Electrodeposition 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 CuO NPs are prepared by electrodeposition (EDL) using formaldehyde-based solutions of different compositions. EDL Cu NP films displaying a prominent surface plasmon (SP) band around 680 nm were stabilized using benzoic acid (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 NaAuCl₃, rinsing, and reduction with NaBH₄. This was followed by deposition from formaldehyde-based EDL solutions of different compositions, optimized for the preparation of Cu or CuO NP films. Stabilization of Cu NPs was achieved using benzoic acid (BTAH) treatment.

**Deposition reaction:** 
Cu deposition: 

\[
[CuT₄]^{2+} + 2 \text{HCHO} + 4 \text{OH} \rightarrow \text{Cu} (s) + \text{H}_2 \text{CO}_3 (g) + 2 \text{H}^+ + 2 \text{H}_2 \text{O}
\]

CuO deposition: 

\[
2 \text{CuT}^{2+} + \text{HCHO} + 5 \text{OH} \rightarrow \text{Cu}_2 \text{O} (s) + \text{HCOO}^- + 3 \text{H}_2 \text{O} + 4 \text{H}^+
\]

**Cu NPs: oxidation in air**

- **At room temperature:** (a) SP band change for an EDL 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 EDL 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**

- **20 mM HCl (pH 1.7):** Disolved
- **PBS (pH 7.4):** Corroded
- **0.5M NaOH (pH 13.7):** Corroded

(a) Spectral changes for 9 min EDL 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.)

**Corrosion inhibition**

- **BTAH:** Stored under air
- **BTAH adsorption:** Stored under air

(Top-left) Ex-situ extinction spectra of a Cu NP film after inhibition treatments with benzoic acid (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.

**Conclusion:**
Cu ELD on glass or quartz primed with Au seeds can be tuned to produce Cu NP films or CuO NP films, by choice of the ELD solution composition. Cu NP films can also be obtained by chemical reduction of the CuO 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 nanos'lands.**

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