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Electronic Supplementary Information (ESI)

Mechanism of selective gold extraction from multi-metal chloride solutions by electrodeposition-redox replacement

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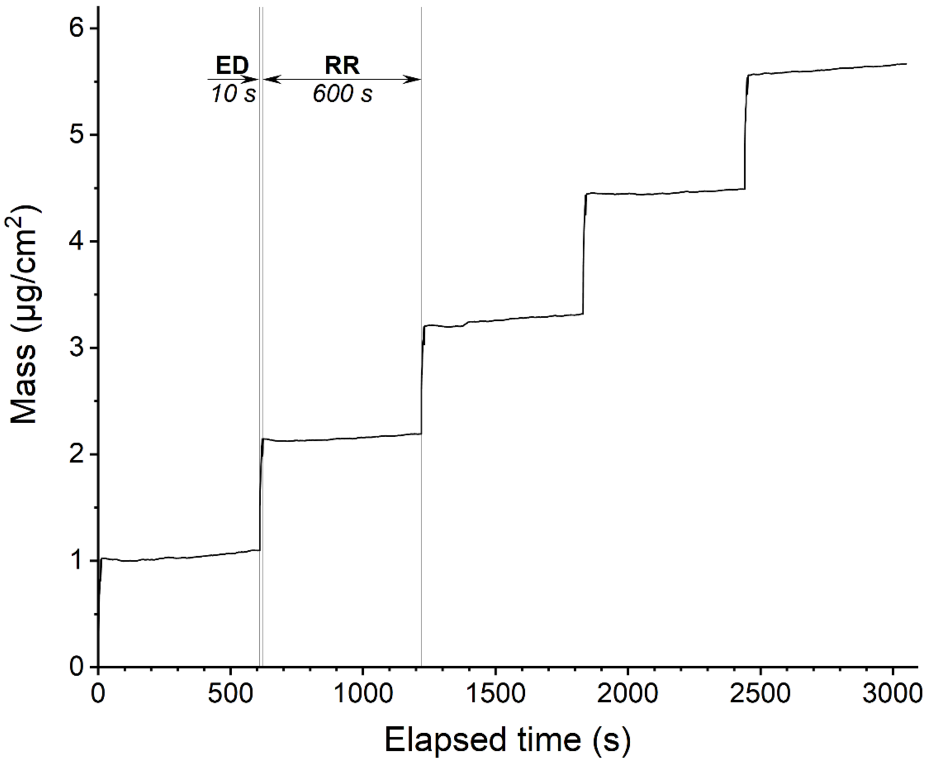

Fig. S1 Mass change during EDRR cycles in aqueous 4.5 M NaCl solution containing 0.5 mM Au without copper.

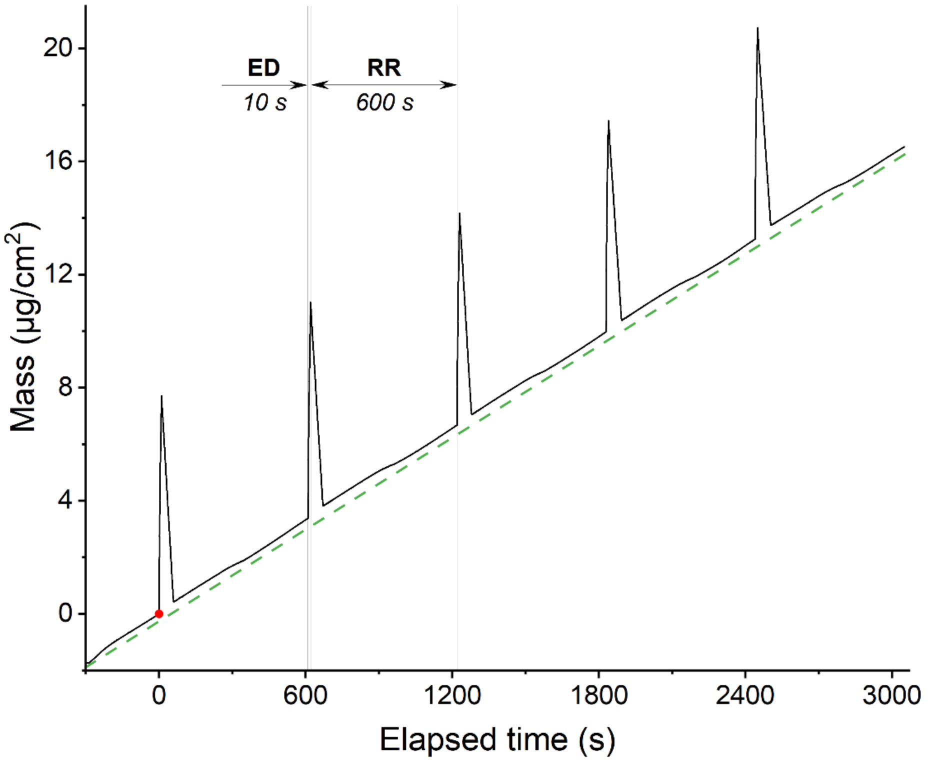

Fig. S2 Mass change during EDRR cycles in aqueous 4.5 M NaCl solution containing 0.5 mM Au + 60 mM Cu(I). The red dot indicates the moment, at which the potential was applied to the system for the first EDRR cycle. Steady mass buildup begins even before that, as shown by dashed line.

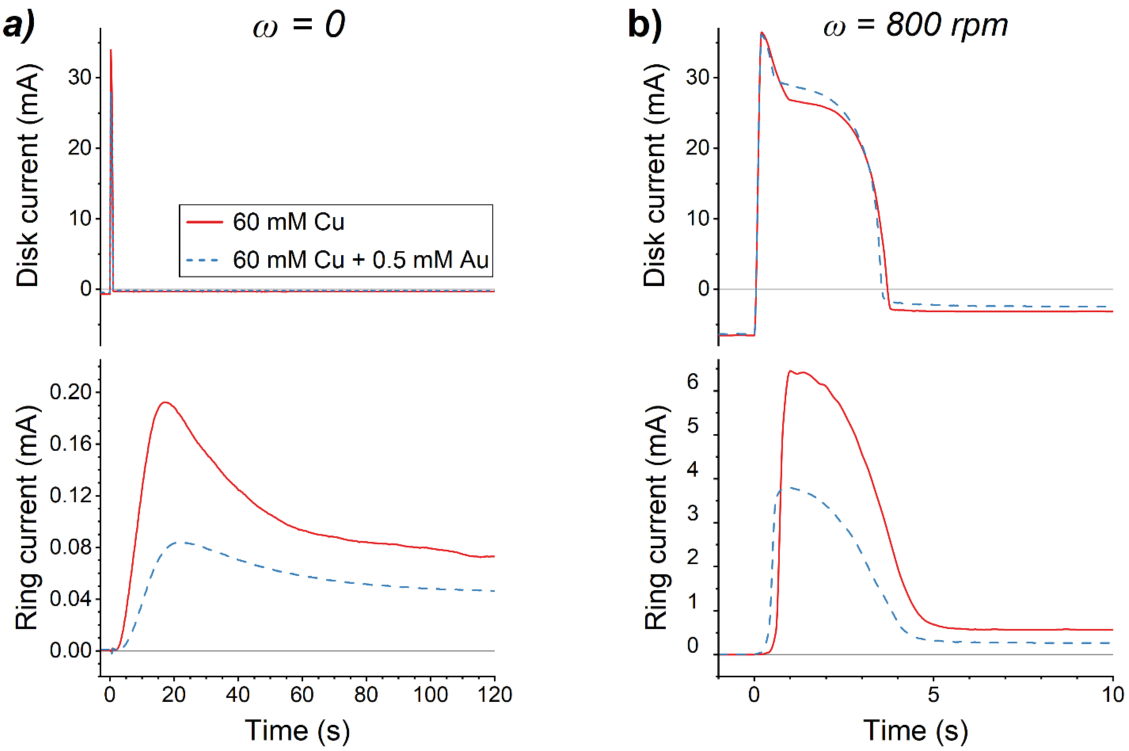

Fig. S3 RRDE current vs. time curves recorded in aqueous 4.5 M NaCl solution at a) 0 rpm and b) 800 rpm (applied potentials: disk E_D = 0.1 V vs. Ag/AgCl, ring E_R = 0.65 V vs. Ag/AgCl).

Fig. S3a validates the presence of copper(I) species as, after a short copper deposition period, the disk electrode was set to the copper dissolution potential (0.1 V vs. Ag/AgCl) while the ring was set to the Cu(I)/Cu(II) oxidation potential (0.65 V vs. Ag/AgCl), so that anodic current observed on the ring electrode indicates the Cu(I)/Cu(II) reaction. When cuprous species are depleted in the solution, the current reaches a plateau after approximately 100 s. The effect of gold ions on the dissolution would be indistinguishable from the disk electrode alone, but the ring current shows a clear difference when the solution also contains Au species, i.e. a smaller amount of copper(I) species is oxidized on the ring electrode in the presence of Au in the solution. This further enhances the explanation that cuprous ions are involved in the precipitation of dissolved gold species via homogenous reduction.

A clearly different behavior is observed when the electrode was rotated (Figure S3b): the dissolution from the disk seems to have two separate steps due to the morphology of the deposit. The sharp peak at the beginning is attributed to the loss of poorly adhered material (particulates or agglomerates) while the presence of a small plateau immediately after this sharp peak indicates that a more uniform, compact coating is being dissolved.[1,2] However, the ring electrode behaves in a similar manner as the static electrode, even though the depletion of copper(I) is achieved faster (5 s when rotating *cf.* 40-60 s when static), due to the enhanced mass transport that results from the electrode rotation.

References

1 A. I. Danilov, E. B. Molodkina and Y. M. Polukarov, *Russ. J. Electrochem.*, 2000, **36**, 1092–1100.
2 A. I. Danilov, E. B. Molodkina, A. A. Baitov, I. V. Pobelov and Y. M. Polukarov, *Russ. J. Electrochem.*, 2002, **38**, 743–753.

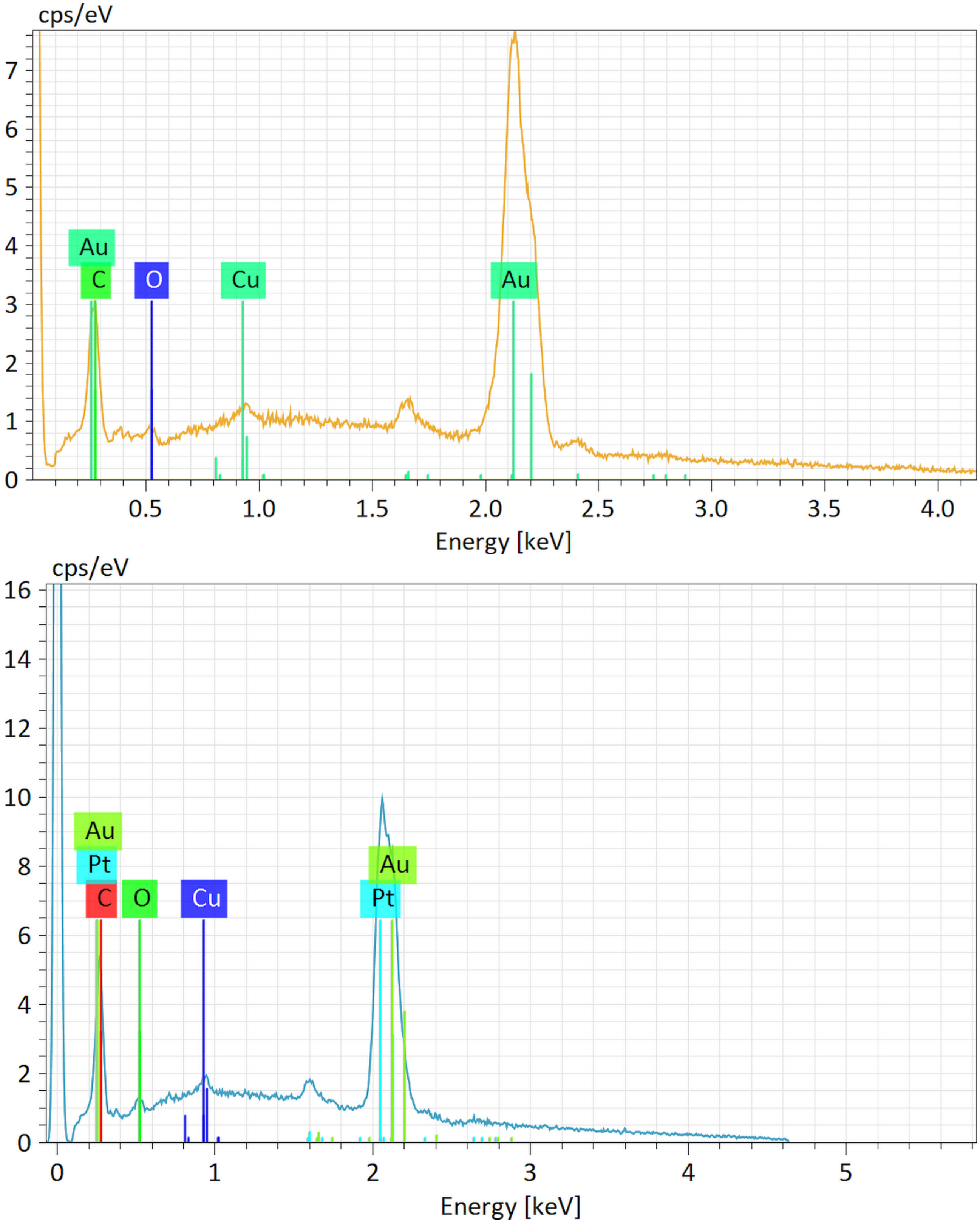

Fig. S4 EDS spectra of the final gold deposit after 50 cycles of EDRR in aqueous 4.5 NaCl solution (top) and 1:2 ChCl:EG (bottom). Background signal from platinum coated QCM crystal is excluded from calculations in Table 3.