fig. 3. When the temperature was set to 180°C, the set temperature was attained after heating for 30 min and remained constant since then. In contrast, during the 200°C synthesis, a striking exothermic peak (the arrow in Fig. 3)

was observed shortly after the temperature of the solution approached the set temperature after heating for 26.5 min, resulting in the occurrence of a violent reaction and abrupt gas generation. This exothermic phenomenon may accelerate the reduction reaction and therefore reduce the synthesis time.

Henceforth, the reduction behaviour of CuO particles will be discussed according to synthesis temperature and time. The SEM images of the used CuO powder are shown in Fig. 4. The particles

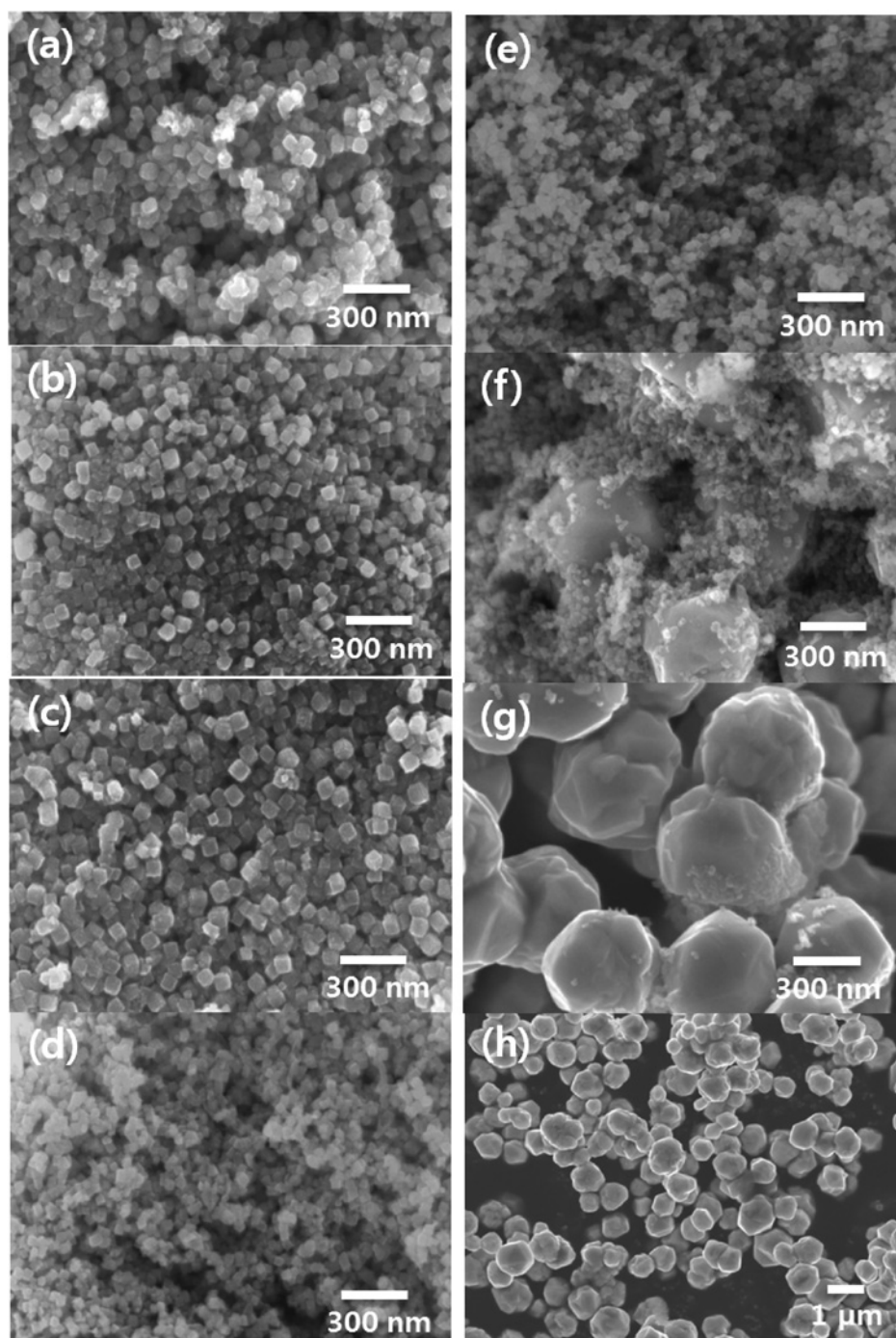


Fig. 5 SEM images of particles collected at different reaction times during synthesis in triethanolamine solvent at 180°C after

a 30 min
b 35 min
c 40 min
d 45 min
e 50 min
f 55 min
g, h 60 min

are several tens of micrometres and visible at low magnification, however they consisted of numerous tiny particles which are aggregates of nanoparticles, as can be seen in Figs. 4*b* and *c*.

Figs. 5 and 6 show the SEM images and XRD patterns of particles collected after different reaction times during synthesis at 180°C.

After the synthesis proceeded for 30 min, the solution just approached the set temperature of 180°C and new particles of cubic shape were formed on the surfaces of the CuO particles. The formed particles were indexed as Cu₂O phase based on the appearance of new peaks observed in Fig. 6. The intensities of the Cu₂O peaks were maximised after 15 min of additional synthesis time, resulting in the decrease and eventual extinction of the CuO peaks. After the additional time, the population of cubic Cu₂O nanoparticles reached a maximum, and then they were transformed into smaller nanoparticles of irregular polyhedral shapes. With the formation of the smaller nanoparticles, the peak intensity of the Cu₂O phase decreased. When the time approached 55 min, pure Cu peaks could be detected, indicating the formation of completely different particles several hundreds of nanometres in size among the smaller particles. The smaller nanoparticles were completely transformed into Cu particles after 5 min of additional reaction time, indicating that the total synthesis time should be 1 h. As a result, the particles collected after 1 h of the reaction showed only Cu peaks.

Figs. 7 and 8 show the SEM images and XRD patterns of particles collected after different reaction times when the synthesis was carried out at 200°C. Novel nanoparticles, different from the initial CuO nanoparticles, were observed with the appearance of Cu₂O peaks in the XRD spectrum after only 20 min of reaction time. The initial CuO peaks rapidly disappeared and the maximum Cu₂O peak intensities were observed after 5 min of additional reaction. At this time, nanoparticles of irregular polyhedral shapes were mainly observed. Particles around 100 nm in size, which seem to be aggregates of polyhedral nanoparticles, also existed in the sample. Finally, the Cu₂O particles were completely transformed into Cu particles at an abruptly high rate by the aid of the exothermic reaction observed in Fig. 3 after 5 min of additional reaction time. Although the phase transformation during the synthesis at a peak temperature 200°C proceeded at an enhanced rate, the sequence of the reduction reaction by which the initial CuO particles are finally transformed into Cu through the formation of a Cu₂O phase was identical to that observed at a lower temperature.

The reduction of CuO particles in triethanolamine could be interpreted based on the sequential reactions illustrated in Fig. 9.

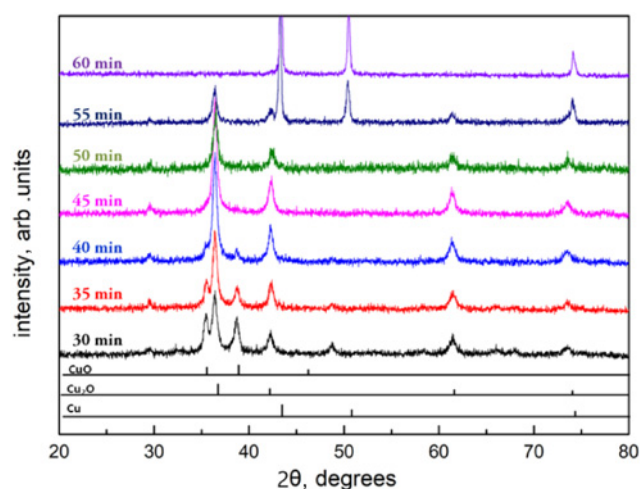


Fig. 6 XRD patterns of particles collected at different reaction times during synthesis in triethanolamine solvent at 180°C

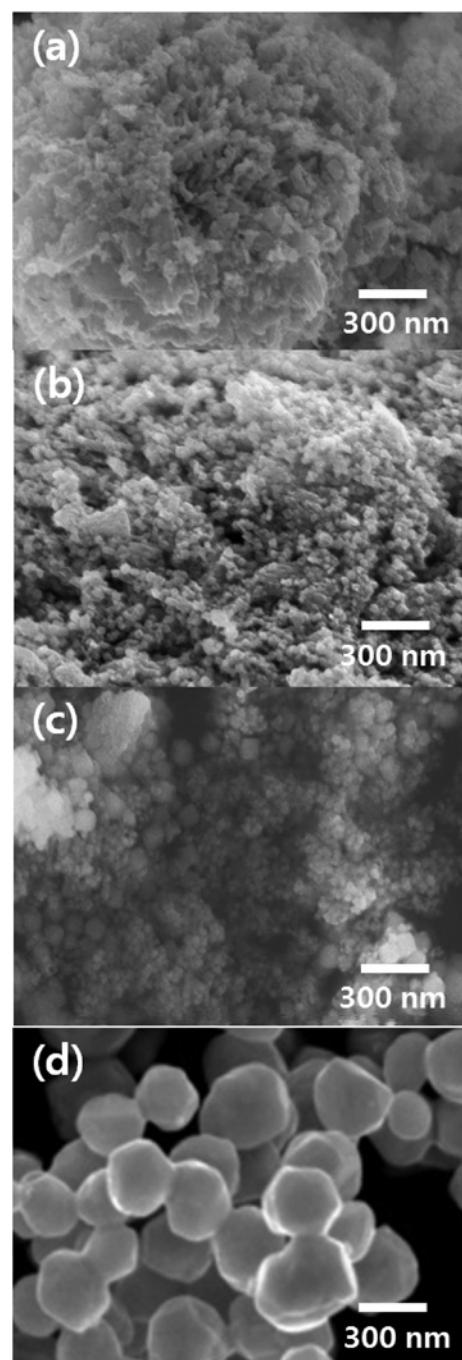


Fig. 7 SEM images of particles collected at different reaction times during synthesis in triethanolamine solvent at 200°C after

- a 15 min
- b 20 min
- c 25 min
- d 30 min

Triethanolamine has three hydroxyl groups, which can be easily oxidised [29, 30]. The triethanolamine is first transformed into aldehyde by the oxidation reaction involving donating hydrogen ions and electrons from the hydroxyl groups [31]. Hence, CuO can be transformed into Cu₂O by accepting the hydrogen ions and electrons, forming cubic-shaped nanoparticles. Subsequently, the aldehyde is transformed into nitrilotriacetic acid by taking O ions away from the transformed Cu₂O [31]. Simultaneously, pure Cu particles are formed from the aggregates of the Cu₂O nanoparticles and the average size decreases with increasing synthesis temperature.

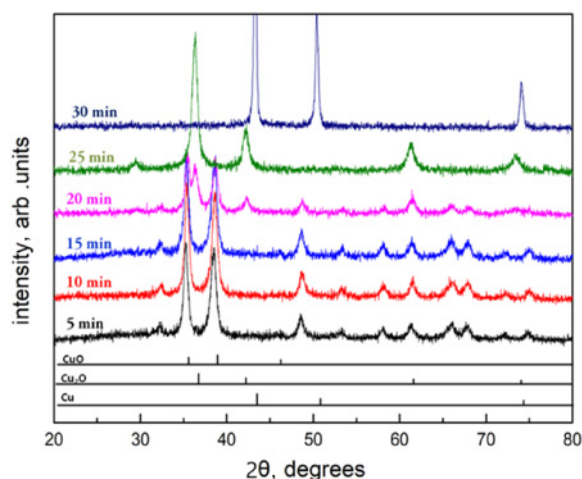


Fig. 8 XRD patterns of particles collected with different reaction times during synthesis in triethanolamine solvent at 200°C

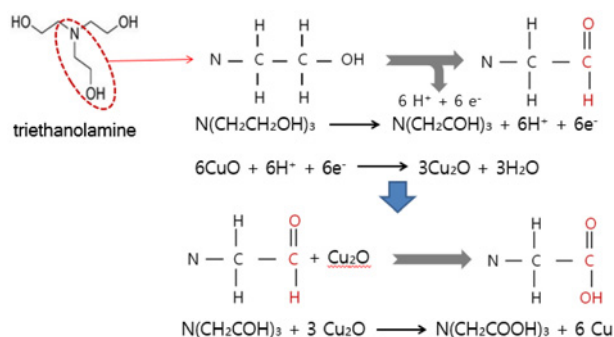


Fig. 9 Oxidation pathways of triethanolamine to aldehyde and nitrilotriacetic acid owing to dehydration of the –OH groups

Most of the reported methods for the wet chemical synthesis of Cu particles were performed using expensive Cu precursors [13–16] or under inert atmosphere [15, 17–19, 25]. Severe agglomeration between synthesised Cu particles or long synthesis time [14] was also reported. When compared with the methods, the synthesis method proposed in this Letter is competitive and has discrimination.

The particles with little agglomeration are beneficial for the mixing process using viscous resin formulation [32]. The submicrometre Cu particles can indicate enhanced sinterability owing to extended surface area. Thus, fabricated particles are suitable for a filler material for sinter-bonding which is required to endure high temperature and transfer effectively heat [33–37].

4. Conclusion: Cu particles of 216–821 nm in average size, indicating acceptable dispersity, were synthesised via a simple solvothermal process, without the need for reducing or protective agents, using a CuO powder precursor and triethanolamine solvent. The average particle size and the required synthesis time were found to decrease proportionally with increasing synthesis temperature. However, the synthesis at 235°C induced an excessive increase of gas pressure in the reaction flask. The synthesis at 200°C induced an abrupt increase in the solution temperature shortly after approaching the set temperature, unlike that at 180°C. During the synthesis at 180°C, the CuO completely disappeared with the appearance of Cu₂O nanoparticles after 45 min and pure Cu particles were formed from the aggregates of Cu₂O nanoparticles after 60 min. Meanwhile, in the 200°C synthesis, the complete disappearance of CuO was observed after just 25 min and pure

Cu particles were formed via the formation of Cu₂O nanoparticles with only 5 min of additional reaction time. CuO might be changed to Cu₂O by accepting the hydrogen ions and electrons released during the transformation of triethanolamine into aldehyde. Subsequently, pure Cu could be formed by removing O ions from Cu₂O during the continuous transformation of the aldehyde into nitrilotriacetic acid.

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6 References

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