

Oxidative and Colloidal Kinetics of Size-Controlled Copper Structures through Surface Plasmon-Regulated Examinations for Broadband Absorbance

A. R. Indhu^[a] and Gnanaprakash Dharmalingam^{*[a]}

Out of all the candidate plasmonic metals, copper has noteworthy optical characteristics and is also economically favourable for use. However, the stability of plasmonic copper nanomaterials against the loss of the plasmonic property is a setback. The present work is on the synthesis of oxidation-stable copper micro/nanoparticles (CuMps/NPs) at ambient conditions with chosen precursors, antioxidizing agents, polymeric capping agents and chelating ligands. The Surface Plasmon Resonance (SPR) response of the synthesized Cu structures and their morphological analyses are studied. XRD

data revealed changes in crystal structure such as crystallite sizes, lattice distortions and dislocation densities as a result of variations in the synthesis conditions. We present from these analyses micro/nanostructures of oxidation-stable plasmonic Cu. The validation of the aggregation and oxidation stabilities of the different synthesized samples make them a worthy choice for multiple plasmonic applications, along with showing the synthesis protocols as viable approaches for achieving such structures with a markedly increased shelf life.

1. Introduction

Plasmonic nanoparticles command enormous attention due to their unique thermal, electrical, and even catalytic properties apart from their optical characteristics. Plasmonic metal nanoparticles like Au, Ag, Cu, Pd, and Pt in particular are well-explored due to their high free electron density, tailorable dielectric constant, specificity for particular reactions and having their optical limit in the UV-Vis due to higher electron densities than other plasmonic materials, among other benefits. Among these candidates, copper nanoparticles (CuNPs) have high thermal (400 W/mK),^[1] and electrical (59.88×10^6 S/m) conductivity, catalytic activity (due to its diverse coordination chemistry) and importantly a facile tunability in plasmonic property through uncomplicated manoeuvres such as during and post-synthesis (including controlled oxidation) and hence have potential in a wide array of applications such as in photothermal therapy,^[2] photocatalysis^[3] and photovoltaics.^[4] High-temperature applications are usually excluded due to high sensitivity and susceptibility towards oxidation (the same being a cause for worry even in atmospheric temperatures and ambient). Researchers have employed numerous methods like chemical reduction,^[5] sol-gel,^[6] photochemical,^[7] microwave,^[8] reverse micelles,^[9] microemulsion,^[10] hydrothermal^[11] and electrochemical^[12] to synthesize and stabilize Cu particles. In the case of different oxides of Cu like Cu₂O, CuO dampens the localized surface plasmon resonance (LSPR)^[13] intensity of the

metal core (Cu) with an associated increase in band gap and hole mobilities. The oxidation problem can be precluded by multiple means, as has been reviewed recently by our group^[14,15] through the addition of ligand molecules, capping agents, or stabilizing agents viz., polyvinyl pyrrolidone (PVP),^[16] cetyl trimethyl ammonium bromide (CTAB),^[17] L-ascorbic acid (AA),^[18] Sodium dodecyl sulphate (SDS),^[19] and ligand molecules like ethylene diamine (EDA).^[20] Usually, molecules which can play a dual role of reducing as well as capping are intuitively preferred due to advantages such as less intensive post-processing to isolate the CuNPs. More than one phenomenon can dictate the capping stability of such dual-role antioxidant ligands. For example, the reduction/capping effect has been reported to be caused by coordinating lone pairs of electrons between AA (or its intermediates, as discussed in the reaction mechanism section) and the copper ion to form a complex compound,^[21] wherein AA have been thought to disperse copper ions and catalyse the reduction of Cu²⁺ inside nanoscopic templates.^[18] Another mechanism through which oxidation stability is possible is the dispersion effect of the oxidation product of L-AA on CuNPs after the completion of reduction, where L-AA is first converted into dehydroascorbic acid and after a sequence of reactions (as discussed later in this study), a polyhydroxy structure whose extensive number of hydroxyl groups can facilitate complexation to the reduced CuNPs by inter and intramolecular hydrogen bonding, preventing aggregation. With these insights, we have explored the impact of using AA alone or in combination with two well-known capping ligands of PVP and triethanol amine (TEA) in this study, with observations of changes in particle surficial features, polydispersity and particle size as a result without a change in morphology. PVP's role as a capping polymer (albeit being a mild reductant due to its high electron affinity in a few cases like Ag, Pt)^[22–24] to exclude aggregation, and TEA has been

[a] A. R. Indhu, G. Dharmalingam
Plasmonic nanomaterials laboratory, PSG Institute of Advanced Studies,
Coimbatore-641004, India
E-mail: dgp@psgias.ac.in

Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/slct.202305087>