Electronic Supplementary Information for:

Photoelectrochemical deposited Sb_2Se_3 thin films: deposition mechanism and characterization

Jia Yang,[a] Yanqing Lai,*[a] Yanyun Fan,[a] Yan Jiang,[a] Ding Tang,[a] Liangxing Jiang,[a] Fangyang Liu,*[a] Jie Lia[a]

[a] School of Metallurgy and Environment, Central South University, Changsha 410083, China

*Corresponding authors:

Yanqing Lai. Tel.: +86 731 88876454. E-mail: laiyanqingcsu@163.com

Fangyang Liu. Tel.: +86 731 88830649. E-mail: liufangyang@csu.edu.cn

The transmittance of electrolytes

The transmittance of electrolytes is illustrated in Fig. S1 and is an important factor affecting incident light harvested by as-deposited film. Fig. S1 (a)~(c) shows the transmittance of the deionized water, the Se electrolyte solution (containing 4.5 mM H_2SeO_3, and 100 mM NH_4Cl, pH = 2.3) and the Sb-Se electrolyte solution (containing 5.5 mM $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$, 4.5 mM H_2SeO_3, and 100 mM NH_4Cl, pH = 2.3). Fig. S1(d) compares the transmittance of the all above solutions, which shows a very similar transmittance in wavelength range of 300~2000 nm, indicating that incident light has no discriminative effect on various ions in electrolyte. The transmittance of electrolytes shows a similar low value in wavelength ranging from 900 to 2000 nm (as a part of infrared), because liquid water has a strong absorption in the infrared[1] blocking the transmission of infrared light. As infrared radiation is an important process of heat transfer, the absorption of the infrared will lead to the rise of

temperature and thermalmotion in electrolytes (photothermal effect). However the temperature variation of 250 ml electrolytes for 30 min illumination is about 3.7 ℃. Such a little temperature rise is ignorable and can not be a dominant factor for the variation of electrochemical behavior. While the transmittance of electrolytes shows a very high value in the wavelength range of 300~900 nm indicating that light in this wavelength range can illuminate on as-deposited films. The light in this wavelength range (4.13~1.38 eV) can be absorbed by as-deposited films for exciting electrons and holes (photoelectric effect) because the band gap[2] of Sb_2Se_3 is approximately 1.3 eV. For xenon lamp spectra, light in the wavelength range of 300~900 nm covers almost total emitted light[3]. Consequently, the influence of illumination on electrochemical behavior is dominated by photoelectric effect rather than photothermal effect.

Figure S1. (a) The transmittance of blank solution (water); (b) the transmittance of solution containing 4.5 mM H_2SeO_3, and 100 mM NH_4Cl (red line); (c) the transmittance of solution containing 4.5 mM H_2SeO_3, 5.5 mM $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$ and 100 mM NH_4Cl (green line); (d) comparison of the transmittance spectra for three solutions of Sb-Se systems.

Potentiostatic polarization curves

Fig. S2 displays the typical potentiostatic polarization curves for revealing the different deposition current densities between the PED and CED process of Sb_2Se_3 at deposition potential of -0.45 V (Fig. S2(a)) and -0.55 V (Fig. S2(b)), respectively. It is obvious that the magnitudes of deposition current densities are enhanced in PED

process. This is an interesting phenomenon, concerning that the cathodic deposition rate of Sb_2Se_3 thin film gets increased under illumination due to the generation of additional photocarriers (photoholes and photoelectrons). As the photocarriers could increase the conductivity of film and promote the electroreduction of ions. The potentiostatic polarization curves and linear sweep photovoltammogram exhibit the same tendency of current density under illumination, which is consistent with the mechanism analysis.

Except the observation above, the reduction current densities of PED process present relatively steady, which is different from the rapidly decreasing reduction current densities of CED process. Because the accumulation of low conductive Sb_2Se_3 films on the surface of cathode, the reduction current densities of CED process show such a rapidly decreasing. PED process can overcome the rapidly decreasing electroreduction rate due to the photosensitive property of Sb_2Se_3 films.

Figure S2. The typical potentiostatic polarization curves for PED and CED Sb_2Se_3 at deposition potential of (a) -0.45 V and (b) -0.55V.

SEM and visual photographs of Sb_2Se_3 thin films

Fig. S3 shows the SEM and visual photograph (right top insets) of Sb_2Se_3 thin films prepared by CED (a), (c) and by PED (b), (d) at different deposition potentials (-0.45 V (a), (b) and at -0.55 V (c), (d)). From the SEM micrographs, it can be observed that PED Sb_2Se_3 films have more homogeneous and smooth morphology. The visual photographs show that film obtained by CED at -0.55 V is semitransparent,

and the film electrodeposited at -0.45 V is much more transparent. However, a significant observation is the evolution of the transparency of Sb_2Se_3 films deposited by PED on SnO_2/glss substrates. Combined with the visual photographs, PED process at -0.55 V is proved to be favorable to improve homogeneous growth of film.

The improvement of Sb_2Se_3 layer in homogeneity should be related to the fact that photons supply an additional energy to the film surface and activate surface processes such as surface diffusion. And the new reduced atoms which hold high kinetic energy can move to appropriate positions and form a more stable lattice plane. The phenomenon has also been observed by Tseng[2] and Yin-Hsien Su[4].

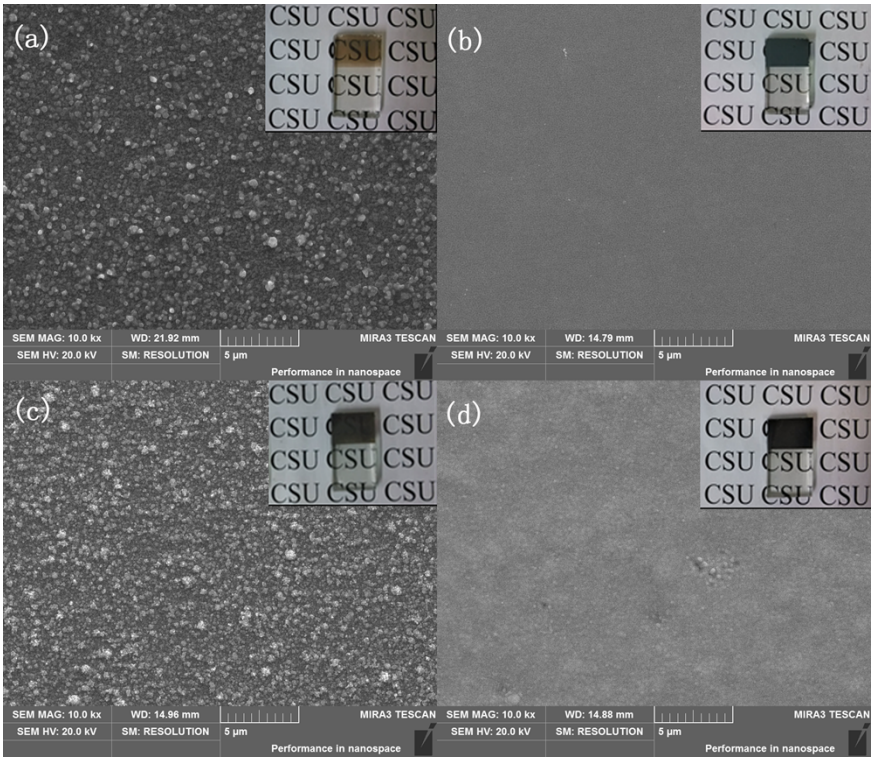

Figure S3. SEM and visual photographs of Sb_2Se_3 thin films (a) prepared by CED at -0.45 V; (b) prepared by PED at -0.45 V; (c) prepared by CED at -0.55V; (d) prepared by PED at -0.55V.

References

1. N. A. Marley, J. S. Gaffney and M. M. Cunningham, *Environ. sci. technol.*, 1993, **27**, 2864-2869.
2. M. Leng, M. Luo, C. Chen, S. Qin, J. Chen, J. Zhong and J. Tang, *Appl. Phys. Lett.*, 2014, **105**, 083905.
3. https://en.wikipedia.org/wiki/Xenon_arc_lamp).
4. Y.-H. Su, T.-W. Chang, W.-H. Lee and B.-H. Tseng, *Thin Solid Films*, 2013, **535**, 343-347.