Supporting Information

Role of polyethyleneimine as an additive in cyanide-free electrolytes for gold electrodeposition

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The concentration of PEI was optimized by electrochemical measurement and material characterization. Different concentrations of PEI, such as 0, 10, 20, 30, 40, 50 mg L\(^{-1}\) were employed to carry out these experiments. The effect of the concentrations of PEI on the gold nucleation process and the morphology of gold electrodeposits were shown in Fig. S1 and Fig. S2, respectively. As displayed in Fig. S1, the cathodic polarization overpotentials are negative shifted with the addition of PEI, while the shift is hardly changed when the concentration of PEI was more than 30 mg L\(^{-1}\). Fig. S2 showed the SEM images of the gold electrodeposits obtained from the DMH-based electrolytes in the presence of different concentrations of PEI, the gold electrodeposits obtained in the presence of 30 and 40 mg L\(^{-1}\) PEI had better surface micromorphology, which were smooth and compact with smallest crystal particles. Based on the electrochemical measurement and material characterization, 30 mg L\(^{-1}\) PEI was selected for further study.

**Fig. S1** Cathodic polarization curves with a scan rate of 1 mV s\(^{-1}\) on the Pt-RDE at 600 rpm, measuring the DMH-based electrolytes in the presence of 0, 10, 20, 30, 40, and 50 mg L\(^{-1}\) PEI.
Fig. S2 SEM images of the gold electrodeposits obtained from the DMH-based electrolytes in the presence of 0, 10, 20, 30, 40, and 50 mg L$^{-1}$ PEI.
Hull cell was employed to study the current density effects on the gold
electrodeposit morphology. And the Hull cell experiments were employed in the gold
electroplating electrolyte in the presence of 30 mg L\(^{-1}\) PEI to determine an optimal
applied current density at 318 K. The Hull cell experiment was carried out at 1 A
current for 10 minutes, macroscopic images of Hull cell gold electrodeposit was
shown in Fig. S3.

![Macroscopic images of Hull cell gold electrodeposit obtained from the DMH-based
gold electroplating electrolyte in the presence of 30 mg L\(^{-1}\) PEI at 1 A current for 10 minutes.](image)

**Fig. S3** Macroscopic images of Hull cell gold electrodeposit obtained from the DMH-based
gold electroplating electrolyte in the presence of 30 mg L\(^{-1}\) PEI at 1 A current for 10 minutes.

As shown in Fig. S3, golden bright gold electrodeposits can be obtained between
2~8 cm. It indicates that golden bright gold electrodeposits can be obtained when the
applied current density was 3.7~35 mA cm\(^{-2}\). And the gold electrodeposits used in this
manuscript were obtained under 8 mA cm\(^{-2}\).

Haring-Blum cell was also employed to study the throwing power of the DMH-
based gold electroplating electrolyte in the presence of 30 mg L\(^{-1}\) PEI under
galvanostatic conditions 8 mA cm\(^{-2}\) at 318 K. The throwing power can be calculated
based Eq. (S1):
\[ T = \frac{K - \frac{M_1}{M_2}}{K - 1} \times 100\% \]  

(S1)

Where \( T \) is the throwing power, \( K \) is the proportion of the distance between the farther cathode and the anode and the distance between the nearer cathode and the anode, \( K=5 \) in our experiments. \( M_1, M_2 \) is the weight of the gold deposit on the farther and nearer cathode, respectively. The average throwing power of the DMH-based gold electroplating electrolyte in the presence of 30 mg L\(^{-1}\) PEI was 80.4\%.
Fig. S4 and Fig. S5 displayed macroscopic and microscopic images of the gold electrodeposits obtained in the absence and presence of 30 mg L\(^{-1}\) PEI under galvanostatic conditions (8 mA cm\(^{-2}\)) for 5 min at 318 K. The gold electrodeposits obtained with bath agitation were both better than that obtained without bath agitation. The current efficiency were around 97% and 92% in the absence and presence of 30 mg L\(^{-1}\) PEI with mild bath agitation, respectively, while they were all about 30% without bath agitation under galvanostatic conditions (8 mA cm\(^{-2}\)) at 318 K. It indicated that bath agitation was very important to enhance the mass transport and improve the macroscopic and microscopic performance of the gold electrodeposit.

**Fig. S4** Macroscopic images of the gold electrodeposits obtained from the DMH-based electrolyte in the absence of PEI (a) with agitation and (b) without agitation, in the presence of 30 mg L\(^{-1}\) PEI (c) with agitation and (d) without agitation.
**Fig. S5** SEM images of the gold electrodeposits obtained from the DMH-based electrolyte in the absence of PEI (a) with agitation and (b) without agitation, in the presence of 30 mg L^{-1} PEI (c) with agitation and (d) without agitation.
Fig. S6 showed the cyclic voltammetry of the fresh and time-aged (more than half a year) gold electroplating electrolytes at 318 K. As displayed in Fig. S6, the curves (a) and (b) are almost overlapped together, which means that the base electrolyte has very good chemistry stability. Contrasting curves (b) and (d), the gold electrodeposition potential of the aged electrolyte with 30 mg L$^{-1}$ PEI was slightly negative than the fresh one so the gold electrolyte with PEI also has good chemistry stability.

**Fig. S6** Cyclic voltammograms with a scan rate of 10 mV s$^{-1}$ on the GCE of the fresh DMH-based electrolyte (a) without PEI, (b) with 30 mg L$^{-1}$ PEI, and the time-aged (more than half a year) DMH-based electrolyte (c) with PEI, (d) with 30 mg L$^{-1}$ PEI.
As displayed in Fig. S7, both the gold electrodeposits obtained in the absence and presence of 30 mg L$^{-1}$ PEI performed a close combination with the substrate.

**Fig. S7** Cross-sectional SEM images of the gold electrodeposits obtained from the DMH-based electrolyte (a) in the absence of PEI and (b) in the presence of 30 mg L$^{-1}$ PEI.