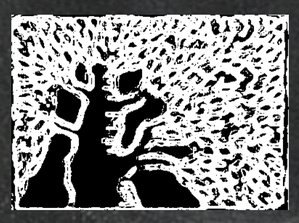

CHEMICAL DEPOSITION OF MORPHOLOGICALLY CONTROLLED Cu_2O NANOCRYSTAL FILMS AND THEIR pH DEPENDENT GALVANIC REPLACEMENT.

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Nanostructured cuprous oxide (Cu_2O) is an intriguing direct bandgap semiconductor material with potential applications as a UV-Vis light absorber in solar cells, a photocatalyst for the degradation of organic pollutants, a negative electrode in Li-ion batteries, and others.

It is known that the morphology and size of Cu_2O nanoparticles (NPs) may affect their photocatalytic and light-absorption properties. However, the preparation of Cu_2O NPs with morphological control has been largely restricted to colloidal syntheses and electrodeposition on substrates.

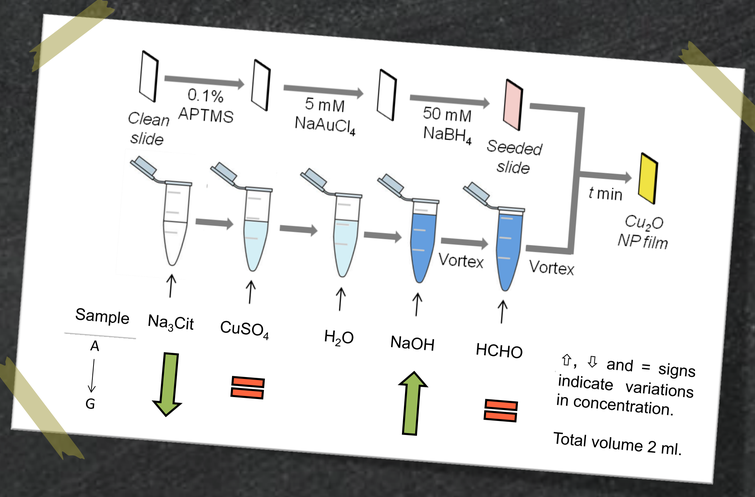
Here we present a chemical (electroless) deposition (CD) approach to direct preparation of Cu_2O nanocrystal (NC) films on substrates, using $CuSO_4$-HCHO-Citrate-NaOH solutions. Our method shows a high degree of morphology control. The average NC size can be varied by controlling the deposition time, while the crystallographic structure is determined by the solution composition. The NC films were studied by SEM, TEM, GIXRD and UV-Vis spectroscopy.

The supported Cu_2O NCs were used to study their galvanic replacement (GR) reactions with metal salts in solutions of different pH. The resulting structures of the replaced Cu_2O NPs showed high dependence on the solution's pH, producing from Cu_2O particles decorated with smaller metal (Me) NPs to supported Cu_2O@Me nanoarchitectures.

SAMPLE PREPARATION

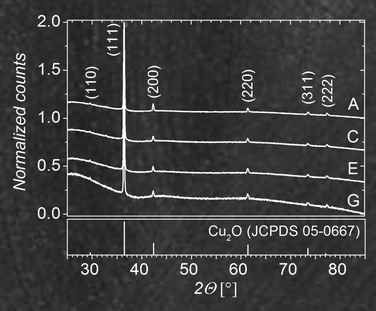
Au seeds were produced in-situ on glass or quartz slides.

Cu_2O NC films were chemically deposited from formaldehyde-based solutions of different compositions (A to G), optimized for the preparation of Cu_2O NCs with precise morphology.



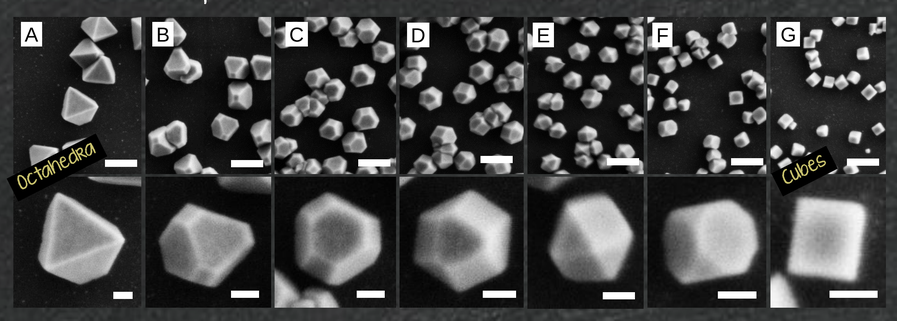
CHARACTERIZATION

Grazing Incidence XRD



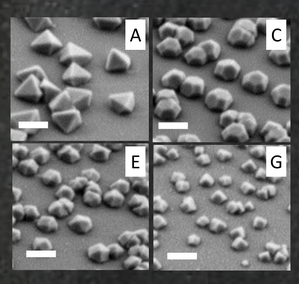
SEM images

Scale bars: Top - 200 nm, bottom - 50 nm.



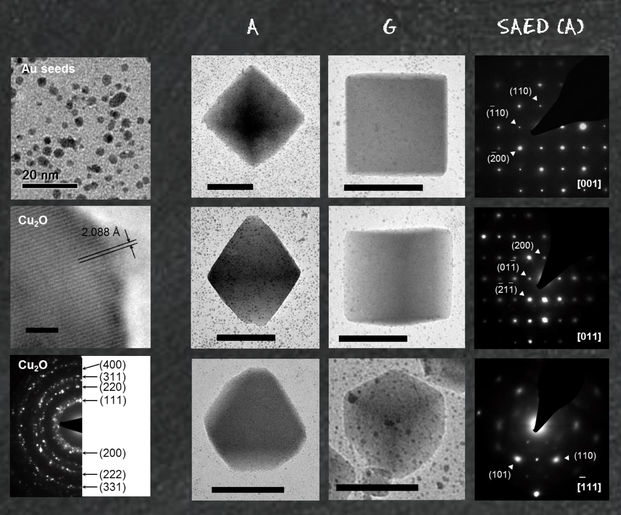
Tilted Angle SEM (45°).

Scale bars: ~200 nm.



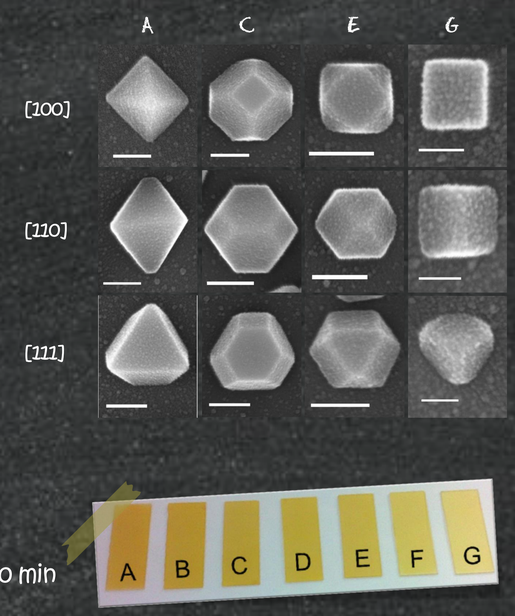
TEM images (Cu_2O NCs prepared after seeding of carbon-coated grids). Scale bars: A - 100 nm, G - 50 nm.

Corresponding SAED patterns from octahedra are shown.

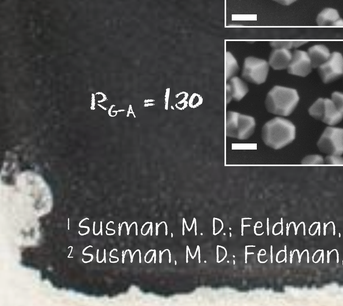


HRSEM (After 3 nm Cr sputtering).

NCs viewed along the indicated directions. Scale bars: A,C,E - 100 nm, G - 50 nm.

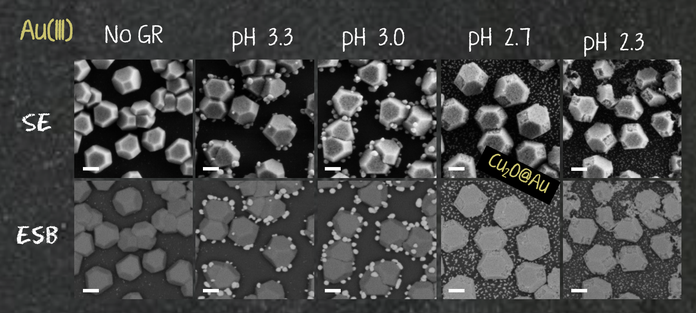


UV-Vis spectroscopy

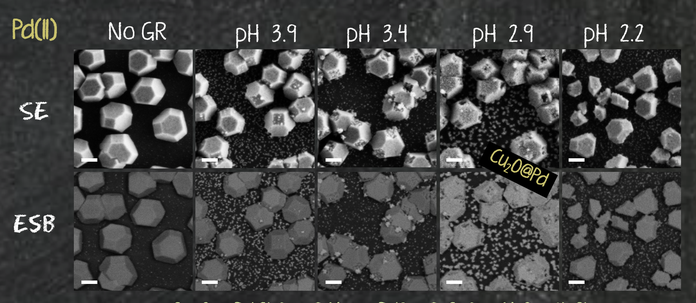


GALVANIC REPLACEMENT (GR)

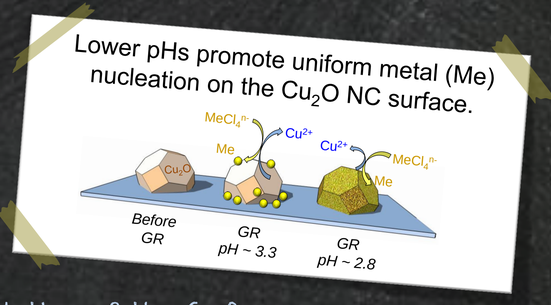
Treatment of Cu_2O NCs with 0.5 mM $MeCl_4^{n-}$ solutions lead to the formation of metal (Me) layers on the Cu_2O NPs, with structures that depend on the solution pH. Scale bars: 100 nm.



$3/2\ Cu_2O + AuCl_4^- + 3\ H^+ \rightarrow Au^0 + 3\ Cu^{2+} + 3/2\ H_2O + 4\ Cl^-$

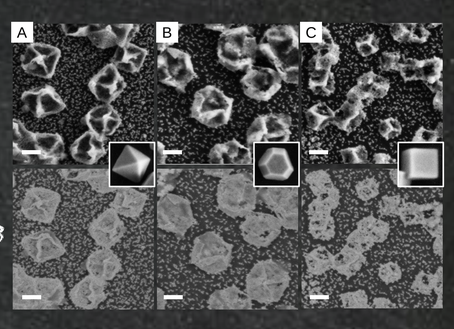


$Cu_2O + PdCl_4^{2-} + 2\ H^+ \rightarrow Pd^0 + 2\ Cu^{2+} + H_2O + 4\ Cl^-$



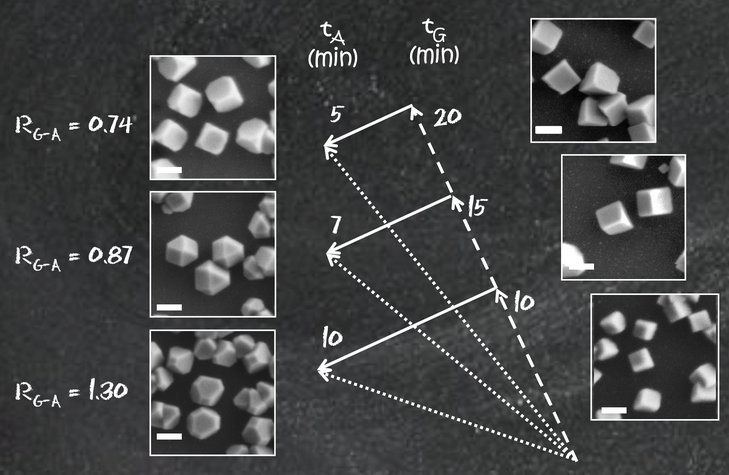
Dissolution of the Cu_2O cores

Cores of Cu_2O@Au NPs were dissolved in 10 mM HCl to reveal the NP surface structure. Scale bars: 100 nm.

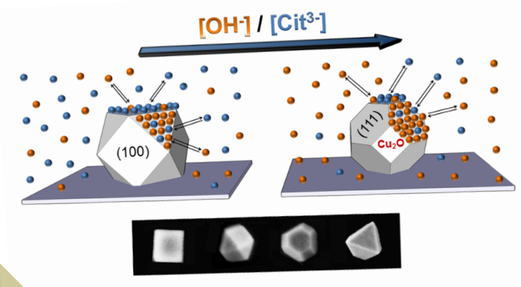


SEQUENTIAL DEPOSITION

Morphological and size control can also be achieved by sequential immersion of the slides in solutions A and G, and controlling the deposition times. Scale bars: 100 nm.



Competitive adsorption of citrate and OH^- anions on {100} and {111} facets, dictates the nanocrystal morphology.



CONCLUSIONS

1) Cu_2O NC films with precisely controlled morphology can be prepared by CD. The morphology is determined by competitive adsorption of citrate and OH- on {100} and {111} facets. The average NC size is determined by the deposition time.

2) The Cu_2O NC morphology can be shifted by sequential immersions in different growth media (*e.g.*, solutions A and G).

3) NPs are truncated on the substrate side and strongly adhere to it (pass the Scotch tape test).

4) Structures obtained by GR reactions of Cu_2O NCs with metal salts are highly dependent on the solution pH. Metal-decorated Cu_2O NPs, Cu_2O@Me, and metal nanocages, can be produced under appropriate conditions.

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[1] Susman, M. D.; Feldman, I.; Vaskevich, A.; Rubinstein, I., *Chem. Mater.* 2012, 24(13), 2501-2508.

[2] Susman, M. D.; Feldman, I.; Vaskevich, A.; Rubinstein, I., - *Submitted.*