Electroless deposition of morphologically controlled Cu_2O nanoparticle films and their photocatalytic activity

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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.

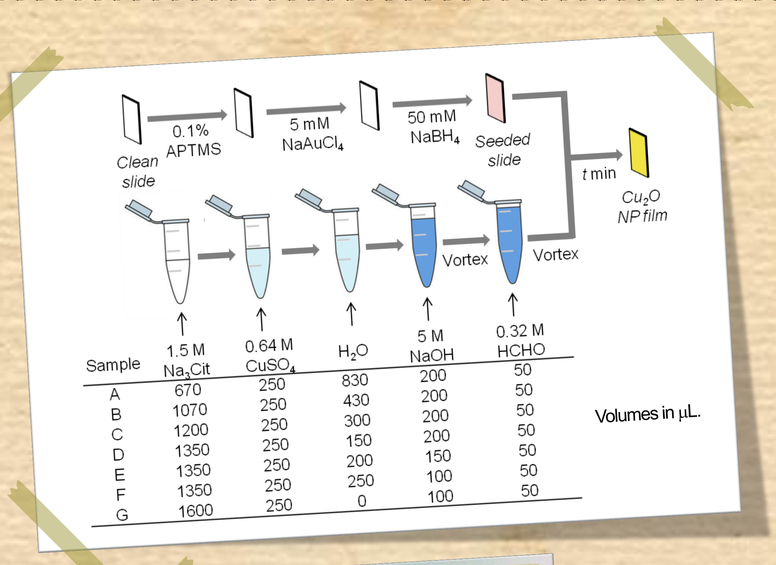
Here we present an electroless (chemical) deposition (ELD) approach to direct preparation of Cu_2O NP films on substrates, using $CuSO_4$-HCHO-Citrate-NaOH solutions. Our method shows a high degree of morphology control. The average NP size can be varied by controlling the deposition time, while the crystallographic structure is determined by the solution composition. The latter derives from the parameter γ = [NaOH]/[Citrate] ratio, which correlates with $R = r_{\langle 100\rangle}/r_{\langle 111\rangle}$ during crystal growth, where r_i is the growth rate perpendicular to the i-plane.

The NP films were studied by SEM, TEM, GIXRD and UV-Vis spectroscopy, and their photocatalytic activity towards the degradation of a model organic contaminant, methyl orange (MO), was evaluated and correlated with the NP morphology.

SAMPLE PREPARATION

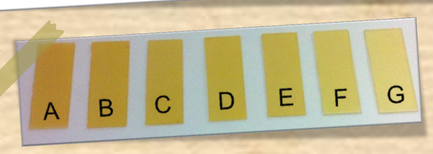
Au seeds were produced *in-situ* on glass or quartz slides by self-assembly of 3-aminopropyl trimethoxysilane (APTMS), immersion in $NaAuCl_4$, rinsing, and reduction with $NaBH_4$.

Cu_2O NP films were chemically deposited from formaldehyde-based solutions[1] of different compositions (A to G, prepared according to the table), optimized for the preparation of Cu_2O NPs with precise morphology.



Sample	1.5 M Na_3Cit	0.64 M $CuSO_4$	H_2O	5 M NaOH	0.32 M HCHO
A	670	250	830	200	50
B	1070	250	430	200	50
C	1200	250	300	200	50
D	1350	250	150	200	50
E	1350	250	200	150	50
F	1350	250	250	100	50
G	1600	250	0	100	50

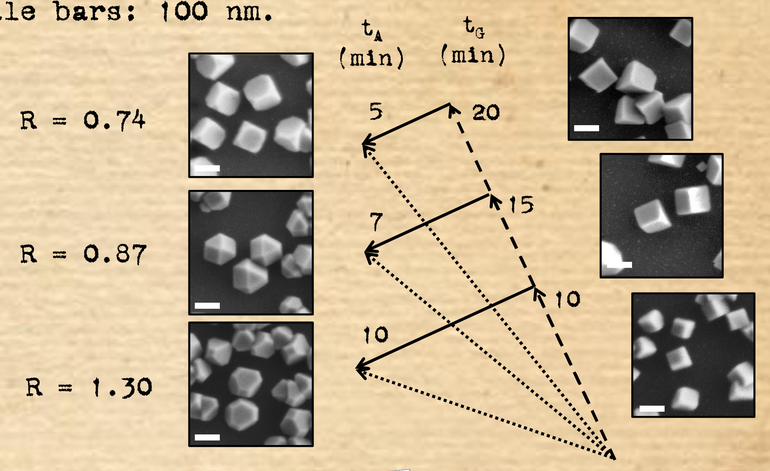
Volumes in µL.



t = 10 min

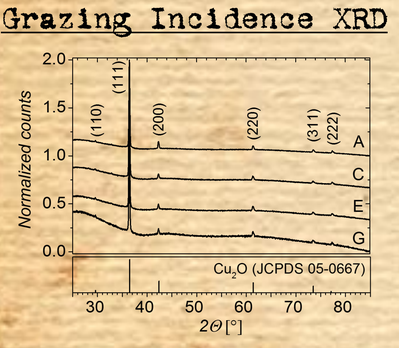
SEQUENTIAL DEPOSITIONS

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.



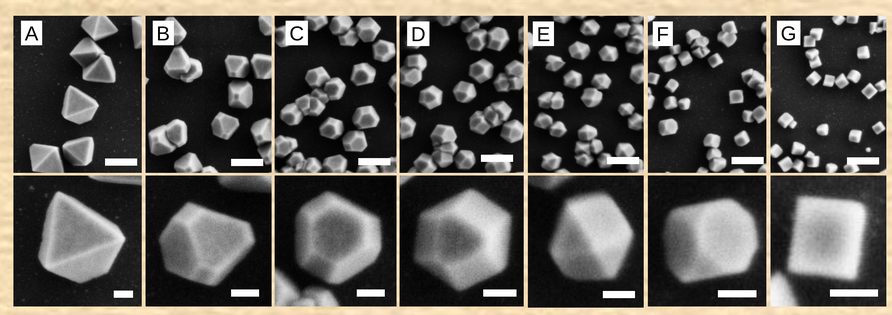
CHARACTERIZATION

Grazing Incidence XRD

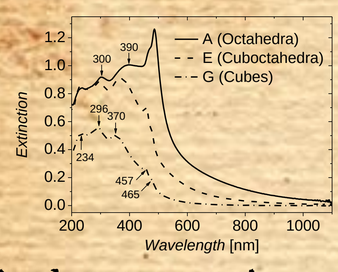


SEM images

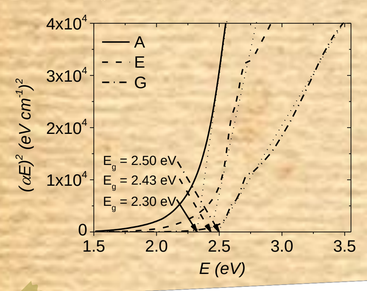
Scale bars: Top - 200 nm, bottom - 50 nm.



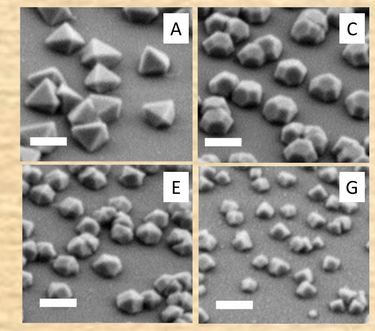
UV-Vis spectroscopy



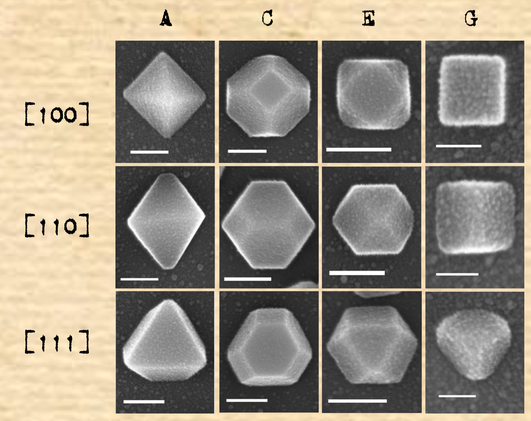
Band-gap energies calculated from absorption spectra.



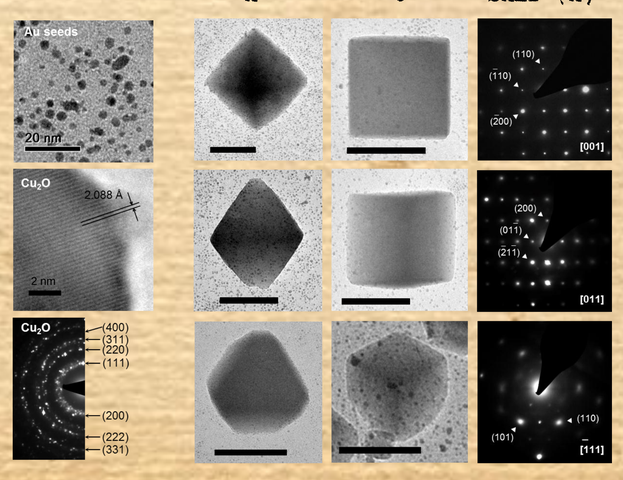
Tilted Angle SEM (45°). Scale bars: ~200 nm.



HRSEM (After 3 nm Cr sputtering). NPs viewed along the indicated directions. Scale bars: A,C,E - 100 nm, G - 50 nm.



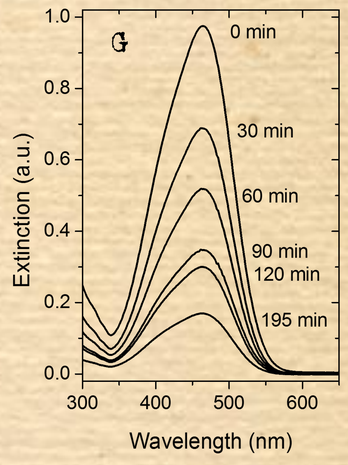
TEM images (Cu_2O NPs prepared after seeding of carbon-coated grids). Scale bars: A - 100 nm, G - 50 nm. Corresponding SAED patterns from octahedra are shown.

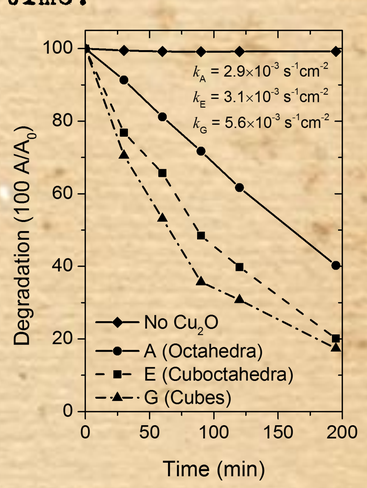


PHOTOCATALYTIC PROPERTIES

Photocatalytic activity under natural light illumination

Methyl orange (MO) photodegradation was followed by UV-Vis spectroscopy, plotting the MO extiction maximum as a function of time.

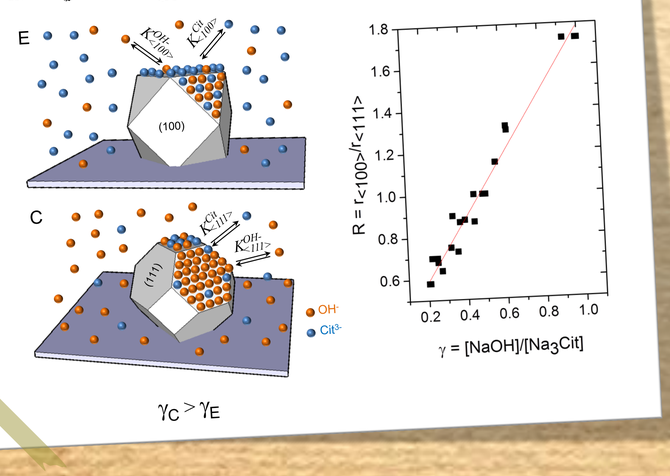




Assuming pseudo-first order reaction, degradation rate constants (k_i) were normalized to the exposed Cu_2O surface area (estimated from SEM images) and followed the order:

cubes > cuboctahedra > octahedra.

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



CONCLUSIONS

1) Cu_2O NP films with controlled morphology can be prepared by ELD. The morphology is determined by competitive adsorption of citrate and OH^- on ⟨100⟩ and ⟨111⟩ facets. Average NP size is controlled by the deposition time.

2) The Cu_2O NP morphology can be shifted by sequential immersion in different growth environments (solution A or G), for controlled times.

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

4) NP films show efficient photocatalytic activity towards MO degradation, being higher for cubes and lower for octahedra. The Cu_2O catalysts can be easily recycled.

[1] Susman, M. D.; Feldman, I.; Vaskevich, A.; Rubinstein, I., *Chem. Mater.* 2012, ASAP article.

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