

Supplementary information file

Facile synthesis of nanostructured gold for microsystems by the combination of electrodeposition and dealloying

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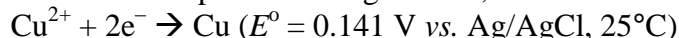
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1. Underpotential codeposition of AuCu alloy (CV measurements)

Using the (111)-oriented Au electrode, electrochemistry of the AuCu alloy formation was evaluated. Figure S1a shows that Cu was underpotentially deposited in the potential range of 0.40–0.05 V, and was overpotentially deposited below 0.05 V. These data were consistent with the Nernst potential, 0.041 V (*vs.* Ag/AgCl, 25°C), which is calculated for the Cu deposition using 20 mM,



In the underpotential deposition (UPD) region, two broad peaks were observed in the negative scans, and the corresponding stripping peaks were observed in the positive scans. The stripping peak located at more positive potential of 0.32 V is assignable to UPD of Cu on Au(111) surface as Cu^{+} ions, and the peak located at 0.16 V is assignable to the further reduction to Cu atoms.¹ On the other facets like Au(100), such Cu UPD was reported to occur in a similar potential range,² that is the underpotential codeposition of Cu with Au is considered to occur in this potential range.

Au was deposited in the potential range more negative than 0.95 V. The deposition commenced at the more positive potential than the standard potential, $E^{\circ} = 0.803 \text{ V}$ (*vs.* Ag/AgCl), because of the absence of Cl^{-} ions in the solution. Then, a limiting diffusion current was observed in the potential range more negative than 0.62 V. During the positive scans, oxidation current was observed above 0.90 V. This is attributable to Au dissolution due to the Cl^{-} anions dissociated from the AuCl_4^{-} anions.

AuCu was deposited using a mixture of the two solutions for the Cu deposition and the Au deposition, that is, the limiting diffusion current for Au should be half of that observed for the Au deposition. Apparently, in the UPD potential region observed in the case of Cu deposition on Au (*i.e.*, 0.4 to 0.05 V), the CV trace for the AuCu deposition exhibited a reduction current. Especially, below 0.30 V, the reduction current increased with negative potential sweep. This is attributable to the underpotential codeposition of Au and Cu. Thus, the deposition potentials of 0.1 V and 0.15 V were tested, and as shown below, the 0.15 V was chosen.

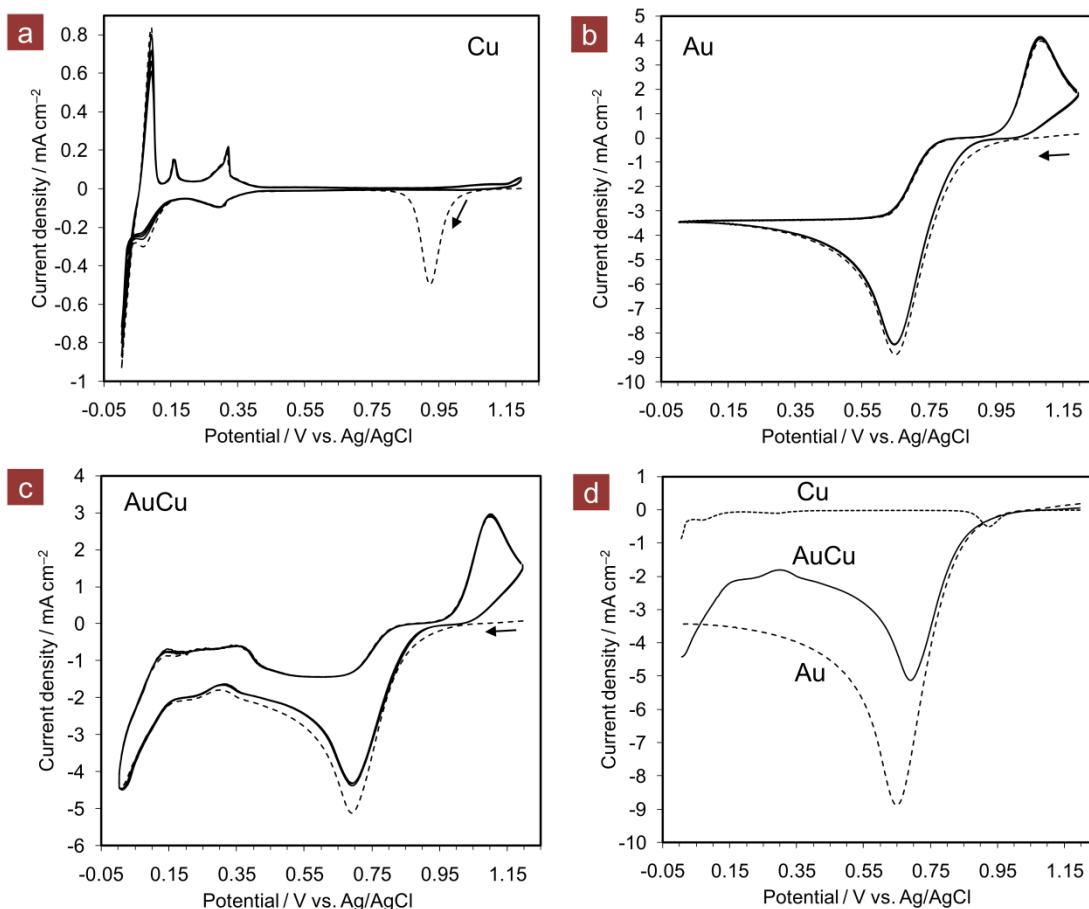
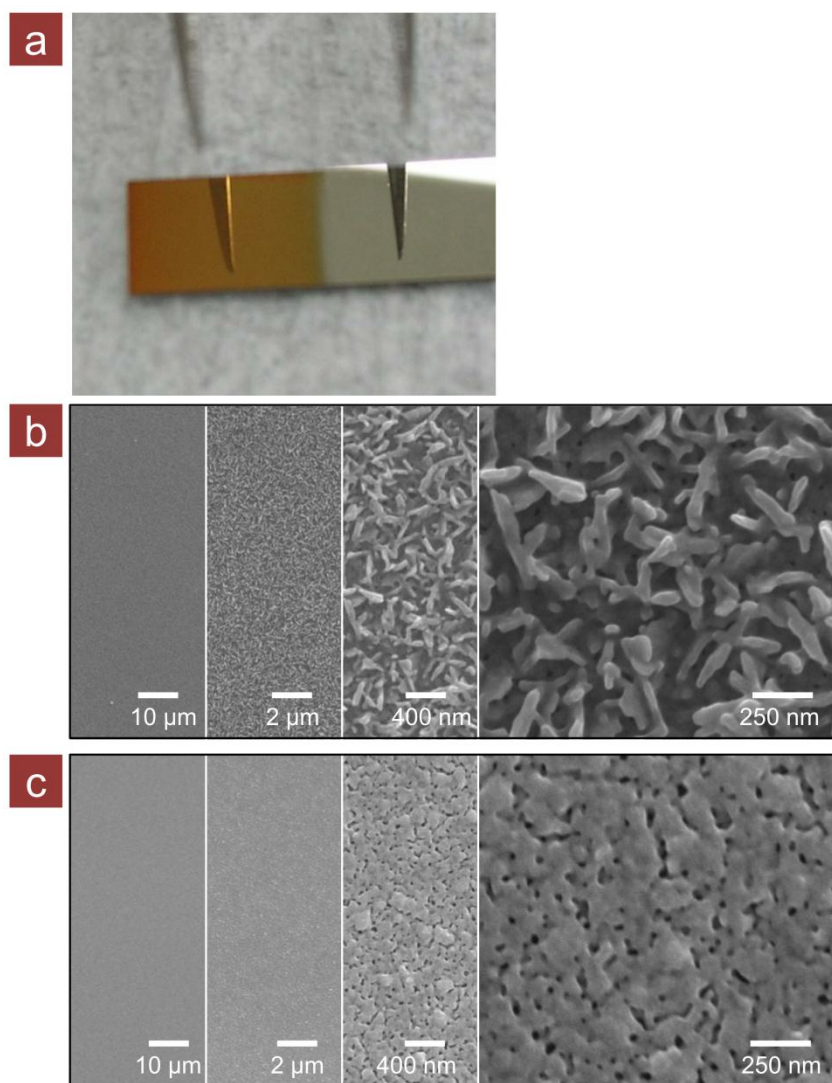


Figure S1 Cyclic voltammograms for determining synthetic conditions at 50 mV s^{-1} for 5 cycles. (a) Cu deposition in a solution containing 20 mM CuSO_4 and 500 mM H_2SO_4 . (b) Au deposition in a solution containing 20 mM KAuCl_4 and 500 mM H_2SO_4 . (c) AuCu deposition in a solution containing 10 mM CuSO_4 , 10 mM KAuCl_4 and 500 mM H_2SO_4 . (d) Comparison of the first negative scans. The working electrode was Au film prepared by electron-beam evaporation. All the measurements were carried out at room temperature.

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2. Dependence of the nanostructure on deposition potentials



5 **Figure S2** Observation of Au nanostructures synthesized by the combination of electrodeposition and dealloying. (a) Photograph of the sample on a Pt substrate. Deposition potential was 0.15 V. (b, c) SEM images of the sample on a Au substrate. (b) Deposition potential was 0.15 V. (c) Deposition potential was 0.10 V.

3. Dependence of the nanostructure on dealloying potentials

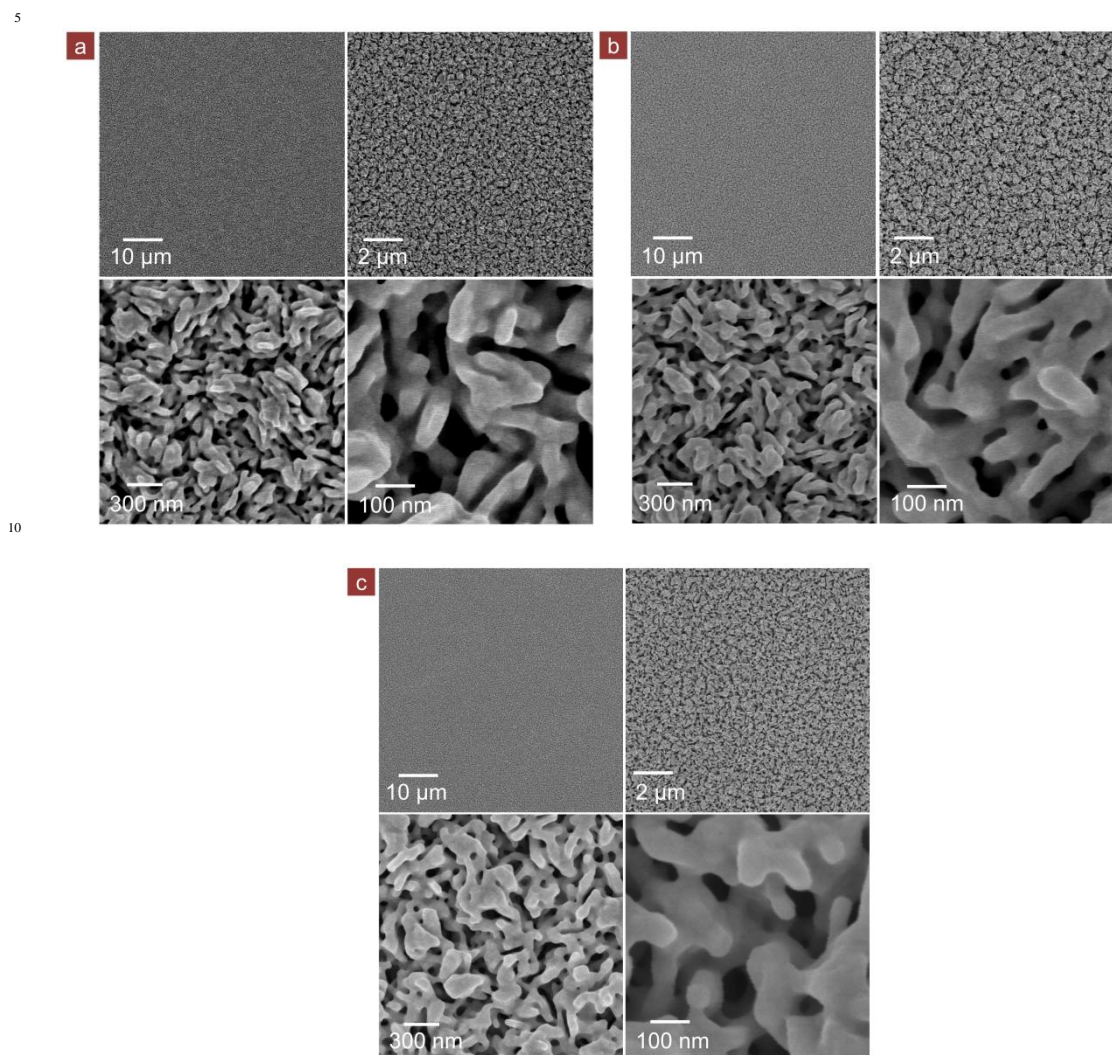


Figure S3 SEM images of Au nanostructures formed by dealloying at a different potential: (a) 0.9 V, (b) 0.95 V, and (c) 1.0 V.

4. Au nanostructures with and without dealloying (SEM observation)

The films (without dealloying) were recovered from the electrochemical cell in two ways. One was taken out as soon as possible after stopping the potential control. The other one was taken out by flushing out the deposition solution with pure water under potential control at 0.15 V (during deposition). The film prepared by the former way was shiny black, and the composition was determined to be $\sim\text{Au}_{95}\text{Cu}_5$. The film prepared by the latter way was shiny brown, and the composition was $\text{Au}_{71}\text{Cu}_{29}$. Even though the compositions were different, the microstructures of the two samples were the same (Fig. S4e-h). Moreover, they were apparently different from the dealloyed one (Fig. S4a-d). The spongelike nanostructures observed on the surface (Fig. S4h) was probably formed by corrosion by oxidation with air or galvanic displacement of Cu with Au.

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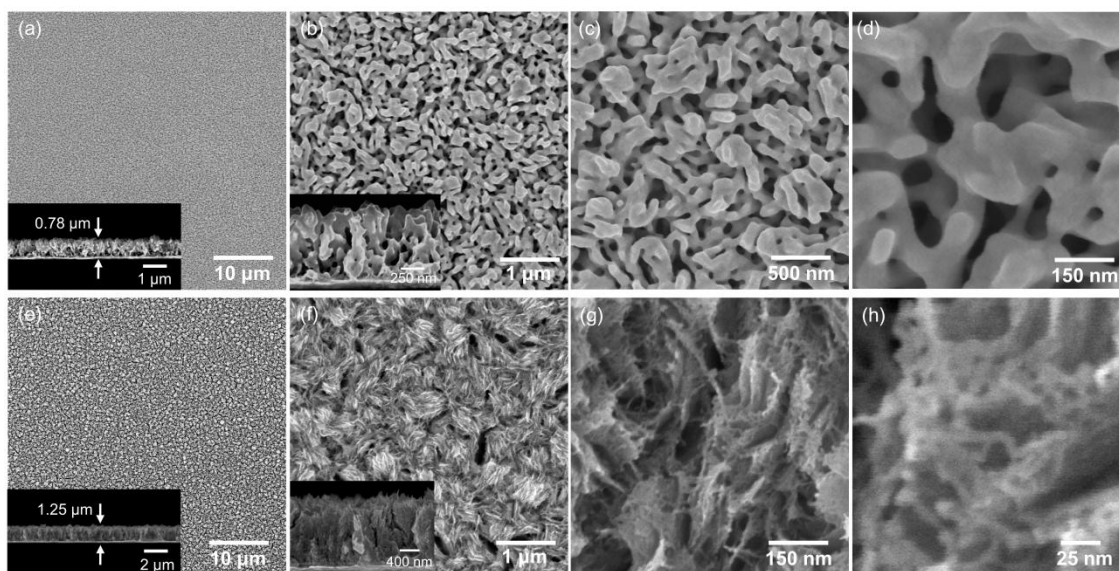


Figure S4 SEM images of Au nanostructures formed by dealloying (a-d) compared with those of electrodeposited film without dealloying process (e-h).

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5. Additional XRD patterns

The crystal structure of the thin film deposited on Si substrate was also analyzed by X-ray diffractometry (XRD) at a fixed incidence angle of 1.0° (RINT2500HF from Rigaku) by applying Cu $K\alpha$ irradiation at 40 kV, 350 mA. This arrangement clarified the peaks originating from the synthesized porous Au layer, by reducing the background originating from the extremely sharp peaks of the (111)-oriented Au substrate obtained by 2θ - θ scan (Fig. S5, inset). Thus, only the Au(220) peak of the substrate is considered to influence on the XRD patterns of the samples (Fig. S5, curve c).

The XRD pattern of the nanoporous Au film exhibited sharp peaks with diffraction angles located at 38.32° , 44.38° and 64.76° . These angles were almost consistent with those of a fcc lattice of pure Au ((111) plane: 38.18° ; (200) plane: 44.37° ; (220) plane: 64.56° ; JCPDS 89-3697).

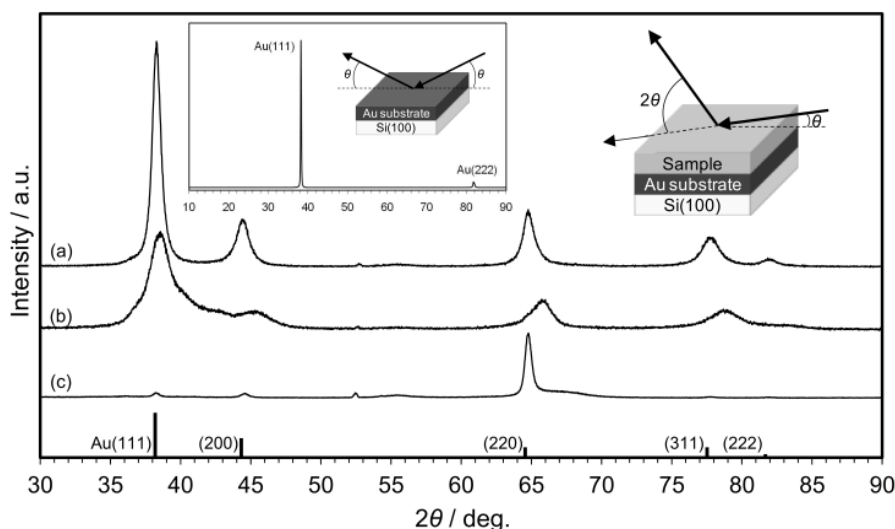


Figure S5 XRD pattern of the nanostructured Au film (a), compared with those of a film without dealloying (b) and a Au substrate prepared by electron-beam evaporation (c). The sample without dealloying was taken out from the cell after stopping the potential control. The data was collected at an incidence angle θ of 1.0° (inset, top right). The inset data was collected for the Au substrate by 2θ - θ scan. The bottom vertical lines show the peak positions and relative intensities of pure powder Au.

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6. Additional TEM images

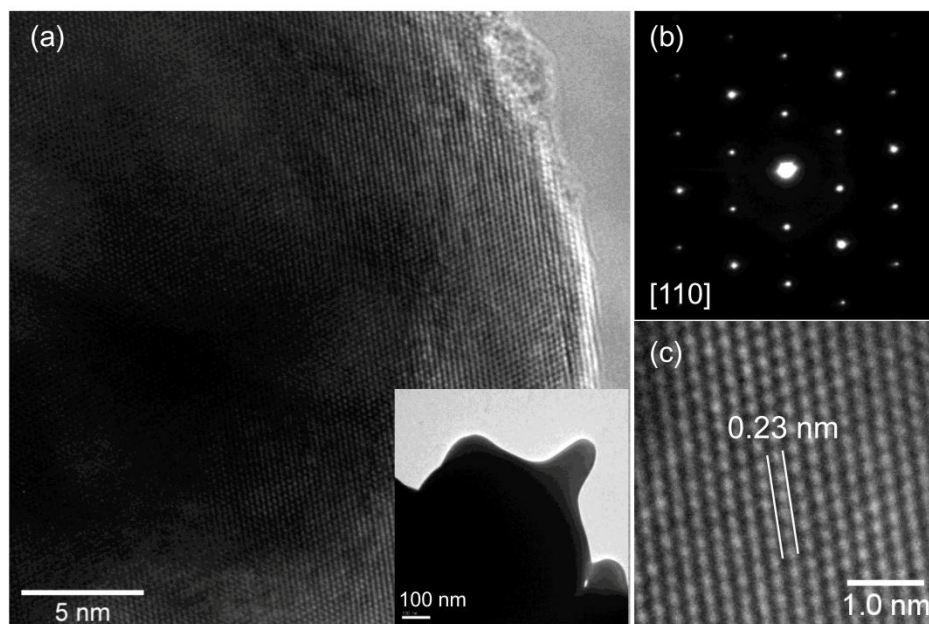


Figure S6 Additional TEM images of the Au nanostructures synthesized by the combination of electrodeposition and dealloying. This sample is the same one as shown in the text.

References

1. E. Herrero, L. J. Buller and H. D. Abruna, *Chemical Reviews*, 2001, **101**, 1897-1930.
2. A. Kuzume, E. Herrero, J. M. Feliu, R. J. Nichols and D. J. Schiffrin, *Journal of Electroanalytical Chemistry*, 2004, **570**, 157-161.