Synthesis of Copper Nanoflakes

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[Note: The findings of this investigation will be published in a scientific paper by the laboratory. Consequently, this report has been modified to leave out certain important details which must remain undisclosed prior to the date of publication. Whilst the background information remains untouched, the experimental procedure and the better part of the discussion of results (including data analysis and representation of trends) has been removed or been intentionally rendered vague. Please thus refer to the academic paper that will soon be published for a fuller overview of this investigation.]

1. INTRODUCTION

The alarming CO_2 levels and climate change are pushing a transition from the use of fossil fuels to renewable energy. In the past years, there has been growing interest in converting solar energy to chemical energy and renewable fuels via electricity and sunlight. These processes require catalysts that can lower the activation energy barrier,[1] enabling the conversion to valuable products.

The study of nanomaterials for energy conversion and catalysis is a growing and promising field as the scaling down of bulk material to well-defined structures of nanoscale dimensions results in interesting electrical, optical, magnetic and chemical properties, due to quantum effects.[2] For instance, lower-dimensional structures of copper may control the separation of photogenerated electrons from electron holes, affecting the transfer charge-carrier distance and the activation energy barrier.[3] More generally, nanocatalysts allow reactions to occur in milder conditions, and tuning their morphology allows to control the selectivity of a reaction towards a desired product whilst reducing the occurrence of side reactions.[4] This, along with a larger surface area to volume ratio which increases the number of exposed active sites, make many nanoparticles higher-efficiency catalysts.[5]

Among those nanomaterials are copper nanoflakes of high aspect ratio (small thickness and large surface area), which expose the (111) facets of the face-centred cubic crystal of copper. Copper-based catalysts are of great interest because of their rare ability to sustain carbon-carbon bond formation on their surface, leading to the formation of multicarbon products.[6] Different facet orientations have specific atomic arrangements and so electronic configurations, which influence their photocatalytic properties as well as their reactive sites and surface energy, affecting the selectivity of various possible chemical reactions.[7] For instance, Luc et al. have demonstrated that the Cu (111) facet shows high Faradaic efficiency in the electroreduction of CO_2/CO into acetate,[8] a chemical used in water treatment, amongst other applications.[9]

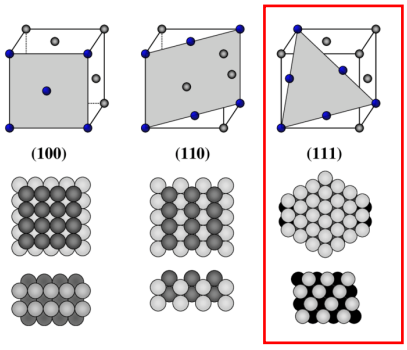
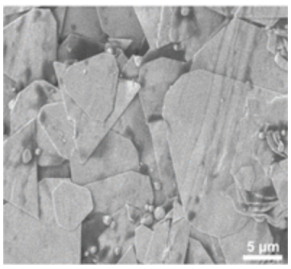
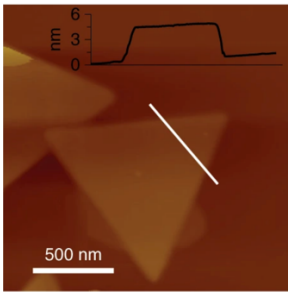
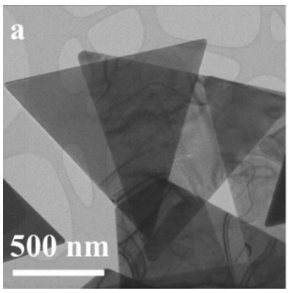
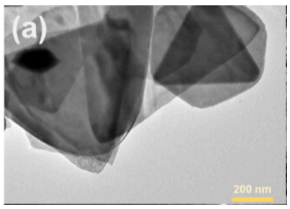
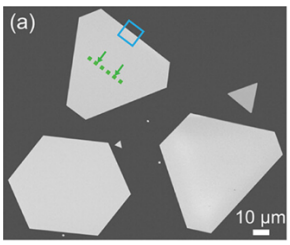


Figure 1: Facets of a face-centered cubic crystal

To be able to understand and quantify the results of such a reaction, several studies focus on the surface activity of copper via operando techniques, which probe the structural changes and active sites of catalysts whilst they are operating.[10] For such investigations, a high purity material must be used to clearly record and understand the complex reactions ongoing at the surface. However, it remains a challenging task to grow high quality and high aspect ratio copper nanoflakes in an efficient and systematic manner. Table 1 summarises the state of the art on synthesis efforts for the growth of copper nanoflakes/nanoplates, and it also displays a method for gold nanoflakes of quality that is hopefully attainable and reproducible for copper.

Table 1

Paper	Method	Result/size	Image
Copper Nanoplates for Printing Flexible High-Temperature Conductors (2022) Authors: Aaron Shang et al.	Reduction of copper chloride by glucose. Iodide as a capping agent, and HDA as a ligand.	Densely packed copper flakes. The largest ones appear to be around 7μm.	
Two-dimensional copper nanosheets for electrochemical reduction of carbon monoxide to acetate (2019) Authors: Wesley Luc et al.	L-ascorbic acid (100mg) reduces $Cu(NO_3)_2$•$3H_2O$ (50 mg) in aqueous solution (15.0mL deionised water). Stabilised via Hexamethylenetetramine (HMTA, 100mg) and Cetyltrimethylammonium bromide (CTAB, 100mg). Heated to 80°C for 3h in an oil bath. Resulting products collected by centrifugation.	Average edge length of ~1.7±0.5μm and thickness of ~5nm.	
Alternative route for electrochemical ammonia synthesis by reduction of nitrate on copper nanosheets (2020) Authors: Xianbiao Fu et al.	Same as “Two-dimensional copper nanosheets…”, but CTAB is replaced by Tetradecyltrimethylammonium bromide (TTAB). The collected nanosheets are redispersed in ethanol.	Average edge length of ~1.8 ±0.5μm, and thickness of ~6nm.	
Sub-1 nm Cu_2O Nanosheets for the Electrochemical CO_2 Reduction and Valence State–Activity Relationship (2023) Authors: Ping Wang et al.	Same as “Two-dimensional copper nanosheets…”.	-	
High Aspect Ratio Au Microflakes via Gap-Assisted Synthesis (2022) Authors: Fatemeh Kiani and Giulia Tagliabue	Solution of ethylene glycol, $HAuCl_4$ as precursor, and halide ions as shape directing agents (KI, KBr, KCl). Two glass substrates immersed in growth solution, on which flakes grow.	Lateral size as high as 250μm, thickness as low as 10nm with an average of 21nm.	

As can be seen, synthesis efforts for copper flakes have resulted in sizes limited to a few microns, or flakes that are not well separated from undesired side products such as nanorods, for example. In the case of gold however, Kiani et al. have developed a simple yet effective method of growing ultrathin and large area flakes.[11] Consequently, this paper aims to adapt the method for copper based nanoflakes. Due to the different natures of the

materials, such an adaptation requires thorough investigation of all the synthesis parameters. The next section explains the conceptualising of the synthesis procedure, as well as the optimisation of several key parameters for the gap assisted synthesis of copper nanoflakes.

2. EXPERIMENTAL APPROACH

The synthesis of nanostructures is generally divided into two categories: top-down and bottom-up approaches. The former relates to the scaling down of thin films or bulk materials, whereas the latter allows for the assembly of atoms or molecules into larger, more complex structures.[12] A bottom-up approach is followed in this experiment, which can be further described as a chemical synthesis.

A precursor, such as copper nitrate, copper sulphate, etc., provides the copper ions that will form the final structure. A reducing agent is used to convert the copper cations to metallic form. Then, the formation of the nanostructures can be divided into two stages; nucleation when the individual atoms come together, and the growth which concerns the rest of the formation of a specifically-shaped crystal.[13] In this second stage, capping agents, which are molecules that bind to the nanostructure surface and prevent their agglomeration,[14] are in general used to control the addition of atoms on specific surfaces, thus directing the overall shape of the nanoparticle.[15]

There are various chemical synthesis approaches, each offering a different advantage depending on the desired end product. Among these methods are microwave[16] or light[17] assisted growth, solvothermal methods where an autoclave is used to reach high pressure and temperature,[18] chemical vapor deposition[19] and wet-synthesis where chemical reactions occur in solution.[20] This last method has the advantages of simple operation and low cost, which potentially allow its scaling up for widespread production of the chosen nanoparticles, and is the method most adapted to the synthesis of copper nanoflakes, as the existing literature shows.

As a reference point, we have adapted a synthesis procedure from Luc et al, who have synthesised copper nanosheets using dissolved Cu (II) nitrate trihydrate, L-ascorbic acid, CTAB and HMTA as a solution that is heated to 80°C in an oil bath for three hours. This produced triangular Cu nanosheets with an average edge length of ~1.7±0.5μm, and thickness of ~5nm. This synthesis recipe was combined with the gap assisted growth method developed by Kiani et al. for Au nanostructures. By placing glass substrates in the form of cover slips in the solution as the reaction is taking place, two major improvements are expected; the on-substrate growth of nanoparticles means higher quality as aggregation, bending and small-particle contamination are avoided (as opposed to

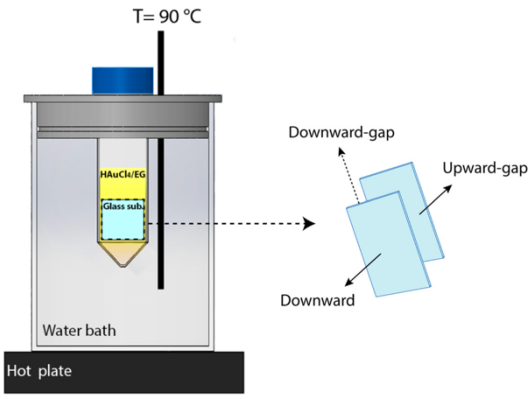


Figure 2: Schematic of the Set-Up Used in "High Aspect Ratio Au Microflakes via Gap-Assisted Synthesis"

methods like post-synthesis drop-casting),[21] and the positioning of two of the glass substrates, in this case around 43 µm away from each other, create a gap that, by changing the accumulation and diffusion of ions present in solution, favours the lateral growth of the flakes. A description of the resulting experimental procedure and a list of the investigated parameters is provided below.

3. EXPERIMENTAL PROCEDURE

[The details of the experimental procedure were taken out of this report but will be available in the scientific paper published by the laboratory.]

The analysis of the resulting copper flakes was performed by optical microscopy and atomic force microscopy. With the images obtained by optical microscopy, lateral dimensions of the nanoflakes were analysed using a commercial software (ImageJ). Atomic force microscopy (AFM) measurements allowed for detailed characterisation of the surface roughness and thickness of the flakes. In AFM, a cantilever interacts with the surface of the sample, and the atomic forces between the two are recorded and analysed to create an image.[22] Along with being an imaging instrument of high precision, the atomic force microscope enables the measurement of electrical or mechanical properties.[23]

Many parameters can be tuned to reach the optimal aspect ratio of the nanoflakes. Growth time, reaction temperature and rate of temperature increase were controlled, as well as the type, freshness and concentration of the precursor, reducing agent and capping agents. The effects of different added reactants were also studied. Each parameter is discussed in further detail in the following section.

4. RESULTS AND DISCUSSION

- Cetyltrimethylammonium bromide (CTAB)

Many synthesis procedures for nanoparticles use surfactants (surface-acting agents) as capping agents. Surfactants are a type of molecule composed of a hydrophilic head and a hydrophobic tail, that decreases the surface tension between two materials.[24] Large enough concentrations (above critical micelle concentration) result in the formation of micelles, ball-like clusters of the surfactant molecules, with the hydrophilic heads facing the polar solvent (in our case water), and the hydrophobic tails encapsulating a non-polar material (nanoparticle). This process of micellization occurs as a stabilisation mechanism to lower the free energy of the system, and the surfactant thus adsorbing to the nanoparticle contributes to shaping it and controlling its growth.[25] However, surfactants have disadvantages. When the nanoparticles are then to be used for their intended purposes, surfactants stay adsorbed on their surface, which reduces the electrochemically active surface area.[26] In the specific application of copper flakes reducing carbon dioxide, the long

chains of the surfactant molecules prevent CO_2 from reaching the surface, and also affect the measure of the catalytic efficiency of the flakes, as some of the detected carbon atoms or compounds actually come from the surfactant instead of the CO_2. Even if these adsorbed molecules can be removed through processes such as thermal annealing, these are not ideal as they induce aggregation of the nanoparticles and changes to their shape.[27] Surfactant-free syntheses are thus generally preferred, which is why initially, only CTAB was used in this investigation, without the additional surfactant HMTA.

Up to synthesis n°14.1, CTAB was consistently used, but two different types were investigated, and with quantities ranging from 50mg to 200mg. Although flakes were observed in some syntheses, they were rarely well distributed or in large enough quantities to be able to conduct statistical analysis. The main problem encountered with the use of CTAB was that unidentified structures were produced instead of well-defined copper flakes. Such structures are shown in Figure 3.

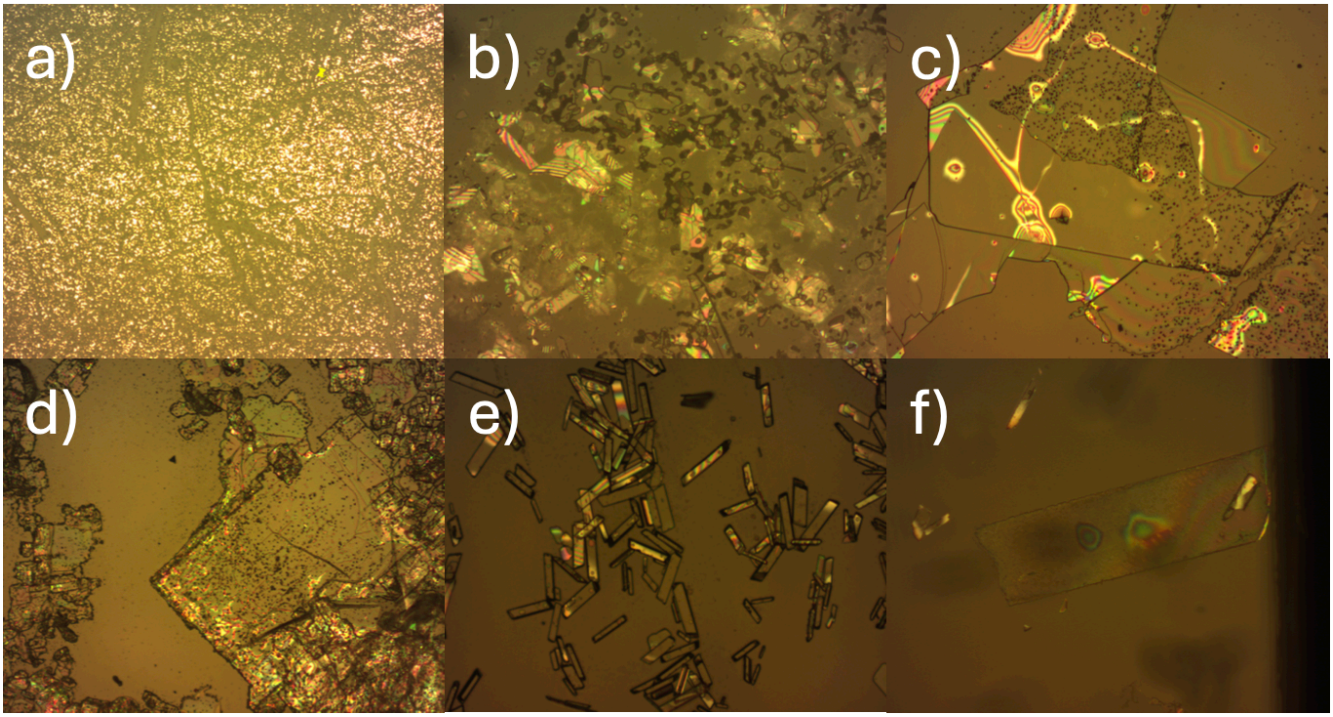


Figure 3: Structures observed a) at 55°C (s5) b) with two times the quantity of both L-ascorbic acid and CTAB (s10.3) c) with smaller quantity of L-ascorbic acid (s12.1) d) after 3 hours (s13.1) e) and f) with added KBr (13.3)

Because of this, no trend could be recorded. Both the concentration of CTAB and that of L-ascorbic acid were varied, but the results were too inconsistent and unreliable. At high concentrations, the solutions were super-saturated. Different types of residues were seen on the glass substrates. Moreover, it was recorded that changing the CTAB to a fresher one of high purity yielded worse results. This could relate to studies conducted on the effect of CTAB on nanoparticle formation that have reported significant differences in yield depending on not only the supplier,[28] but also the lot number of CTAB.[29] One study proposes the idea that an iodide impurity found in the commercialised CTAB is responsible for favouring the growth of these particular nanoparticles, and so, even if in very low

concentrations, this impurity completely affects the efficacity of CTAB as a shape-directing agent for, in that particular case, the formation of gold nanorods.[30]

- Qualitative remarks on syntheses 1-14.1

The flakes were often concentrated near the sides of the glass substrates. This is related to the diffusion of ions in the solution. The diffusion becomes more difficult as the distance within the gap increases.

Increasing the L-ascorbic concentration resulted in more nucleation (greater number of small particles/flakes), which can be attributed to the very role of L-ascorbic acid as a reducing agent that is to break down the precursor, and so allow the reformation of the copper ions into new particles.

One precursor type yielded much better results than the others. The exact reason for this is unknown, but it is expected that different chemical compounds, due to differences in bond length, type, etc. react differently, producing varying results.

- Temperature and Heating Rate

The reaction temperature influences the synthesis of nanoparticles, as it affects the rate of the reaction, and notably the nucleation stage, as high temperatures favour the reduction of the precursor ions.[31] Whilst some papers report that high temperatures thus result in a greater number of smaller flakes, it has been shown that this ceases to be true when precursor concentration is increased,[32] which we will discuss later. It is also believed that high temperatures create nanoparticles that are more uniform, in lesser amounts of time.[33]

The heating rate may affect the formation of nanoparticles. Mountrichas et al. have put forward the idea that a low heating rate results in a broader size distribution because nucleation occurs over a longer period and so the flakes have varying amounts of time to grow, whilst high heating rates lead to better defined nucleation.[34]

[Results not discussed in this report]

- Precursor type and concentration

Whilst the copper atoms that make up the nanoparticles are unchanged when varying precursor type, the same cannot be said of the different formation mechanisms and so overall morphology of the flakes, as the differences in molecular structure of the compounds affect their decomposition.[35] Precursor type was shown to affect the morphology of the particles produced, with some precursors resulting in 3D structures instead of flakes.

The concentration of precursor is also greatly relevant in nanoparticle synthesis. In “Noble Metal Nanoparticles”, Ignác Capek stresses the importance of supersaturation of reactants in homogeneous nucleation of the nanoparticles.[36] This is supported by the idea that a sufficient amount of precursor atoms is crucial to ensure that the nanoparticles can grow without limit.[37]

[Results not discussed in this report]

- Concentration of Reducing Agent

In chemical nanoparticle syntheses, the reducing agent, in our case L-ascorbic acid, enables the formation of the nanoparticles by reducing the precursor ions. Luc et al. have also put forward the idea that, in their synthesis, L-ascorbic acid contributed to the stability of the flakes against oxidation.[38] However, they also mentioned that an acidic environment is not favourable to growth due to an uncontrolled rate of reduction, and other papers also promote a pH of 7 as the most ideal for copper nanoplate growth.[39]

[Results not discussed in this report]

- Added Reactants

[Results not discussed in this report]

- Note on AFM characterisation

A preliminary AFM characterisation indicated that the flakes were between 100-150nm thick, with a relatively smooth surface. The peaks shown in figure have yet to be explained and could relate to the formation mechanism of the flakes, or to their oxidation.

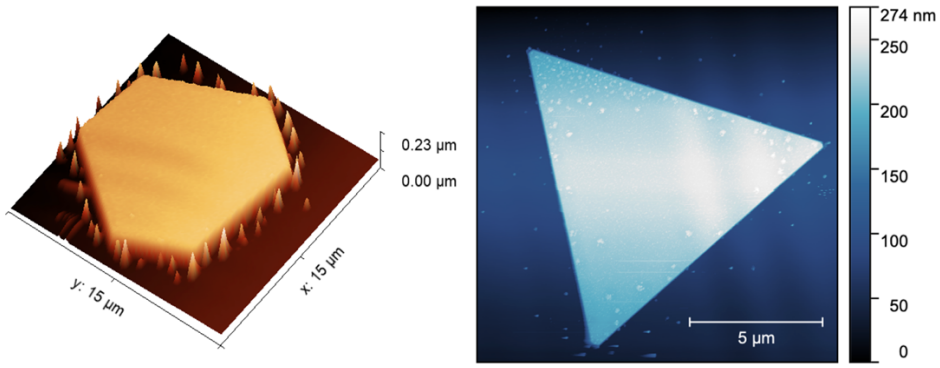


Figure 4: AFM images of the nanoflakes

5. CONCLUSION

High-quality copper nanoflakes of lateral size up to 52 microns were synthesised using a surfactant-free recipe. Various morphologies exposing different facets were also obtained by modifying the recipe. The effects of changing synthesis parameters were explored and trends were established, allowing for greater insight into the formation mechanisms of the flakes.

Various steps are to be taken next to complete the characterisation of the flakes. Their synthesis can be adapted onto conductive substrates to allow exploration of their

properties by Scanning Electrochemical Microscopy (SECM). The flakes could also be transferred, notably via Nanotransfer Printing.[40] In order to each even thinner flakes, they could be chemically etched.[41] Finally, we have yet to understand their photocatalytic activity, to then establish their potential role in CO/CO_2 reduction.

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