Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

One-step Electrodeposition of $CuIn_xGa_{1-x}Se_2$ Thin Films from a Mixture System of Ionic Liquid and Ethanol

Ye Lian, Shanshan Ji, Lei Zhao, Jie Zhang, Peixia Yang, Jinqiu Zhang, Maozhong An*

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

*Corresponding author. Tel./Fax: +86 451 86418616

E-mail address: mzan@hit.edu.cn (M. Z. An)

1. **Unitary cyclic voltammograms**

The cyclic voltammograms (CVs) of unitary system recorded on GCE in the mixture system of ionic liquid and ethanol are presented (Fig. S1).

Fig. S1a is the CV of $BMImBF_4$ mixed with 25 vol.% ethanol containing 10mmol·L^{-1} $CuCl_2$, and there are two gentle reduction peaks of $Cu^{2+/+}$and $Cu^{+/0}$ at -0.09 V, -1.26 V. But the reduction peak of copper is not observed in CV of binary (Cu-Se) system (Fig. 1b).

In the unitary cyclic voltammogram of selenium (Fig. S1b), reductive wave of Se^{4+} to Se^0 is at -0.66 and Se^0 to Se^{2-} at -1.39 V , however the reduction potential of $Se^{4+/0}$ and $Se^{0/2-}$ are -0.78 V, -1.41 V in binary (Cu-Se) system (Fig. 1b). We hypothesise that the negative shift is a result of the higher activation energy needed to form the alloys and therefore, a higher overpotential is required as well.[1]

According to the Fig. S1c, the reduction potential of $In^{3+/0}$ is at -1.25V, it negative shift to -1.77 V in the ternary (Cu-In-Se) (Fig. 1c),[2] quaternary (Cu-In-Ga-Se) system (Fig. 1d) like selenium in binary (Cu-Se) system.

There is a obviously reduction peak of Ga^{3+} at -2.09V in Fig. S1d, and a gentle wave is observed at the same potential in quaternary (Cu-In-Ga-Se) system (Fig. 1d). At first, we hypothesise that the wave in quaternary system is the reduction of gallium or the co-deposition peak of gallium with other element. Afterwards, the XRD pattern of deposited CIGS thin film indicates the existence of gallium alloy and no independent gallium, consequently, we suggest the the wave at -2.09V in quaternary system is the co-deposition peak of gallium with other element.

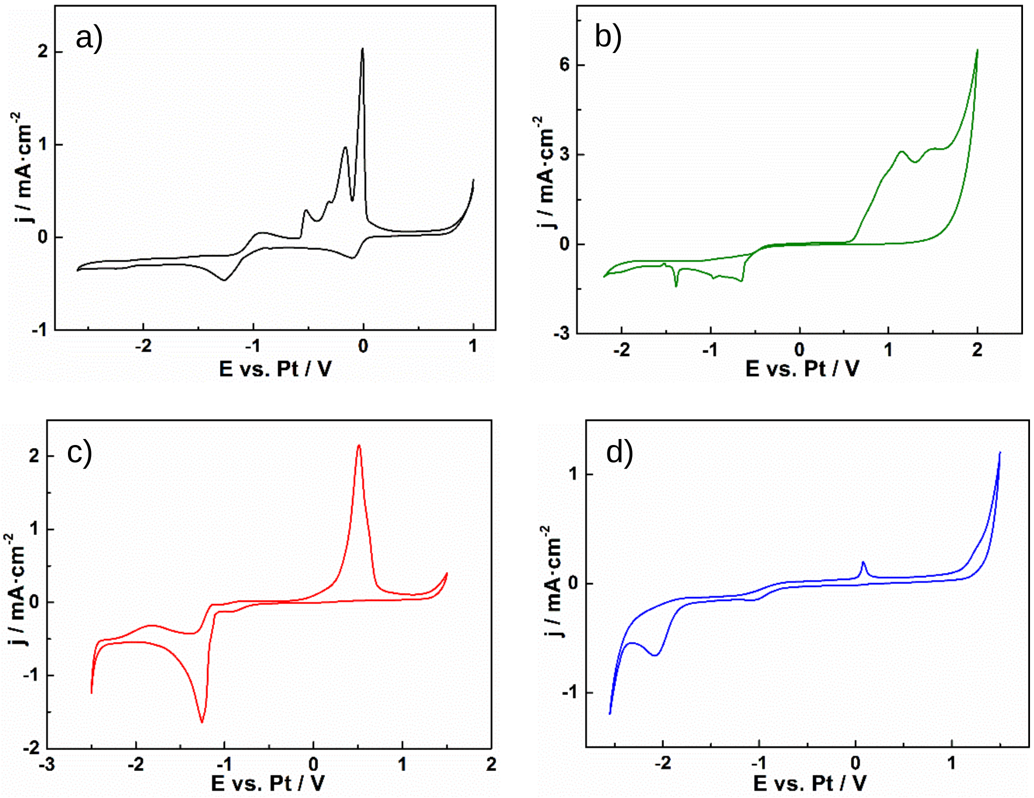

Fig. S1 Cyclic voltammograms recorded for $BMImBF_4$ mixed with 25 vol.% ethanol containing: (a) 10mmol·L^{-1} $CuCl_2$; (b) 20mmol·L^{-1} $SeCl_4$; (c) 25mmol·L^{-1} $InCl_3$; (d) 10mmol·L^{-1} $GaCl_3$ on a GCE electrodes at 40 ℃ with scan rate 10mV·s^{-1}.

2 The calculation method of band gap

Band gap is an important characteristic parameter of semiconductors. Band gap can be measured by UV-vis spectrophotometer, and the data processing is indispensable. The principle is from *Semiconductor Devices Physics and Technology*[3] and the approach is according to the study of Soon Hyung Kang et al.[4]

After the samples are measured by UV-vis spectrophotometer, λ is obtained. According to Eq. (1), we get $h\upsilon$, then Eq. (2) which decides the exact optical bandgap (E_g) can be calculated.

$$h\upsilon(\mathrm{eV})=\frac{1240}{\lambda} \tag{1}$$

$$\alpha = \frac{\mathrm{A}}{h\upsilon}\sqrt{(h\upsilon - E_g)} \qquad (2)$$

In Eq. (2), A is a constant which depends on the transition probability and refractive index of the material, $h\upsilon$ is the radiation energy, and E_g is the transition energy.

Next, plotting the straight line between $(\alpha h\upsilon)^2$ and $h\upsilon$, making use of the extrapolation of the energy axis, the band gap can be obtained.

References

1 J. C. Malaquias, M. Steichen and P. J. Dale, *Electrochim. Acta*, 2015, **151**, 150–156.

2 J. C. Malaquias, D. Regesch, P. J. Dale and M. Steichen, *Phys. Chem. Chem. Phys.*, 2014, **16**, 2561–2567.

3 S. M. Sze, *S.M. Sze*, .

4 S. H. Kang, Y. K. Kim, D. S. Choi and Y. E. Sung, *Electrochim. Acta*, 2006, **51**, 4433–4438.