

Electronic Supplementary Information

A composite additive used for a new cyanide-free silver plating bath

(II): an insight by electrochemical measurements and quantum

chemical calculation

Anmin Liu ^{a, *}, Xuefeng Ren ^b, and Maozhong An ^c

^a School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin, 124221, China.

* E-mail: anmin0127@163.com, liuanmin@dlut.edu.cn

^b School of Food and Environment, Dalian University of Technology, Panjin, 124221, China.

^c State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China.

CV measurements at various sweep rates on 3 mm GCE were performed in the absence and presence of additive to study the silver electrodeposition behavior, including the control step of silver electrodeposition, the transfer coefficient, and the diffusion coefficient influenced by additives. The results are shown in Fig. S1.

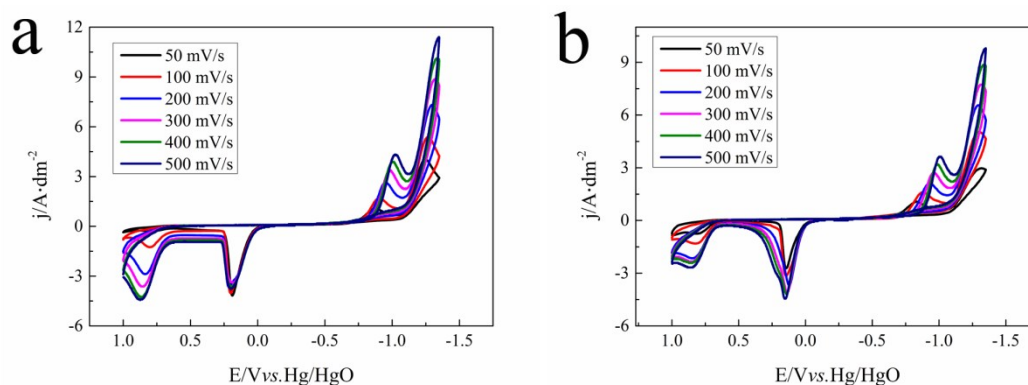


Fig. S1 Cyclic voltammograms with different sweep rates on the GCE of the silver electroplating baths, (a) without additive and (b) with additive.

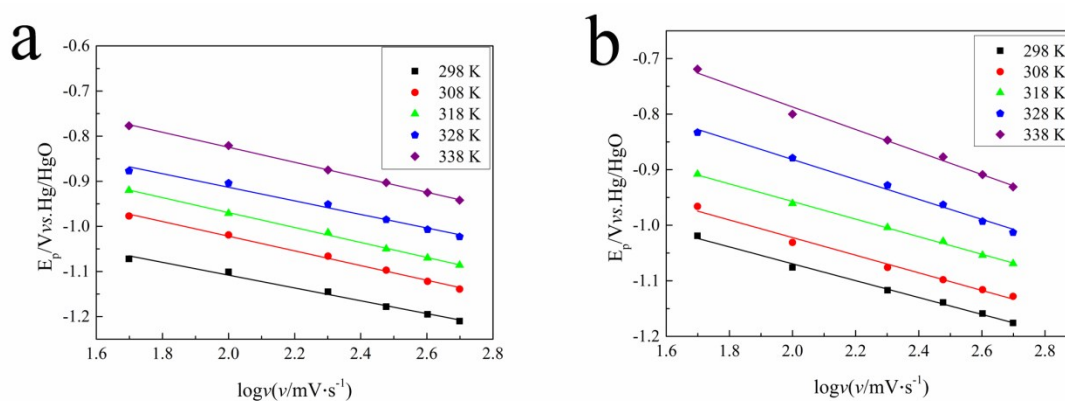


Fig. S2 The peak potential (E_p) of CV with various sweep rates versus $\log \nu$ of the silver electroplating baths, (a) without additive and (b) with additive.

As displayed in Fig. S1, the cathodic peak current density j_p increases and cathodic peak potential E_p shifts negatively with the increase of the sweep rate. At the same time peak potential E_p plotted vs. $\log \nu$ gives a linear response in the both condition as displayed in Fig. S2. Fig. S3 displays that the j_p versus the square root of the scan rate ($\nu^{1/2}$) of the silver plating baths without and with additive also possess a

linear response in the investigated silver plating baths. These indicate that the silver electrodeposition are both irreversible process in the silver electroplating baths without additive and with additive.¹

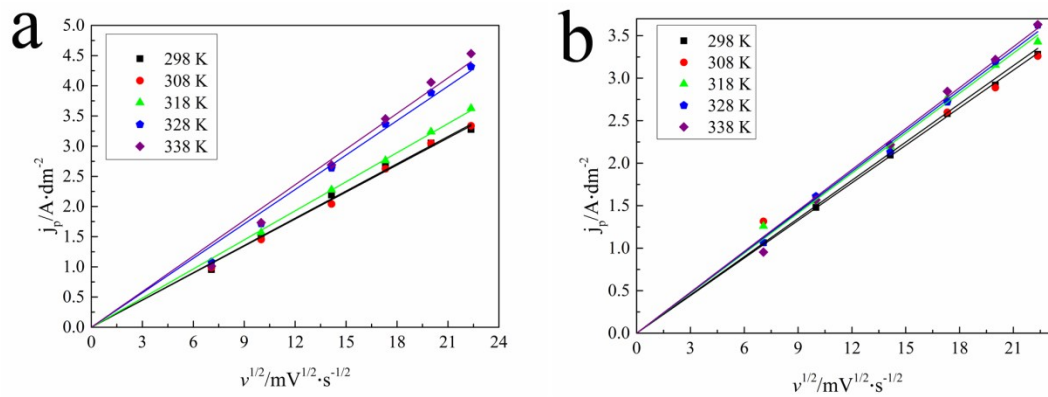


Fig. S3 The peak current density (j_p) of CV with various sweep rates versus $v^{1/2}$ of the silver electroplating baths, (a) without additive and (b) with additive.

Charge transfer coefficient (α), a measure of symmetry barrier in non-reversible (quasi- and irreversible) electrode processes, can be determined from the shift of the E_p (ΔE_p) when sweep rate increase 10 times according to equation (S1)^{2, 3}:

$$\alpha n_\alpha = 1.15RT / (\Delta E_p F) \quad (\text{S1})$$

Where n_α is the number of the transferred electrons in the rate determining step, F is the Faraday constant, and T is the measurement temperature.

As the silver electrodeposition process is total irreversible, the relationship between the cathodic peak current density (j_p) and the square root of the scan rate ($v^{1/2}$) can be expressed as equation (S2):

$$j_p = 0.4958nF^{3/2}c(\alpha n_\alpha D)^{1/2}v^{1/2}(RT)^{-1/2} \quad (\text{S2})$$

Where j_p is the cathodic peak current density, n is the number of electrons involved in the silver electro deposition reaction ($n = 1$), F is the Faraday constant, D is the diffusion coefficient, v is the scan rate, R is the gas constant, T is the temperature, and

c is the concentration of electroactive ions in the bath ($c = 0.088$ M). The fitted j_p vs $v^{1/2}$ plots, presented in Fig. S3, possess a zero intercept and a linear response, indicating that the nucleation process is under diffusion control in the silver electroplating bath, both with and without additive. According to equation (S1) and (S2), the αn_α and diffusion coefficient (D) were calculated at various temperatures, as displayed in Table S1.

Table S1 The diffusion coefficient (D) calculated from CV curves at different temperatures on GCE.

T/K	Without additive			With additive		
	$\Delta E_p/V$	αn_α	$D_0/10^{-8} \text{ cm}^2 \text{ s}^{-1}$	$\Delta E_p/V$	αn_α	$D_0/10^{-8} \text{ cm}^2 \text{ s}^{-1}$
298	0.138	0.214	1.532	0.157	0.188	1.672
308	0.162	0.188	1.772	0.162	0.188	1.785
318	0.166	0.189	2.101	0.161	0.196	1.943
328	0.146	0.223	2.589	0.180	0.181	2.222
338	0.165	0.203	3.131	0.212	0.158	2.676

As displayed in Table S1, the diffusion coefficient was slightly reduced with the addition of additive, indicating that the ion transfer was slightly inhibited in the silver plating bath with additive. Thus the influence of additive on the silver deposition is mainly on the electrochemical behavior, corresponding to the conclusions of the EIS measurements. However, with the increase of temperature, the diffusion coefficient was increased. This proves that the silver electrodeposition process can be accelerated by heating the bath.

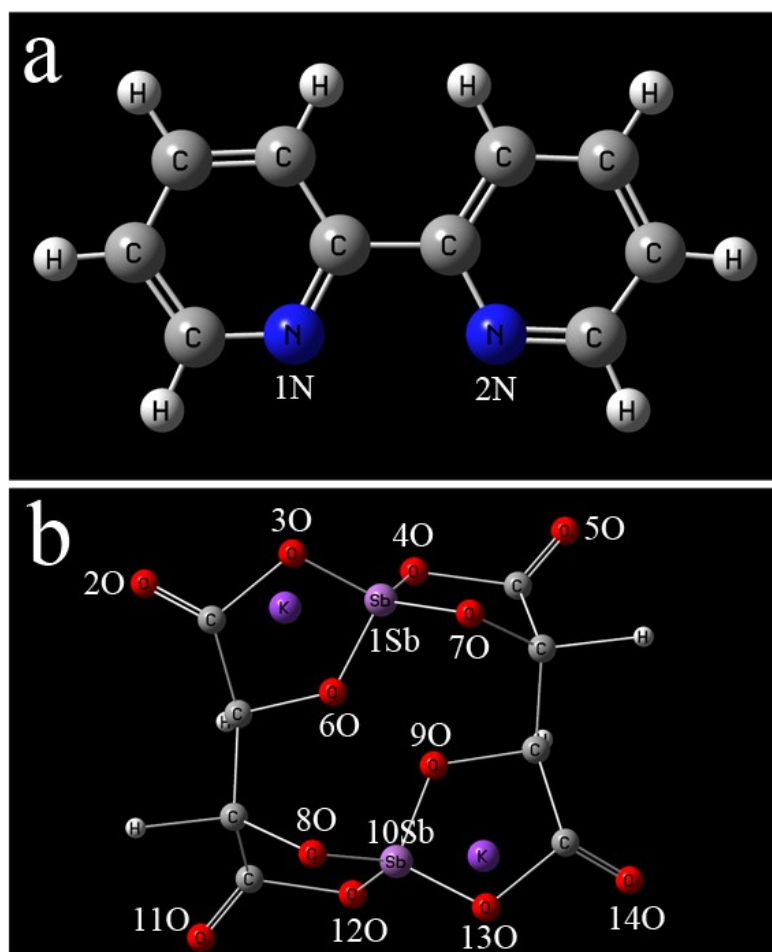


Fig. S4 Optimized structures of (a) BPY and (b) PAT with atom label symbols.

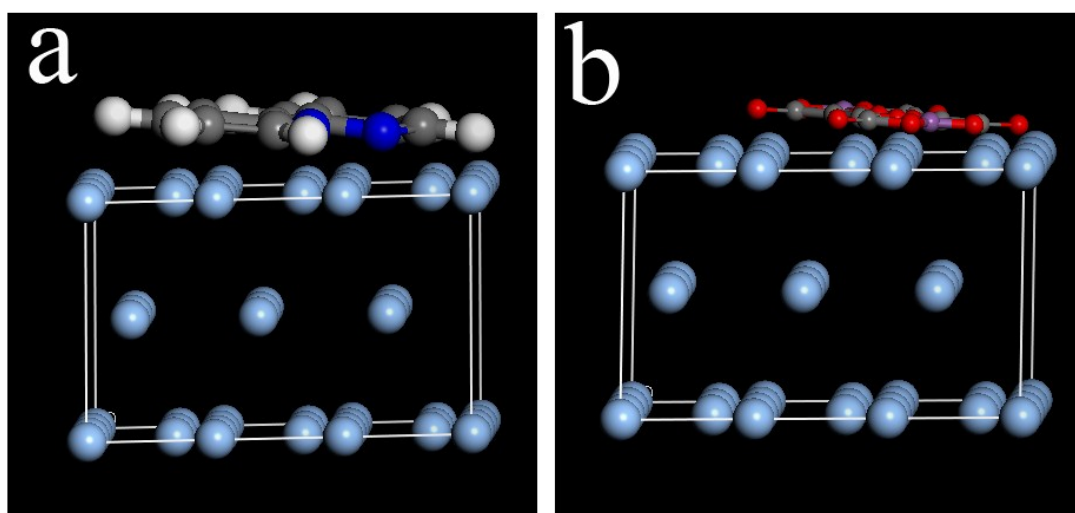


Fig. S5 Interface structures of (a) BPY and (b) PAT²⁻ on Ag (111).

References

1. M. Jayakumar, K. A. Venkatesan and T. G. Srinivasan, *Electrochim. Acta*, 2007, **52**, 7121-7127.
2. X. Yang, M. An, Y. Zhang and L. Zhang, *Electrochim. Acta*, 2011, **58**, 516-522.
3. M. Jayakumar, K. A. Venkatesan and T. G. Srinivasan, *Electrochim. Acta*, 2008, **53**, 2794-2801.