**Electrochemical Growth of Spatially Organized Copper Microwire Arrays within Biomineralized (Dentine) Templates**

Joe Harris, Jun Wang, Mei Li, Daniela Plana, Michele E. Barbour, David J Fermin* and Stephen Mann*

**Supporting Information**

**Fig. S1.** (a) Distribution in thickness for copper microwires produced within dentinal tubules. (b) SEM image of a cross-sectioned metallized dentine composite showing ordered array of Cu microwires within the biomineralized matrix (c) XRD powder pattern of ground sample of metallized dentine composite showing for peaks for Cu (*), Cu$_2$O (3), apatite (2) and brushite (1).
**Fig. S2.** Cyclic voltammogram of a dentine-masked electrode recorded in an electrolyte solution of 0.2 M CuSO$_4$, 0.75 M H$_3$BO$_3$ and 1 M Na$_2$SO$_4$ prior to the application of the electrodeposition potential. Scan rate: 0.1 V s$^{-1}$. The relatively large negative potential for Cu electrodeposition and the significant tilt in the voltammetric responses originate from a large uncompensated resistance (estimated as 2.5 kΩ) introduced by the porous template. Despite the large resistance and the corresponding shift in potentials, a peak associated with diffusion controlled deposition of Cu can be observed between -0.5 and -1.0 V, while the corresponding Cu stripping peak is present at 0.2 V.
**Fig. S3.** Cyclic voltammogram of an unmasked electrode recorded in an electrolyte solution of 0.2 M CuSO₄, 0.75 M H₃BO₃ and 1 M Na₂SO₄. Scan rate: 0.1 V s⁻¹. A peak associated with diffusion controlled deposition of Cu is evident at -0.5 V, a characteristic nucleation loop can be seen between 0.0 and -0.2 V and a Cu stripping peak is evident at 0.5 V.

**Fig. S4.** Optical image of a template-masked working electrode after completion of electrodeposition showing bulk copper dendritic deposits on the template surface. The uncompensated resistance sharply decreased as the deposit grew over the dentine template.