

Electronic Supplementary Information (ESI)

Electrodeposition of Nanostructured Cobalt Selenide Films towards High Performance Counter Electrode in Dye-Sensitized Solar Cells

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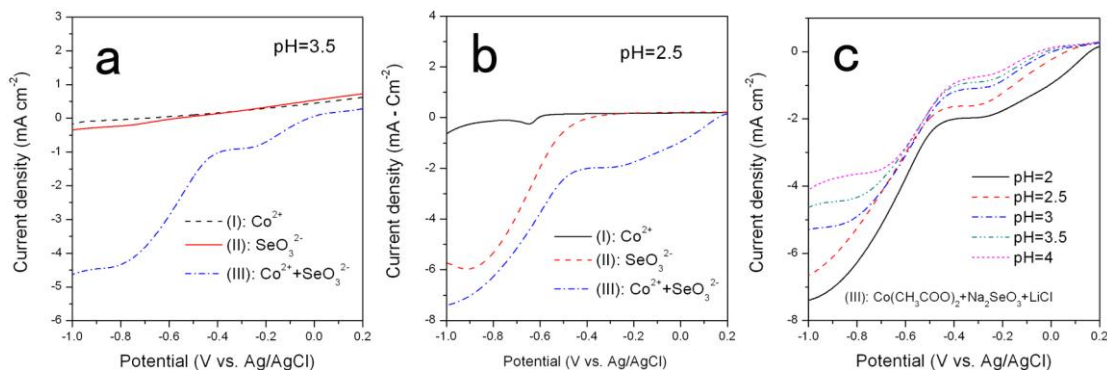


Figure S1. Linear-sweep voltammetry curves of various electrodeposition systems. (a) cathodic sweeps under the pH3.5 for I, II and III electrolyte systems, respectively. (b) cathodic sweeps under the pH2.5 for I, II and III electrolyte systems, respectively. (c) cathodic sweeps of different pH value for the electrolyte system III.

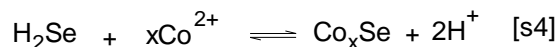
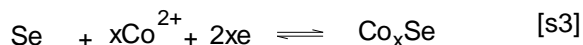
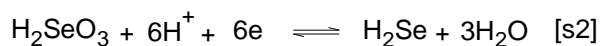
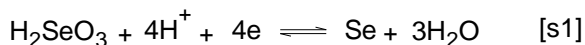
In order to obtain an optimized electrochemical deposition condition, the electrochemical behavior of Co²⁺ and SeO₃²⁻ on FTO glass were firstly studied by a Linear-sweep voltammetry (LSV). The testing solutions contain (I) 20 mM Co(CH₃COO)₂, (II) 20mM Na₂SeO₃ and (III) 20 mM Co(CH₃COO)₂ and 20 mM Na₂SeO₃, respectively. The parallel test solutions were adjusted to the same pH value.

Fig. S1a shows the typical cathodic sweeps at pH3.5 of (I), (II) and (III) solutions, respectively. For the Co(CH₃COO)₂ and Na₂SeO₃ solutions, there are no obvious peaks at the pH value. While for the Na₂SeO₃/Co(CH₃COO)₂ solution, there are two distinct cathodic peaks, which both attribute to the formation of cobalt selenide. According to the previous literature, the low cathodic peak at -0.2 V attributes to a four-electron Se deposition (Eq. S1) which followed by the surface-induced reduction of Co²⁺ to form the cobalt selenide (Eq. S3).^{1,2} The cathodic peak at -0.8 V can be ascribed to a six-electron process, where Co²⁺ directly react with the product of six-

electron process (H_2Se) to form cobalt selenide, which corresponds to Eq. S2 and Eq. S4 respectively.¹

In the case of much lower pH value (<3), the LSV curve of (II) solution system shows obviously different from that of high pH value (>3). Fig S1b shows the typical cathodic sweeps for various solution systems under pH2.5 condition. It is shown that, for solution (II), an obvious reduction peak appeared at the potential range of -0.6 ~ -1.0V. This peak is corresponding to the reaction of Eq. S2 according to the previous literature.¹ There is an initial reductive feature in the potential range from -0.3 ~ -0.5 V, which may correspond to the four-electron predeposition of selenium on FTO substrate, similar to that reported by other groups.^{1, 3, 4} While, at higher pH value, as $[\text{H}^+]$ decreases, lower concentration of H_2SeO_3 result in inhibition of reaction [S1]. So, there is no obvious peak observed for solution system (II), in the case of pH3.5 (Fig. S1a).

However, for the cathodic sweep curve of solution system (III), the curves of pH2.5 is very similar to that of pH3.5, indicating the two processes involving the formation of CoSe can take place in the pH range. Fig. S1c is the cathodic sweep of different pH value for (III) solution system. In the case of pH2.0~4.0, the curves are very similar but with different current density. In order to facilitate the generation of cobalt selenide, in our case, the deposition bias was uniformly selected at -0.8 V.



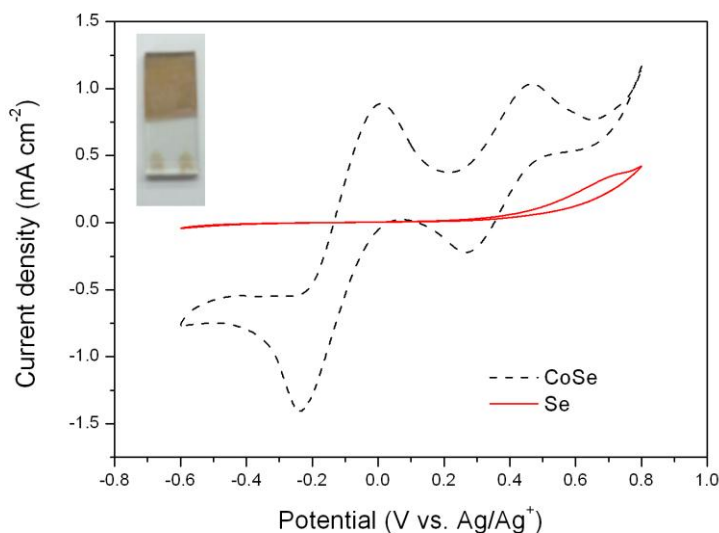


Figure S2. Cyclic Voltammetry (CV) curves of the electrodeposited Se electrode (solid red line) compared with that of the cobalt selenide electrode (black dotted line). Inset is a photograph of the electrodeposited Se electrode.

Preparation of amorphous Selenium electrode. The amorphous Se electrode was prepared by electrochemical deposition method similar to the preparation of cobalt selenide electrodes. The typical deposition bath was a 50 mL aqueous solution containing 20 mM Na₂SeO₃, and 100 mM LiCl. The pH value of applied solution was adjusted to 2.5 by hydrochloric acid.

The electrochemical behavior of cyclic voltammetry for amorphous Se electrode compared with that of CoSe electrode is exhibited in Fig. S2. The inset of Fig. S2 shows a photograph of the amorphous Se electrode, which exhibited a dark red color distinctly different from cobalt selenide electrodes (Fig. 1g).

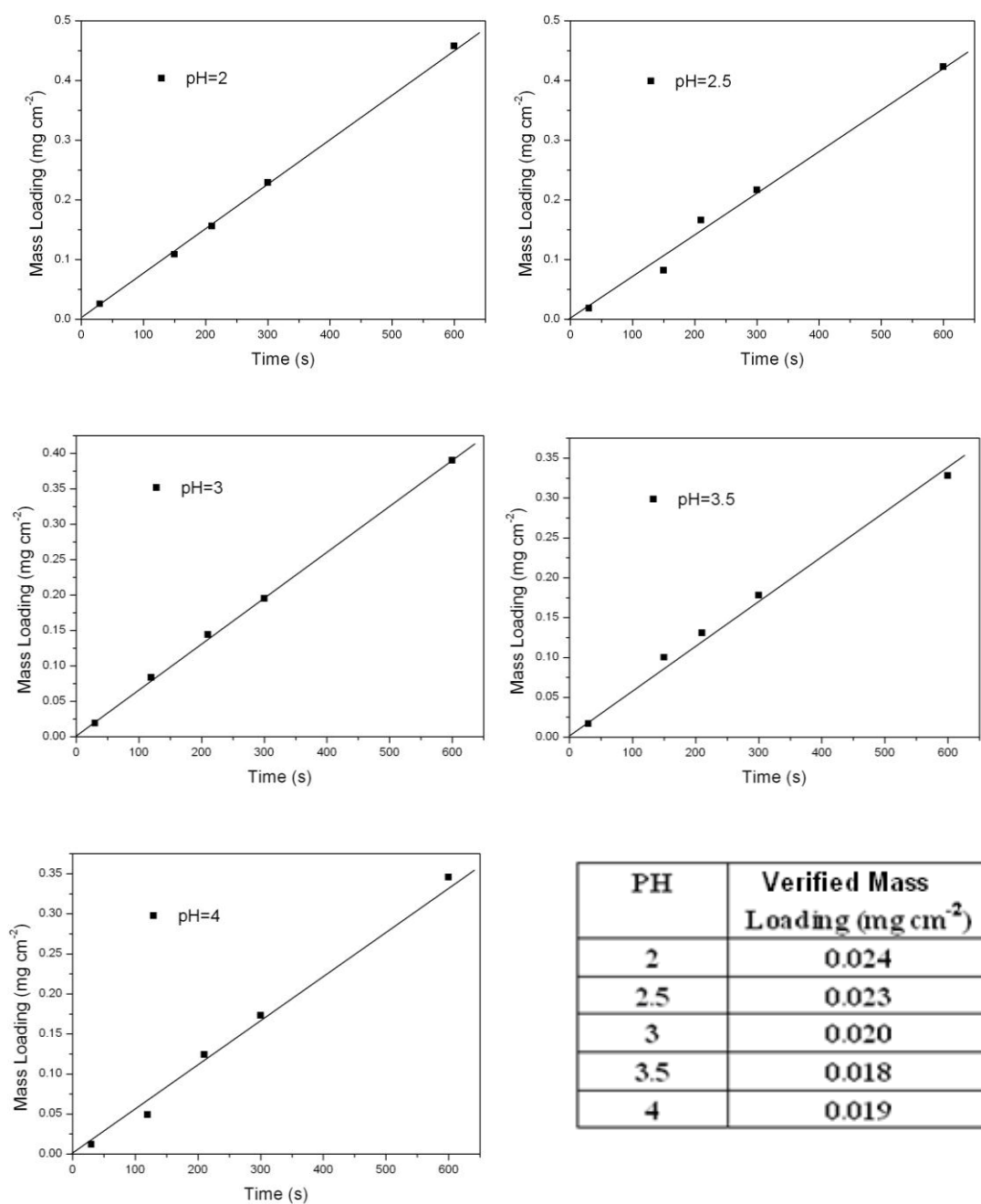


Figure S3. Growth rate curves and the Verified Mass loading under different pH values

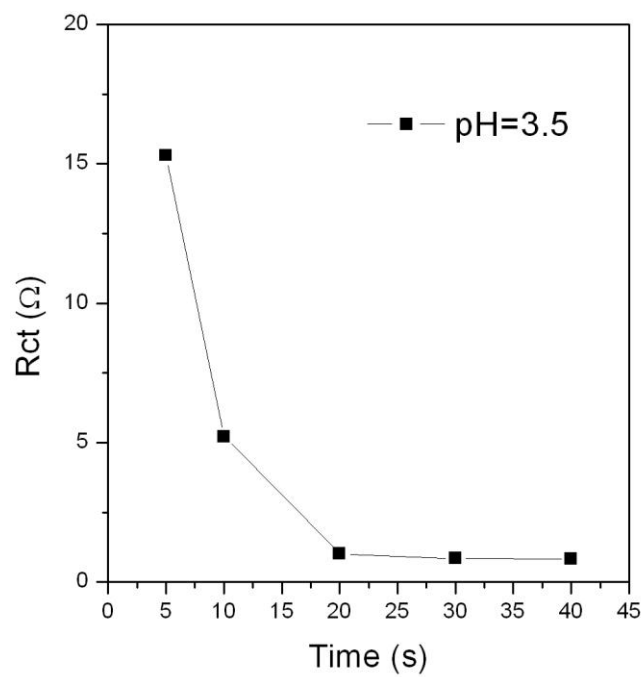


Figure S4. R_{ct} of the cobalt selenide electrodes prepared under various electrodeposition time.

REFERENCE

- 1 F. Y. Liu, B. Wang, Y. Q. Lai, J. Li, Z. A. Zhang, Y. X. Liu, *J. Electrochem. Soc.*, 2010, **157**, D523
- 2 F.A. Kröger, *J. Electrochem. Soc.*, 1978, **125**, 2028
- 3 T. A. Sorenson, T. E. Lister, B. M. Huang, J. L. A. Stickney, *J. Electrochem. Soc.*, 1999, **146**, 1019
- 4 Y. Q. Lai, F. Y. Liu, J. Li, Z. A. Zhang, Y. X. Liu, *J. Electronanal. Chem.* 2010, **639**, 187