

## Electronic Supplementary Information

### **A Composite Additive used for an Excellent New Cyanide-free Silver Plating Bath**

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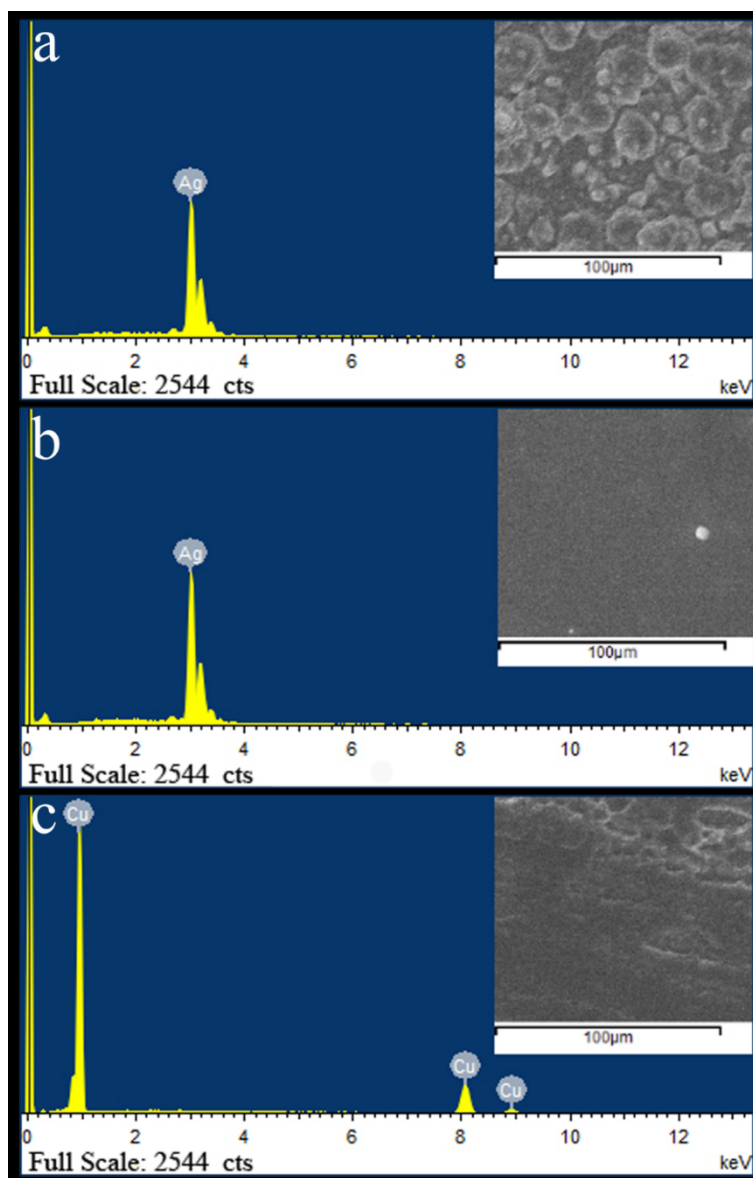
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EDS analysis was carried out to examine the composition of the copper substrate as well as the silver deposit obtained from the cyanide-free silver plating baths without and with the introduced composite additive. Fig. S1 displays the EDS patterns of these samples. The inset is the surface morphology.

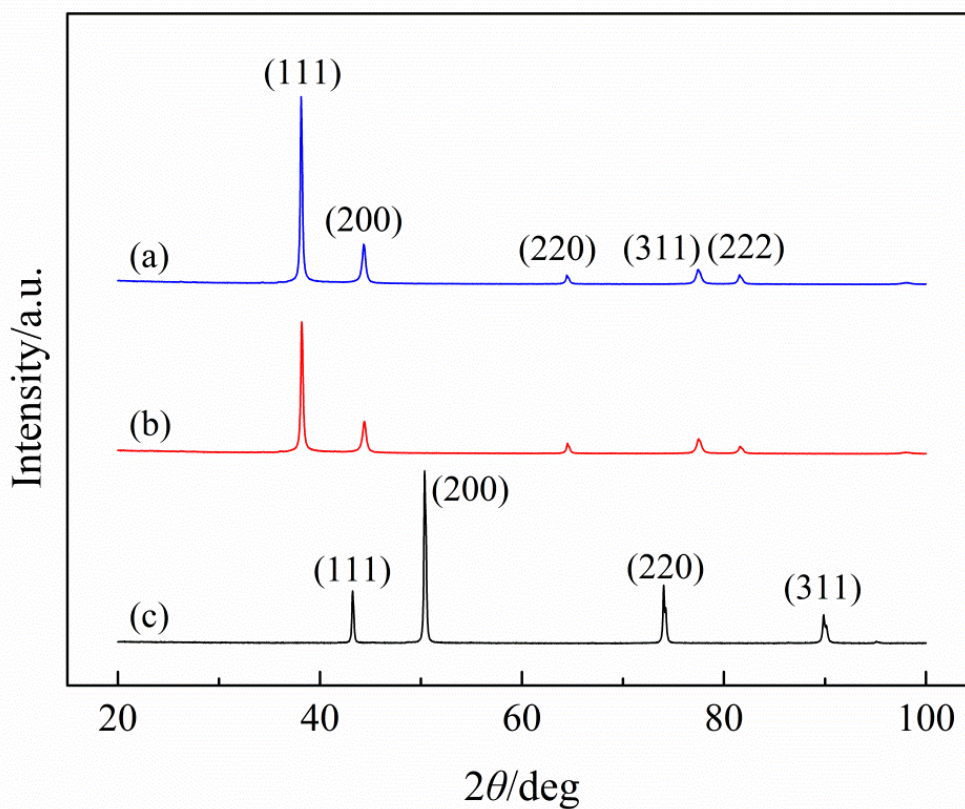
As shown in the EDS patterns, there are only silver signals on the silver deposits obtained from cyanide-free silver plating baths without and with the introduced composite additive. The copper substrate had different EDS patterns compared with the silver deposit, indicating that the deposit obtained from the cyanide-free silver plating bath is pure silver and the purity of the silver deposit was very high.

For application in microelectronics, aerospace, automotive, and jewelry industries, the anti-tarnish abilities and electrical properties of the silver deposits are severely compromised by impurities. Thus, the silver deposit obtained from the cyanide-free bath could be used in microelectronics, aerospace, automotive, and jewelry applications due to its high purity.



**Fig. S1** The EDS patterns of (a) Silver deposit obtained from the basic bath without the introduced composite additive, (b) silver deposit obtained from the bath with the introduced composite additive, and (c) copper substrate.

X-ray diffraction (XRD) patterns of the silver deposits obtained from cyanide-free silver plating bath with and without the introduced composite additive as well as the copper substrate were displayed in Fig. S2.



**Fig. S2** The XRD patterns of (a) Silver deposit obtained from the bath with the introduced composite additive, (b) silver deposit obtained from the basic bath without the introduced composite additive, and (c) copper substrate.

As displayed in Fig. S2 (a) and (b), all peaks can be indexed to silver (111), (200), (220), (311), and (222) crystal face without any additional peak observed, which illustrates that the silver deposits obtained from the cyanide-free silver plating bath with and without the introduced composite additive possess high purity. As displayed in Fig. S2 (c), there are four obvious peaks indexed to copper (111), (200), (220), and (311) crystal face at different  $2\theta$  values with silver deposits. This indicates that the deposit obtained from the cyanide-free silver plating bath is pure silver and the purity of the silver deposit was very high.

The diffraction peak intensity of the (111) facets for the silver electrodeposits

obtained from the cyanide-free silver plating baths with and without the introduced composite additive is larger than that of other peaks, indicating that in the both baths with and without additive the deposition of silver were both expected to occur preferentially on Ag (111) facets. All the peaks of the silver deposit obtained from the cyanide-free plating baths with the introduced composite additive are narrower than those without additive. This indicates that the grain sizes of the silver deposits are much smaller with the addition of the introduced additive into the cyanide-free silver plating bath, corresponding to the results of SEM and AFM measurements.