Growth of Cu_2O Nanocubes from Seeds in Microwells

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Abstract

This project focused on the growth of Cu_2O nanocubes in microwells from nanoparticle "seeds." The seeds were first formed by the reduction of copper sulfate with ascorbic acid in the presence of the surfactant poly(ethylene glycol) (PEG). Upon reaction within the microwell, the seed solution formed a larger single crystal. By varying the amount of precursor seed particles available in the reaction, nanocubes of different sizes were formed. The surfactant was removed from the surface of the nanocubes using ethanol. The nanocubes were characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Introduction

Inorganic nanoparticles of defined size and shape possess unique and tunable optical and electronic properties.[1,2] Consequently, such materials hold great promise for applications in catalysis,[3] photonics,[4,5] electronics,[6] and biological diagnosis.[7,8] Many of the applications of nanomaterials depend upon the size, shape, and crystallinity of the particles. These properties are commonly controlled in solution-phase nanoscale synthesis via nucleation and growth mechanisms in the

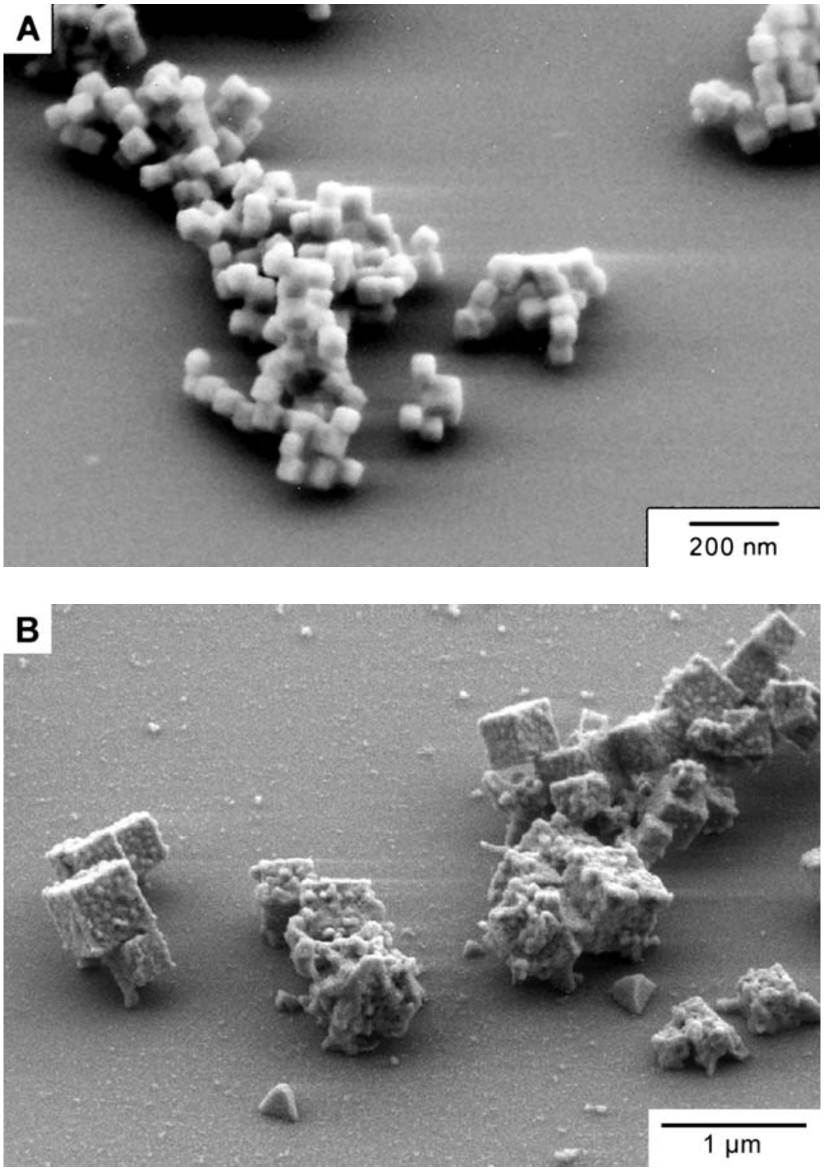

Figure 1: SEM images of bulk Cu_2O nanocubes. (a) Monodisperse 75 nm cubes made from the procedure in which NaOH and ascorbic acid were mixed together before addition to the $CuSO_4$-PEG solution. (b) Cubes of different edge lengths made from the procedure in which NaOH was added one minute before addition of ascorbic acid.

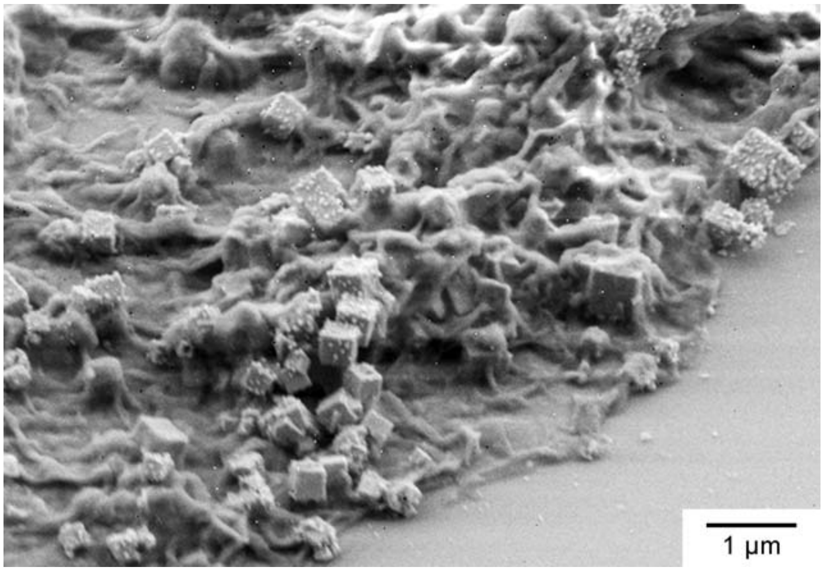

Figure 2: Cu_2O nanocubes synthesized using diethyl ether as the surfactant. Despite centrifugation and resuspension to clean off the cubes, a messy layer remained on the substrate.

presence of surfactants under high-temperature reaction conditions.[9,10] Size and shape control are not guaranteed because of possible temperature gradients in the reaction vessel and inhomogeneity in the injection of precursors.

An alternative to high-temperature synthesis is the use of microscale and nanoscale reaction vessels. These miniature reactors are valuable tools in controlling the growth of microparticles and nanoparticles. The wells limit the volume of the reaction so that the quantity of material available to react only forms a single crystal. In this study a seed-mediated approach was used for the formation of Cu_2O nanocubes within microwells. The goal was to control the size of the nanocubes by controlling the concentration of precursors in the starting solution. This control over the mass available in the microwells allowed us to limit the number of seed particles available to form the nanocubes.

Background

Copper(I) oxide, Cu_2O, is a semiconductor with a variety of applications. It can be used as a solar cell material,[11] and it has been shown to catalyze water splitting, although the mechanism is not yet clear.[12,13] Upon photoexcitation, the long-lived excitons in Cu_2O exhibit coherent propagation analogous to that of photons in a laser.[14] The groundbreaking real-time imaging of covalent bonds between the atoms in Cu_2O has broad implications for new materials used in computer components, medical equipment, and other devices.[15]

Cu_2O nanocubes have been synthesized in bulk by the reduction of $CuSO_4$ in the presence of NaOH and the surfactants cetyltrimethylammonium bromide (CTAB) or PEG.[16,17] The surfactant binds nonselectively to the faces of cubic Cu_2O. The average edge lengths of the cubes have been controlled by changing the concentration of PEG and the order of addition of reagents.[18] In these systems dispersions in size and shape may occur because of chemical and thermal inhomogeneity and the process of seed aggregation by Ostwald ripening, which involves the growth of larger particles at the expense of smaller particles. The seed-mediated approach has also been examined in the shape-controlled synthesis of metal nanoparticles.[19,20]

Microwell and nanowell arrays have been used as miniature reactor systems for the growth of microcrystals and nanocrystals.[21,22] Simple precipitation of inorganic salts and syntheses of nanoscale structures have been carried out in such reactors, but the use of microwells to limit the quantity of precursor seeds (instead of molecules or atoms) has not been investigated.

Approach

Bulk Synthesis of Cu_2O Nanocubes

We prepared monodisperse Cu_2O nanocubes according to the procedure by Gou and Murphy[18] with slight modifications (Figure 1a). In bulk, the size of the nanocubes was controlled by varying the concentration of surfactant and the order of addition of reagents. This step served as a confirmation for the growth of nanocubes. Cubes with different edge lengths were sometimes observed in the same sample and suggest that smaller cubes can combine to form larger cubes

(Figure 1b). In the process known as Ostwald ripening, as the nucleated particles grow, smaller cubes coexist with larger cubes until they eventually combine into larger cubes themselves. By carrying out the preparation of Cu_2O nanocubes in microwells, the seed particles should be able to combine together into one single crystal through this ripening process.

It was proposed that the Cu^{2+} ions coordinate loosely to the oxygen atoms of PEG initially in water to cause isotropic capping of the cubic Cu_2O surfaces.[18] Diethyl ether should accomplish the same thing as a surfactant, with Cu^{2+} coordinating to its central oxygen atom. The advantage of using diethyl ether is its lower boiling point, allowing for evaporation from the wells upon completion of the reaction. The volatile nature of diethyl ether, however, also prevented injection of precise amounts of it into the precursor solution. Bulk synthesis results did confirm the formation of cubes by this method, but there remained a messy film of unidentified composition over the substrate (Figure 2). The effectiveness and function of diethyl ether and other polar oxygenated molecules as surfactant for growth of Cu_2O nanocubes are important for future investigations.

Fabrication of Microwells
Microwells were prepared using photolithography and molded with the elastic polymer poly(dimethylsiloxane) (PDMS) (Figure 3).[23] First, SU-8 negative photoresist was used with a chrome mask of 3 mm dots to create a master of wells that were 3 mm in diameter and 1 mm deep. This pattern was replicated against PDMS to generate posts in PDMS, which we used as our PDMS master. The PDMS master of posts was then used for the time and cost-efficient production of arrays of

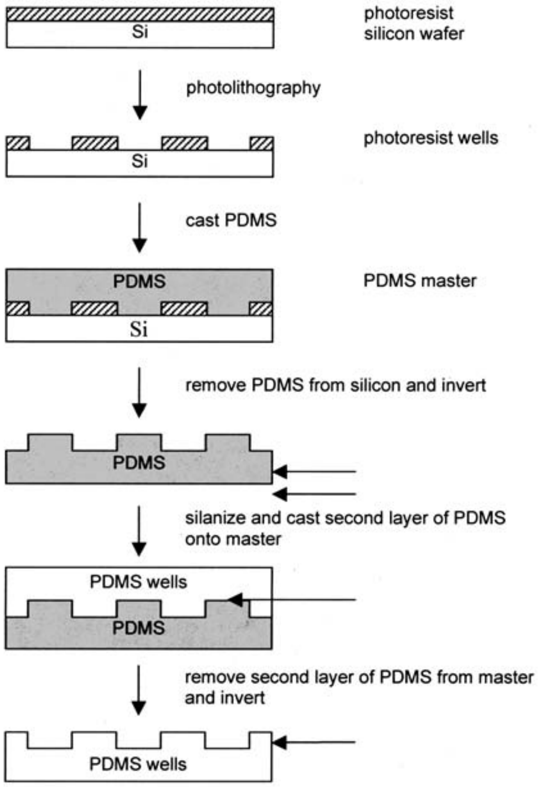

Figure 3: Schematic diagram for the fabrication of PDMS microwells.

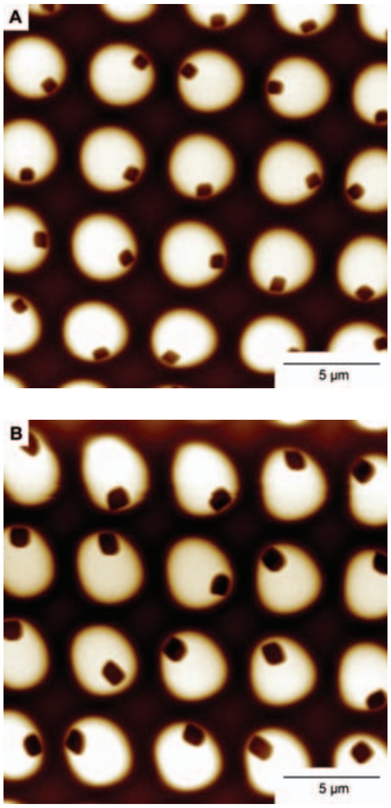

Figure 4: AFM images depicting the mass-limited precipitation of NaCl in microwells filled with (a) a 1 M solution and (b) a 3 M solution. Image colors were inverted to allow for contrast between particles and background.

microwells by casting onto it another layer of PDMS. The advantage of the PDMS master is that it can be used many times, provided the surface is silanized to achieve a hydrophobic interface that prevents damage to either layer of PDMS. Alternative microwell and nanowell geometries can be attained using different photolithography masks, photoresists, and spin-coating speeds and should not intrinsically affect the use of the wells.[23]

The soft material properties of PDMS limit their use as microwells because of the temperature and solvents often necessary in nanoscale synthesis. PDMS cannot be heated above 70° C and is swollen by many organic solvents.[24] The reactions in this study were not affected by such limitations. For the growth of other materials by the high-temperature synthesis route, PDMS wells can be replaced by wells made of harder, inorganic materials such as silicon and silicon dioxide.[25]

Mass-Limited Precipitation of NaCl in Microwells

This step served mainly to illustrate the concept of mass-limited reactions in microwells. We varied the concentration of NaCl solutions to test the method of discontinuous dewetting, a process in which the substrate is withdrawn slowly from the precursor solution.[23] This technique allows wells to be filled rapidly and uniformly by exploiting the differences in the surface free energies of the substrate and the solution. Mass-limited precipitation was observed, as the edge lengths of the single cubes formed from the 1 M solution were uniformly 650 nm, and those from the 3 M solution were 900 nm (Figure 4).

Performing Reactions in Microwells

A starting solution was prepared at room temperature containing $CuSO_4$, PEG as the surfactant, NaOH, and ascorbic acid as the reducing agent. Ascorbic acid was added one minute after the other reagents were mixed. The solution was set on ice to retard the immediate reduction reaction:

$$2\ Cu(OH)_2 + C_6H_8O_6 \rightarrow Cu_2O + C_6H_6O_6 + 3\ H_2O$$

To increase the surface free energy and ensure proper wetting, the PDMS microwells were plasma oxidized for five seconds before they were filled with the seed solution by discontinuous dewetting (Figure 5). The array of filled microwells was covered with a microscope coverglass, and the reaction was allowed to run for 30 minutes. Upon removal of the coverglass, the solvent evaporated from the wells to expose the crystallized Cu_2O cubes. The use of microwells allowed us to limit the mass of precursor (and thus the number of seed particles) available within a prescribed volume. We were then able to examine the aggregation of the seed particles into different-sized nanocubes.

Removal of Surfactant and Characterization

For this study PEG was used as the surfactant, which in bulk nanoparticle synthesis is removed by centrifugation and resuspension in water or organic solvents. Within the microwells, however, the removal of PEG was accomplished by dipping the substrate in ethanol. We also tried to avoid the step of surfactant removal by using diethyl ether instead of PEG as the surfactant. In addition, different methods to prevent immediate evaporation of solvent from the wells were examined.

Results and Discussion

Varied amounts of $CuSO_4$ in the initial solution produced proportional variations in the sizes of nanocubes formed in the microwells. For 0.1 mL to 0.8 mL of a 0.1 M $CuSO_4$ solution in 24 mL of total reaction volume, Cu_2O particles appeared to be rounded cubes with diameters between 300 nm and 450 nm. The rounded and sometimes amorphous appearance of the particles was attributed to the remaining surfactant on the surface of the cubes (Figure 6).

After the samples were dipped and agitated in ethanol for several seconds, the particles exhibited a notable reduction in size and improvement of cubic morphology (Figure 7). The sizes of the cubes decreased to between 200 nm and 300 nm, depending on the amount of $CuSO_4$ (Figure 8). Table 1 summarizes the results of the varied Cu^{2+} concentrations before and after cleaning off the surfactant. The mole ratio of Cu^{2+} : PEG : ascorbic acid was kept constant at 1 : 1.25 : 2.

Although we cannot yet ascertain the cubic morphology of the particles, we are reasonably certain, based on AFM characterization and bulk synthesis results, that Cu_2O has in fact formed nanocubes. The same synthesis in bulk produced nanocubes of varying sizes, and the cubic morphology was governed by the non-preferential coordination of PEG to the cubic faces of the lattice structure of Cu_2O. Current results do not lend themselves to analysis of the exact proportionality of available mass versus cube size; the surfactant layer must be sufficiently

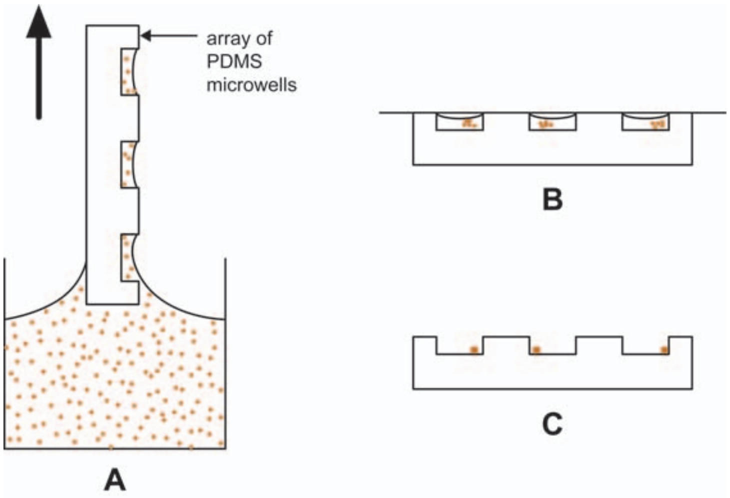

Figure 5: Scheme for performing seed-mediated reactions in microwells. (a) Discontinuous dewetting: a large array of microwells is filled as it is pulled from the bulk seed solution. (b) Microwells are covered to prevent evaporation as the reaction proceeds. Individual seeds begin to aggregate. (c) Covering is removed and solvent is allowed to evaporate, leaving behind a single crystal in each microwell.

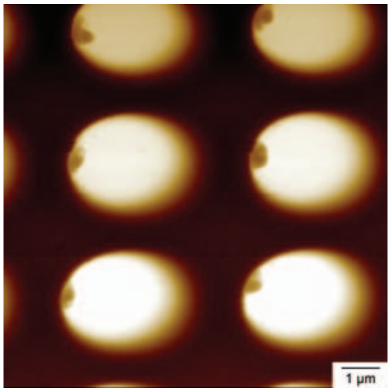

Figure 6: As-grown Cu_2O nanocubes with amorphous surfactant polymer on surface.

removed to obtain accurate measurements of edge lengths. The qualitative analysis presented here does confirm the usefulness of microwells for the mass-limited growth of nanoparticles. The trends in Table 1 clearly support the idea that nanocube size is dependent upon the amount of Cu^{2+} in the seed solution.

Conclusions

Cu_2O nanocubes were grown in microwells that were filled with a precursor solution. Mass-limited, seed-mediated growth was observed, and the initial amount of copper available in the solution was proportional to the size of the crystals in the microwells. Bulk Cu_2O nanocubes were also synthesized by using diethyl ether as surfactant.

Future work would include refinement of the dewetting and growth processes. Discontinuous dewetting of the wells should be performed in a humidity-controlled environment to inhibit the evaporation of solution from the wells before they are covered. Evaporation could also be reduced by using less volatile PDMS-compatible solvents or by fabricating deeper wells to give a lower ratio of surface area to volume. Additionally, the seed-mediated growth process is still one that warrants closer examination. Running the reaction for varying amounts of time could provide insight into the rate of particle formation or Ostwald ripening. To facilitate characterization, alternative surfactants and their subsequent removal may also be investigated. More broadly, the method of crystal growth in microwells and nanowells may be applied to other microscale and nanoscale syntheses in the future because it provides a means of controlling the size of the particles.

Table 1: Effects of Cu^{2+} concentration on size of nanocubes.

Volume of 0.1 M $CuSO_4$ in 25 mL total reaction volume (mL)	**Average edge length of Cu_2O nanocubes as grown (nm)**	**Average edge length of Cu_2O nanocubes after cleaning (nm)**
0.1	300	200
0.2	350	250
0.4	380	280
0.8	450	300

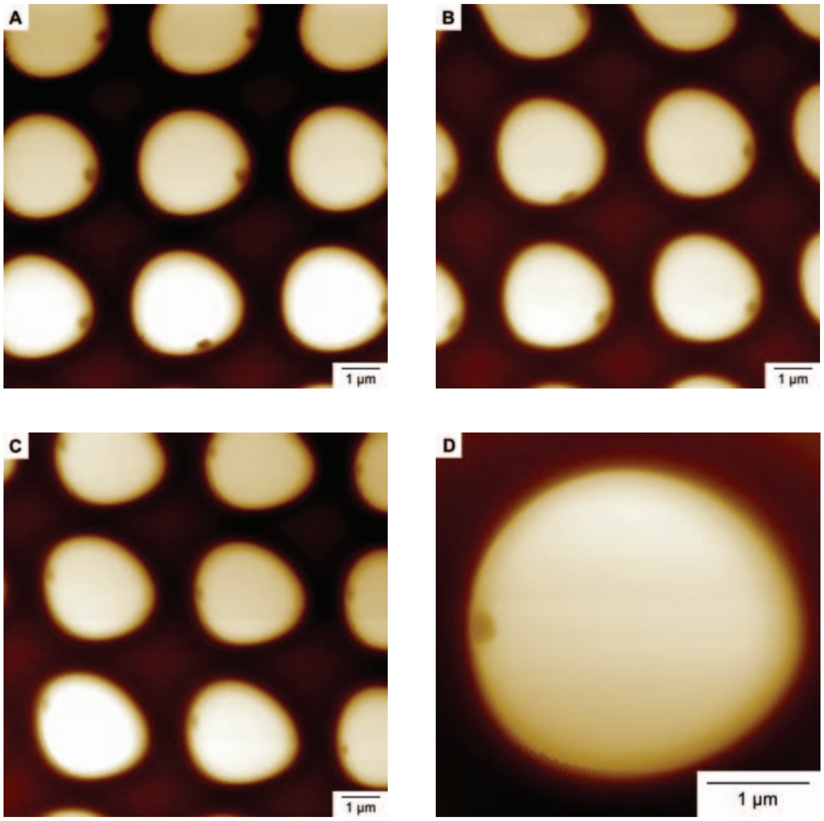

Figure 7: Cu_2O nanocubes in microwells (a) as grown, (b) after dipping in ethanol for three seconds, and (c) after dipping in ethanol for an additional six seconds with agitation. Despite a notable decrease in size and improvement of cubic morphology, further cleaning is required to obtain the crisp edges necessary for accurate determination of edge length (d).

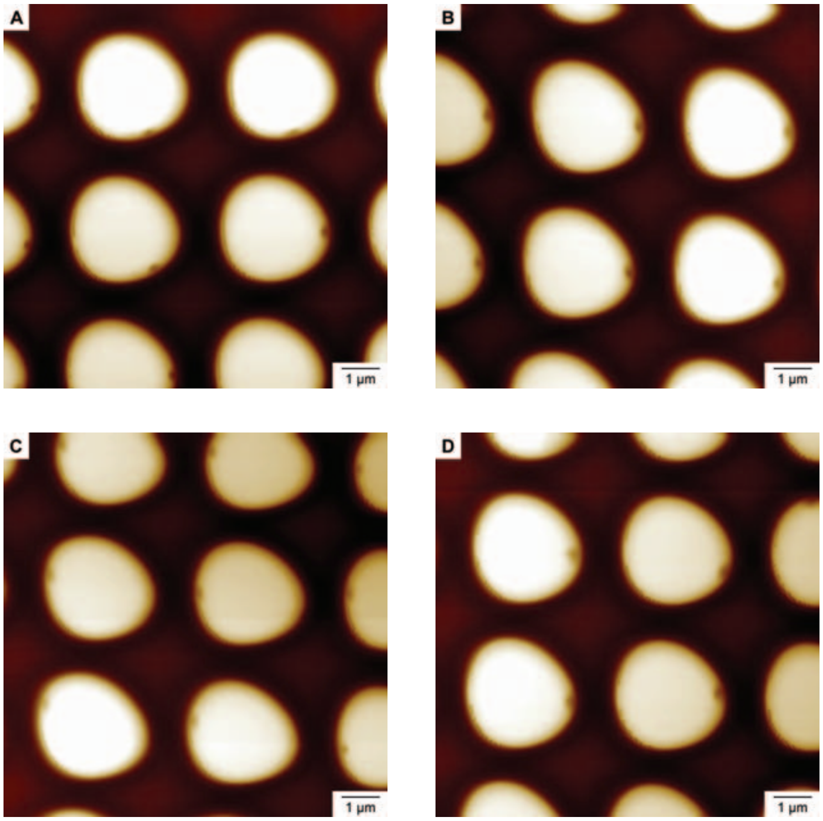

Figure 8: Cu_2O nanocubes in microwells from a starting solution containing PEG, NaOH, ascorbic acid, and (a) 0.1 mL, (b) 0.2 mL, (c) 0.4 mL, and (d) 0.8 mL of 0.1 M $CuSO_4$. Images were obtained after cleaning the nanocubes with ethanol.

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