Photodegradation study of Copper (I) Oxide nanoparticles synthesized with different geometries

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Introduction

•The global community is forced to face an ever growing problem involving energy resources. It is well documented that there is a limited supply of fossil fuels and that consuming these has lead to environmental concerns due to CO_2 emission and greenhouse effect. As a result, there have been intense research efforts to transition into renewable energy sources.

•Among the different renewable energy sources, solar energy is particularly attractive; one hour of direct sunlight provides the same amount of energy the planet consumes in a year[(1)]. In addition, solar energy can be used in the production of fuels such as H_2 through the use of photoelectrochemical cells (PECs).

•Nanomaterial-based photoelectrodes provide unique advantages as the shape can be readily controlled and they provide higher surface area suitable for catalytic reactions.

•Copper (I) Oxide (Cu_2O) has been widely researched as a photocathode for overall water splitting due to its high absorption in the visible range, with a band gap of 2.2 eV, which is favored due to the conduction band lying 0.7V negative of the hydrogen evolution potential and the valence band lying just positive of the oxygen evolution potential[(2)].

•In addition, it is made of abundant, inexpensive, and non-toxic elements, making it suitable for large scale production.

•The major drawback to this material is its photodegradation under conditions required for practical PECs, which hinders its application. A major question is how does this degradation vary for Cu_2O with different exposed crystal facets.

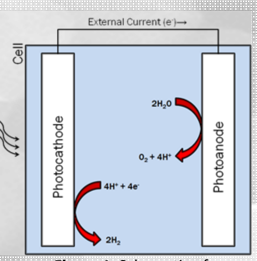
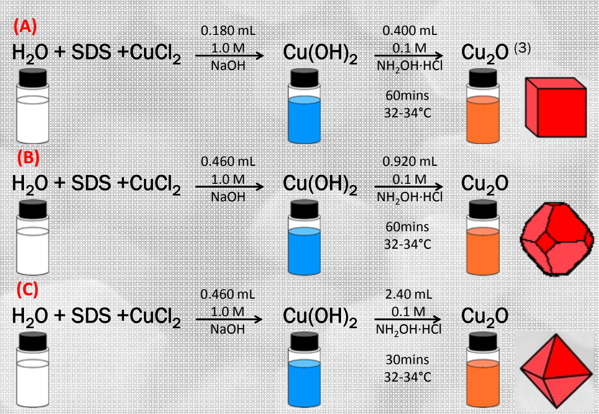
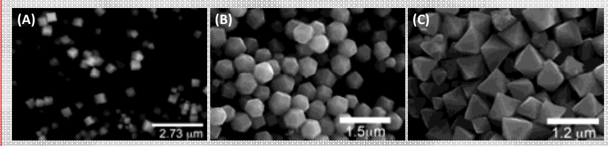


Figure 1. Schematic of a Photoelectrochemical cell

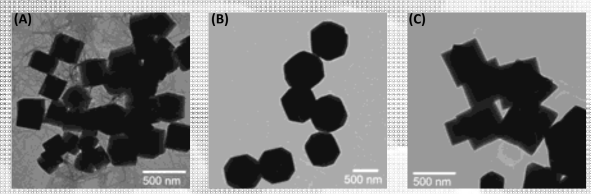
Experimental



Characterization



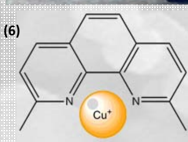
•**Figure 2**. Scanning Electron Micrographs (SEM) of **(A)** cubic **(B)** truncated octahedral and **(C)** bipyramidal geometries obtained from the aqueous synthesis with varying NaOH:NH_2OH•HCl ratios.

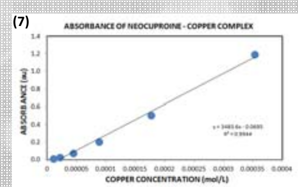


•**Figure 3**. Transmission Electron Micrographs (TEM) corresponding to the geometries directly above.

Device Fabrication

Figure 5. Electrodes were made on Au coated Si wafer, by drop casting 100 µL (5µL increments) of a concentrated sample onto a 0.25 cm² working area masked off by Kapton tape.





To ensure that the electrodes had the same amount of particles, aliquots of the drop-casting solution were exposed to neocuproine. Neocuproine leaches the copper forming the complex illustrated in **Fig. 6**. The absorbance of this complex at 457 nm was used to find the copper concentration from the calibration curve (**Fig.7**)

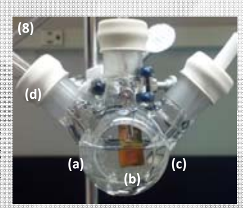
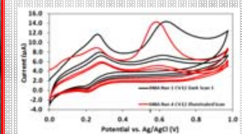
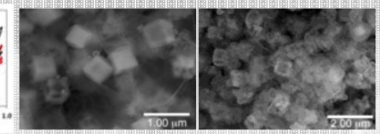


Figure 8. Photograph of custom made PEC with **(a)** Pt mesh counter electrode **(b)** drop cast Cu_2O working electrode **(c)** Ag/AgCl reference electrode **(d)** under N_2 atmosphere.

Results

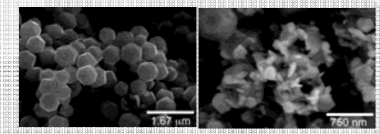


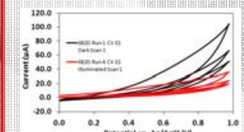
•**Figure 9**. Cyclic Voltammetry (CV) of cubic Cu_2O in buffered (pH 5) 1.0 M Na_2SO_4.



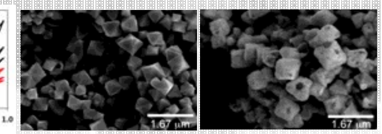
•**Figure 10**. SEM images of different areas of a cubic Cu_2O based electrode after operation.

•**Figure 11**. SEM images of different areas of a truncated octahedral Cu_2O based electrode after operation.





•**Figure 12**. CV of bipyramidal Cu_2O in buffered (pH 5) 1.0 M Na_2SO_4.



•**Figure 13**. SEM images of different areas of a bipyramidal Cu_2O based electrode after operation.

Discussion

• The synthesis outlined can be easily tuned to obtain multi-faceted nanoparticle geometries.
• Drop-casting proved to be a convenient method to create electrodes based on the different geometries, with mechanical stability.
• As can be seen in the CVs, the current decreases significantly after operation of the electrodes independent of the geometry.
• Examination of the electrodes by SEM after operation shows degradation and deposits.
• Preliminary results suggest that the order of particle photodegradation is cubic > truncated octahedral > bipyramidal. However, more detail studies are required.

References

(1) Lewis N.S., and Nocera D.G., PNAS 2006, 103, 15729-15735
(2) Paraccino A., Laporte V., Sivula K., Grätzel M., and Thimsen E., Nature Materials 2011, 10, 456-461
(3) Huang W.C., Lyu L.M., Yang Y.C., and Huang M.H. J. Am. Chem. Soc. 2012, 134, 1261-1267

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