Electroless deposition and stabilization of plasmonic copper nanostructures on transparent substrates

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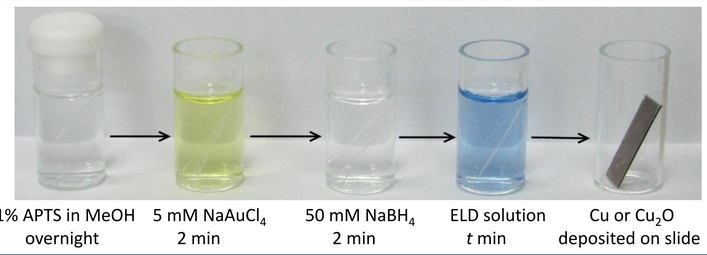
Introduction. Use of Cu nanoparticles (NPs) in localized surface plasmon resonance (LSPR) and surface-enhanced Raman spectroscopy (SERS) has been scarce, compared to the more noble metals Ag and Au, mainly due to its lower stability towards corrosion in aqueous solutions and oxidation in air. Still, Cu might represent an alternative inexpensive material for these applications if chemical stabilization of Cu NPs could be achieved. In the present work we investigate gold-seeded glass and quartz substrates onto which layers of Cu and Cu_2O NPs are prepared by electroless deposition (ELD) using formaldehyde-based solutions of different compositions. ELD Cu NP films displaying a prominent surface plasmon (SP) band around 600 nm were stabilized using benzotriazole (BTAH), a known Cu corrosion inhibitor, allowing the study of their plasmonic properties, such as the refractive index sensitivity (RIS). The dependence of the SP band on the local dielectric environment is shown to provide a useful tool for studying Cu corrosion processes and their inhibition. Stabilization of the Cu NP films is expected to enable their use in optical applications such as LSPR sensing and SERS.

Preparation. Au-seeded substrates were produced in-situ by self-assembly of (3-aminopropyl)trimethoxysilane (APTS) on glass or quartz slides, immersion in $NaAuCl_4$, rinsing, and reduction with $NaBH_4$. This was followed by deposition from formaldehyde-based ELD solutions of different compositions, optimized for the preparation of Cu or Cu_2O NP films. Stabilization of Cu NPs was achieved using benzotriazole (BTAH) treatment.

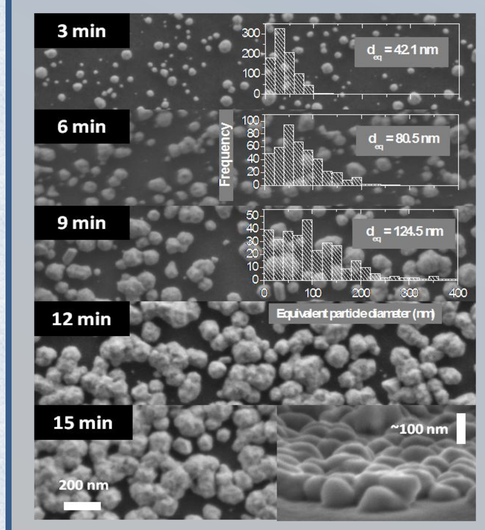


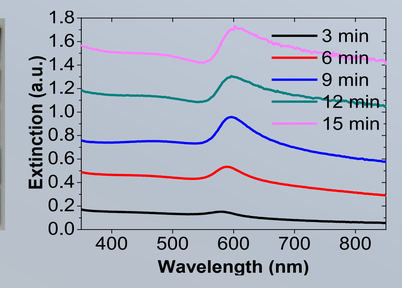
Composition of optimized ELD solutions		
	Cu	**Cu_2O**
$CuSO_4.5H_2O$	8 mM	80 mM
Formaldehyde (HCHO)	200 mM	40 mM
NaOH	0.5 N	
Sodium potassium tartrate (NaKT)	0.177 M	

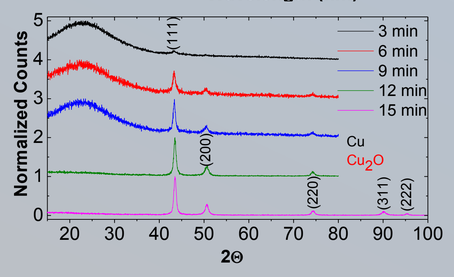
Cu deposition

Deposition reaction:

$[CuT_2]^{2-} + 2\ HCHO + 4\ OH^- \rightarrow$ **Cu (*s*)** $+ H_2\,(g) + 2\ HCOO^- + 2\ T^{2-} + 2H_2O$





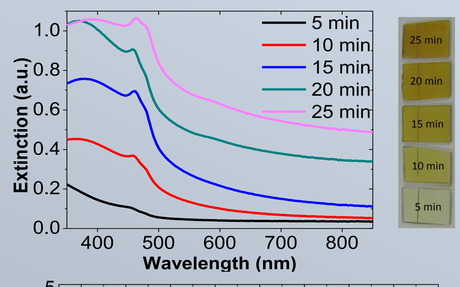


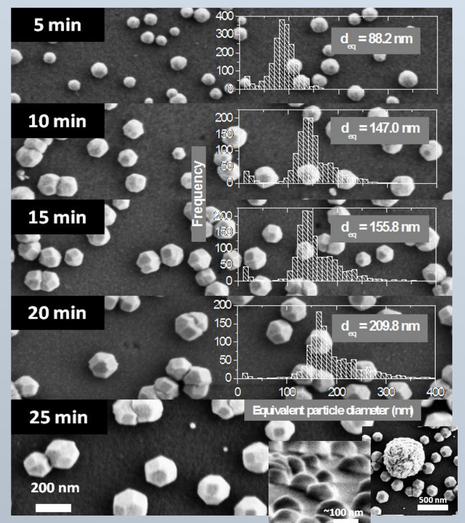
ELD Cu. *(Left)* SEM images of Cu NPs deposited on glass slides for different times. Insets show particle size distributions and a SEM tilted-angle image of the 15 min slide. Also shown are corresponding transmission UV-Vis spectra *(top-right)*, GIXRD data *(bottom-right),* and photographs *(center)* (the latter on quartz). The band around 600 nm in the UV-Vis spectra corresponds to the Cu SP extinction.

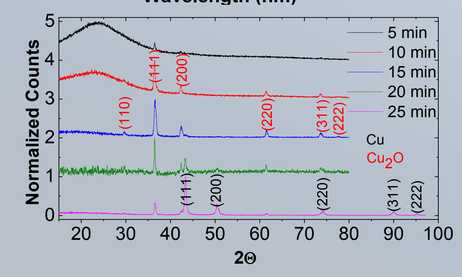
Cu_2O deposition

Deposition reaction:

$2\ [CuT_2]^{2-} + HCHO + 5\ OH^- \rightarrow$ **Cu_2O (s)** $+ HCOO^- + 3H_2O + 4\ T^{2-}$

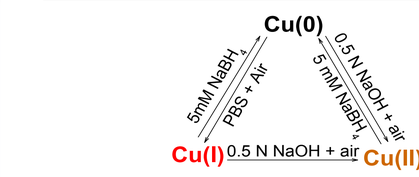


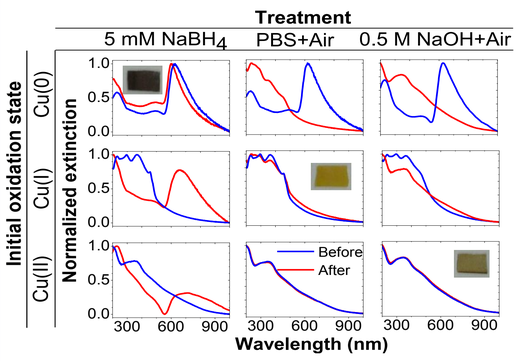




ELD Cu_2O. *(Right)* SEM images of Cu_2O NPs deposited on glass slides for different times. Insets show particle size distributions, a tilted-angle SEM image of the 15 min slide, and co-deposited Cu particles formed after ca. 20 min. Also shown are corresponding transmission UV-Vis spectra *(top-left)*, GIXRD data *(bottom-left),* and photographs (*center)* (the latter on quartz).

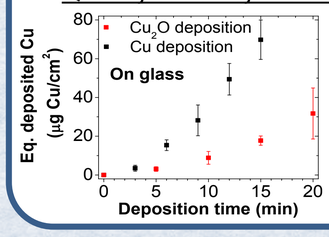
Oxidation states and extinction spectra





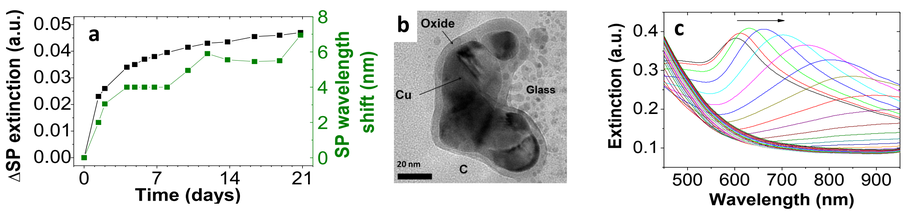
Conclusion: Combinations of chemical reactions allow prediction of the major oxidation state of the deposit.

Quantification of the deposited mass



The deposited mass was quantified using UV-Vis spectroscopy with neocuproine chelator. Similar trends were verified by X-ray fluorescence (XRF), on quartz.

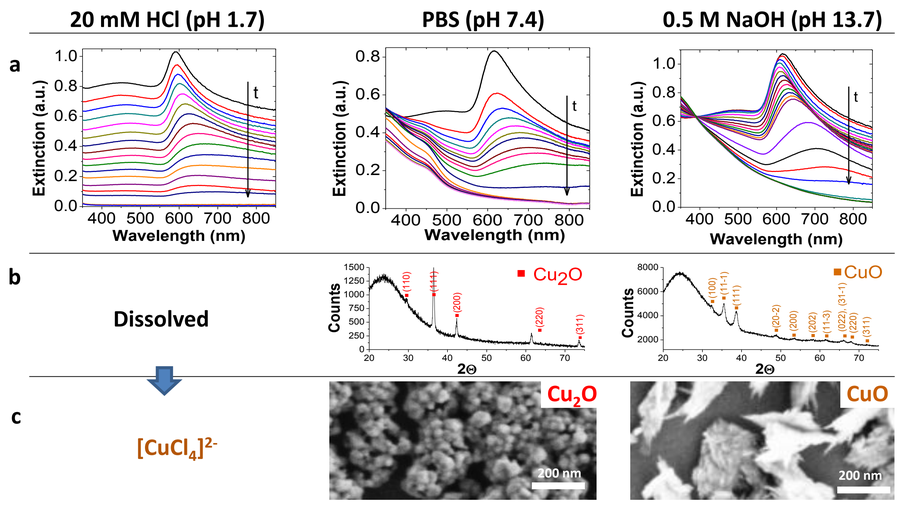
Cu NPs: oxidation in air



At room temperature: *(a)* SP band change for an ELD Cu NP film prepared by 6 min deposition (glass substrate). (*b)* Cross-sectional TEM image (prepared by FIB slicing) of a 2 month oxidized Cu aggregate; note the formation of an oxide shell.

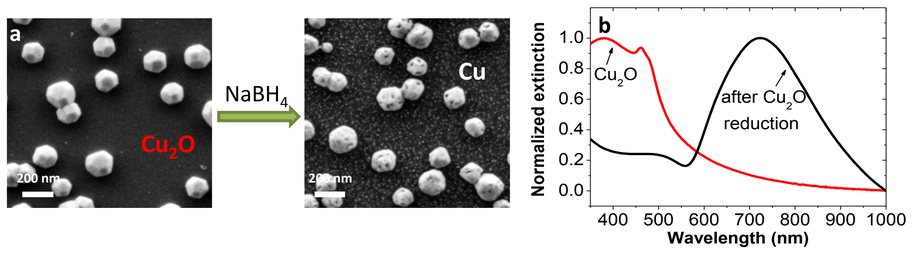
At high temperature: *(c)* In-situ spectral changes for a 6 min ELD Cu NP film, recorded during annealing in air at 225 °C in a special optical oven (1 spectrum/30 s).

Cu NPs: corrosion in aqueous media



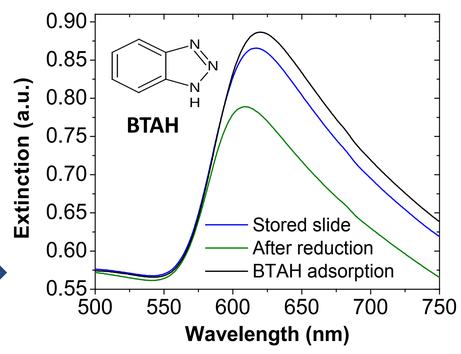
(a) Spectral changes for 9 min ELD Cu NP films undergoing corrosion in aqueous media of different pH, measured under air. Also shown are GIXRD patterns *(b)* and SEM images *(c)* of the supported corrosion products. (PBS = phosphate buffer saline.)

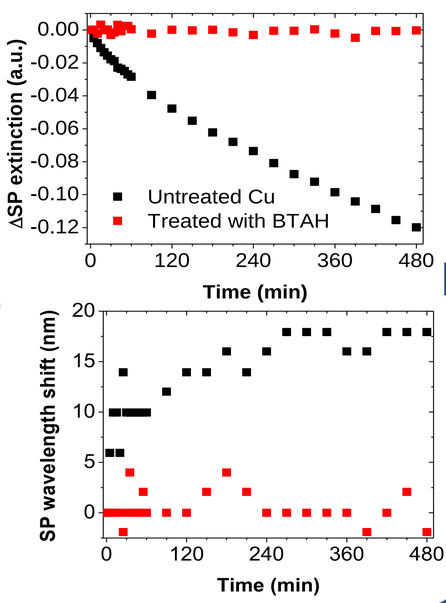
Cu NPs obtained by chemical reduction of Cu_2O NPs



An alternative strategy for producing well-defined Cu NP films is chemical reduction of the Cu_2O nanocrystals. *(a)* SEM images before and after chemical reduction with $NaBH_4$. *(b)* Corresponding transmission UV-Vis spectra.

Corrosion inhibition

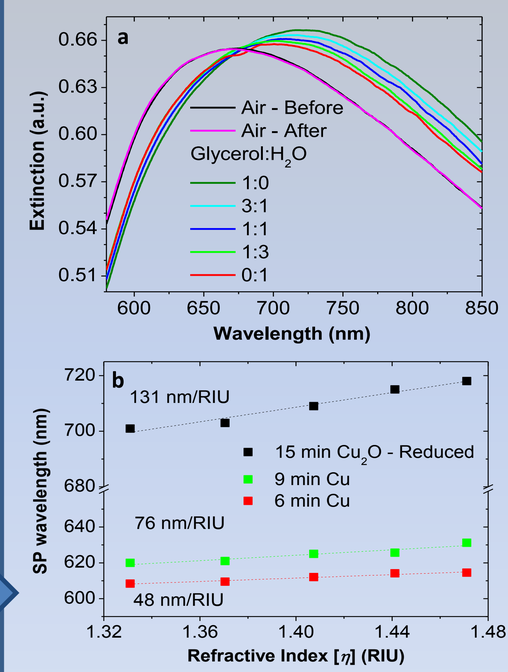




(Top-left) Ex-situ extinction spectra of a Cu NP film after inhibition treatments with benzotriazole (BTAH). *(Top-right)* In-situ SP extinction change for a reduced Cu NP film, measured in water under air. *(Bottom-right)* Corresponding SP wavelength changes.

Refractive index sensitivity

The refractive index sensitivity (RIS) is defined as the SP wavelength shift per unit change of the refractive index (RI) of the contacting bulk medium.



The RIS was measured by immersion of BTAH-protected Cu NP films in water-glycerol mixtures of different volume ratios and RIs. (*a*) Spectra of a Cu NP film (15 min ELD Cu_2O, reduced) immersed in different mixtures; (*c*) Determination of the RIS of the various samples.

Conclusions:

- Cu ELD on glass or quartz primed with Au seeds can be tuned to produce Cu NP films or Cu_2O NP films, by choice of the ELD solution composition. Cu NP films can also be obtained by chemical reduction of the Cu_2O NPs.
- Cu NP films of both kinds show a well-defined localized plasmon extinction band in the visible range.
- Air oxidation of Cu NP films was monitored by following the change of the LSPR band shape. Corrosion of Cu NP films in aqueous media produces different oxidized deposits in solutions of different pH, monitored by LSPR spectroscopy and GIXRD.
- Corrosion of Cu NP films is effectively inhibited by BTAH treatment, suggesting possible applications in LSPR sensing.
- The RIS values of Cu NP films are comparable to those of evaporated Au nanoisland films.[1]

Acknowledgment. We thank Dr. Palle Von Huth for FIB cross-sectioning, Dr. Ronit Popovitz-Biro and Alexander Tesler for TEM imaging, and Dr. Sana Shilstein for XRF measurements.

[1] T. Karakouz; D. Holder; M. Goomanovsky; A. Vaskevich; I. Rubinstein, *Morphology and Refractive Index Sensitivity of Gold Island Films*, *Chem. Mater.* 2009, 21, 5875–5885.

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