

Supporting Information

Electrodeposition of copper for three-dimensional metamaterial fabrication

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Section 1. Surface topography and resistivity characterization

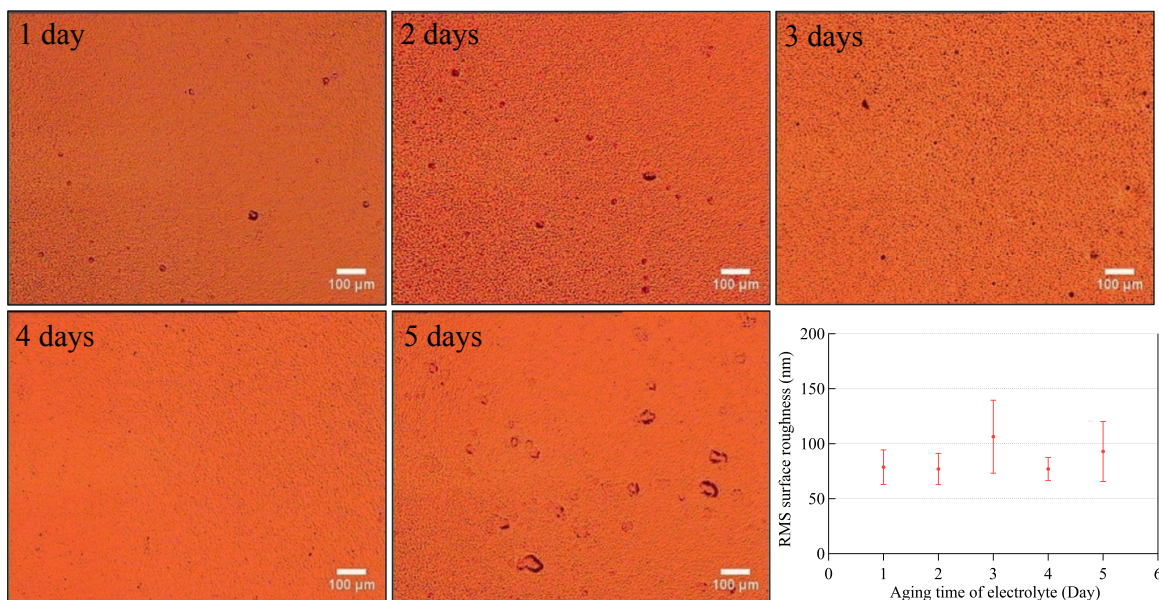


Figure S1. The optical microscope images of the surface topography of 150 μm -thick copper film electrodeposited in a CI-PEG-MPSA-PVP additive system of different aging time and the corresponding RMS surface roughness data. Five different positions on each sample were measured by optical profilometer.

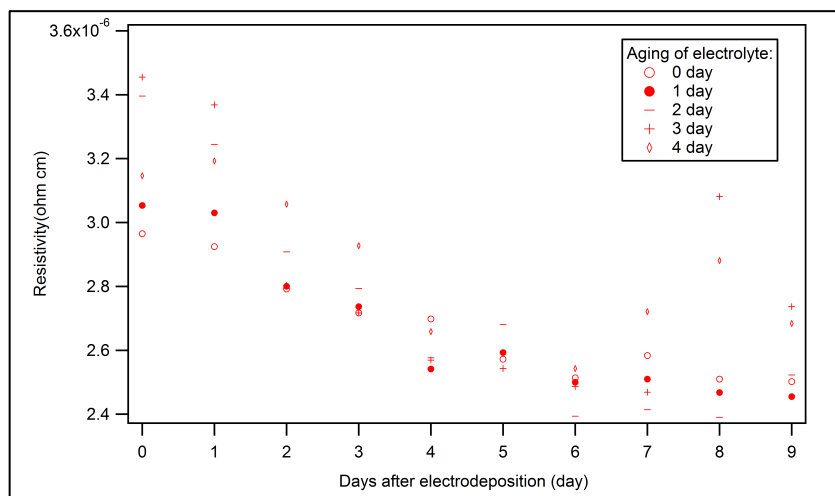


Figure S2. The resistivity transients during aging of 150 μm -thick copper film electrodeposited in aged electrolyte.

In order to investigate the impact of electrolyte aging on the surface topography of copper film, a series of electrodepositions of copper film was carried out using aged electrolyte with a controlled current density of 10 mA/cm^2 . As shown in Fig.S1, all the electrodeposited copper films are bright and only have a few defects. Moreover, they

have a relatively similar RMS surface roughness data with a range from 60 to 100 nm. Both the optical microscope images and the surface roughness data indicate that the aging of the electrolyte does not have a big impact on the surface roughness of electrodeposited copper film.

As is known, the resistivity of bulk copper is $1.7 \mu\Omega \text{ cm}^{-1}$ and the resistivity range of the electrodeposited copper film ranges from 3.0 to $3.4 \mu\Omega \text{ cm}$ immediately after the electrodeposition as shown in Fig. S2. During the aging of the copper films, a 29% decrease in resistivity appears gradually. The resistivity drop is due to the recrystallization and the growth of grain size that resulted in the reduction of grain boundaries². In addition, there is a trend that the copper resistivity increases with bath aging. Also, the resistivity of copper electrodeposited from the electrolyte that was aged 3-4 days increases rapidly after 7 days of environmental exposure. Other work³⁻⁴ has shown that additives in the electrolyte tend to form Cu(I)-accelerator and Cu(I)-Cl-PEG complex during aging that leads to decreasing additive concentration. Therefore, as the electrolyte ages, defect structures increase causing the resistivity to rise in the electrodeposited film.

Section 2. Chemical analysis of additives

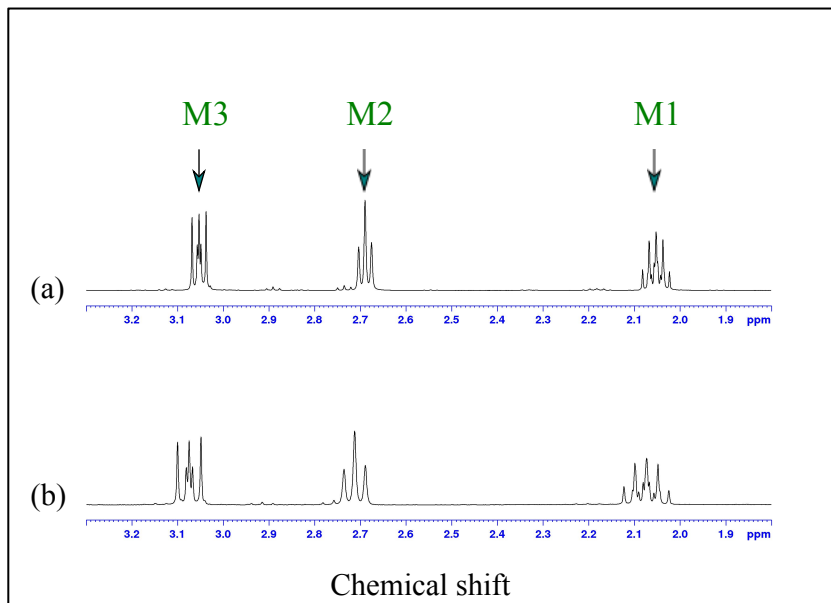


Figure S3. The ^1H -NMR spectra of (a) fresh MPSA and (b) the powder dried from MPSA + DI water solution.

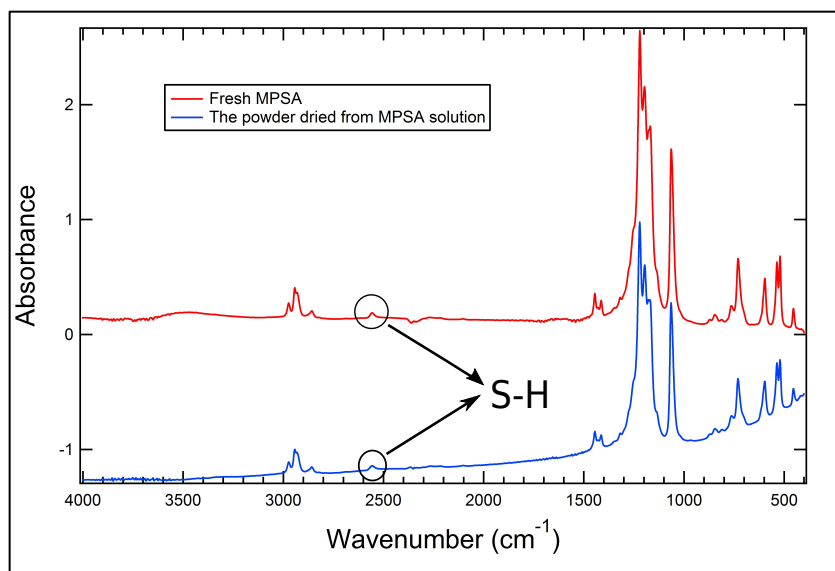


Figure S4. The FTIR spectra of fresh MPSA and the powder dried from MPSA + DI water solution.

Fig.7 shows that MPSA converts to SPS in acid copper solution immediately and SPS would not convert back to MPSA during aging. In contrast with others' work, the present data shows that this conversion process is not reversible, for which two potential causes are likely. First, it may be caused by different experimental conditions such as low PH and the concentration of copper ions. Second, it should be noted that, the extraction

process of MPSA in an acid copper bath involves neutralization, extraction and evaporation. Among those three steps, neutralization is an exothermic process and evaporation is under vacuum and high temperature (55 °C), so overheating might change both the original and regenerated MPSA to SPS, resulting in the appearance of only SPS in the spectra as shown in Fig. 7(b). In order to investigate the impact of the pretreatment on the conversion of compounds, the following tests were conducted: pure MPSA powder was dissolved in DI water first and then evaporated under the same evaporation conditions as before, whose ^1H -NMR spectrum and the FTIR spectrum can be seen in Fig. S3 and Fig. S4. The characteristic peaks of the ^1H -NMR spectrum are the same as that of pure MPSA with an area ratio of 1:1:1. In the FTIR image, both the fresh and evaporated MPSA have the same spectra, especially the weak peak of S-H at 2550 cm^{-1} , which proves again after the evaporation treatment, MPSA would still remain unchanged. So the acid copper bath is likely the reason to drive MPSA to SPS and this process is irreversible in the present experimental conditions.

References

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