Electrodeposition of CuSe Nanosheets films and its growth mechanism

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Abstract. Copper selenide nanosheets films were synthesized successfully by simple electrodeposition method with controlling various experimental parameters. CV was used to study its growth process. It demonstrated that copper selenium is formed by an induced co-deposition mechanism where selenium is deposited first and then the reduction of Cu⁺ is induced, finally the formation of copper selenide nanostructures is finished.

1. Introduction

As a class of multifunctional semiconductors with layered structure, CuSe is identified as p-type semiconductor due to the existence of copper vacancies within crystal lattice, and widely used in solar cells, [1] gas sensors, [2] and photo-detectors. [3] CuSe nanomaterials have been prepared by diverse methods including hydrothermal method, solvothermal method, microwave-assisted polyol process, and mechanical alloying route. [4-6] However, to date, synthesis of copper selenide nanosheets has rarely been reported.

In this paper, novel two-dimensional (2D) CuSe nanosheets films were successfully synthesized via electrodeposition method. The growth mechanism was study carefully using Cyclic voltammograms(CV) technique. It demonstrated that copper selenium is formed by an induced co-deposition mechanism, where selenium is deposited first and then the reduction of Cu⁺ is induced, finally the formation of copper selenide nanostructures is finished.

2. Experimental details

For the deposition of cupper selenium nanosheets film, the electrolyte was prepared by dissolving CuCl₂*2H₂O (2 mM/L), SeO₂ (4.5 mM/L) and KCl(99%)(0.1 M/L) in distilled water. The pH of the solution was adjusted to 1.5 by using 0.2M HCl solution. The electrolyte was not stirred during all the electrochemical measurements and depositions. The electrodeposition was carried out in a conventional three-electrode electrochemical cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode, and gold coated polyethylene terephthalate (PET) was used as working electrode. To obtain high quality nanosheets film, a series of experiments on the basis of orthogonal experimental design were performed to optimize the deposition parameters. The deposition temperatures were varied from 20 °C to 80 °C, and the deposited potentials were varied from -0.02 V to -0.20 V.

3. Results and Discussion
Figure 1. CV of the relative electrolytes. a) 4.5 mM SeO$_2$+0.1M KCl. b) 2.5mM CuCl$_2$+0.1M KCl. c) 4.5 mM SeO$_2$+2.5mM CuCl$_2$+0.1M KCl. The PH values of the electrolytes were adjusted to 1.5. The scan rates were kept at 10mV/S.

To study electrochemical features of Cu and Se induced co-deposition, a series of CV were done on Au coated PET substrates. Figure 1a shows the typical CV containing 4.5mM SeO$_2$ in 0.1M KCl solution. A weak cathodic current begins to flow at +0.12 V (inset in Figure 1a), while the current changes slowly from +0.12 to -0.36 V, after which it increases rapidly and a very strong reduction peak appears at -0.52 V. Combined with the previous results, the assignment of the cathode polarization process can be described as follow. The weak reduction current in the potential ranging from +0.12 V to -0.2 V indicating slow deposition kinetics, corresponds to bulk selenium deposition through four-electron reduction of Se$^{4+}$ to Se$^0$. The process is described by Eq. 1. This characterization qualitatively is similar to the under-potential deposition (UPD) of metals, involving the formation of the first monolayer selenium before the bulk deposition. The followed deposition of Se is, however, prevented by slow deposition kinetics due to the passivating effect of the selenium film. It is verified by the fact that in the second scan, the cathodic current density is much smaller than that observed at the Au surface. For the electrodeposition Se at -0.52 V, it goes through a two-step reaction, the first step of which corresponds to the six electron reduction from HSeO$_3$ to H$_2$Se (Eq. 2), and the second step is a chemical reaction between HSeO$_3$ and H$_2$Se according to Eq. 3. The electrodeposition mechanism of Se in the potential ranging from -0.20 V to -0.52 V is attributed to the competition between four-electron reaction and six-electron reaction. Additionally, the deposition process is influenced by the substrate surface and additional ions, which can change its deposition potential.

$$\text{HSeO}_3^- + 5\text{H}^+ + 4\text{e}^- = \text{Se} + 3\text{H}_2\text{O} \quad \text{Eq. 1}$$

$$\text{HSeO}_3^- + 7\text{H}^+ + 6\text{e}^- = \text{H}_2\text{Se} + 3\text{H}_2\text{O} \quad \text{Eq. 2}$$

$$\text{HSeO}_3^- + 2\text{H}_2\text{Se} + \text{H}^+ + 6\text{e}^- = 3\text{Se} + 3\text{H}_2\text{O} \quad \text{Eq. 3}$$

Figure 1b depicts the CV obtained in 2.5 mM CuCl$_2$+0.1 M KCl solution. The reduction current starts to flow at +0.40V and formed a reduction peak at +0.13V, which corresponds to the transformation of Cu$^{2+}$ to Cu$^+$ as described by Eq. 4. According to Eq.5, the subsequent peak at -0.22V corresponds to the reduction of Cu$^+$ to metallic Cu, and the later process is verified the metallic copper deposition with an unsymmetrical oxidation peak at -0.05 V. [10]

$$\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+ \quad \text{Eq. 4}$$

$$\text{Cu}^+ + \text{e}^- = \text{Cu} \quad \text{Eq. 5}$$

The electrodeposition of CuSe was conducted on Au-PET substrate using 4.5 mM SeO$_2$, 2.5mM CuCl$_2$, and 0.1M KCl as the electrolyte. The CuSe formation mechanism was studied first by CV as shown in Figure 1C. When both Cu$^{2+}$ and Se$^{4+}$ ions are present in the solution, significant change occurs during the initial scan. The first cathodic peak is seen at about +0.1V, which has a small potential shift compared with the reduction of Cu$^{2+}$ to Cu$^+$ measured containing only CuCl$_2$. The phenomena were very common if additional ions were added. The second cathodic peak is at about -
0.1V, which corresponds to the reduction of Cu\(^+\) induced by Se\(^2-\) and thus the CuSe formed before the deposition of metallic Cu. The formation of CuSe is processed by the Eq. 6. As mentioned above, in the first monolayer, Se formed at +0.12 V through UPD-like process, then the Cu\(^+\) in the electrolyte will be combined by as-deposited Se. Meanwhile, Se is being deposited on CuSe at the same deposition potential, which runs the reaction continually. Since the reduction of Se and the remaining of the Cu\(^+\) in the electrolyte can take place at the same time during a large deposit potential about from +0.1 V to -0.2V, the electrodeposition of CuSe may undergo in the same deposit potential range. Thus, it concludes that copper selenium is formed by an induced co-deposition mechanism that selenium is deposited first then the Cu\(^+\) reduction is induced and finally the formation of copper selenide nanostructures is finished. The HSeO\(_3^-\) ions shift the reduction potential of Cu\(^+\) significantly to the negative direction, and the cathodic current increases rapidly at \(-0.3V\) forming a cathodic peak at \(-0.45V\), which corresponds to the formation metallic Cu and is not suitable for formation CuSe, which do not discussed here.

\[
\text{Se + Cu}^+ + e^- = \text{CuSe}
\]

Eq. 6

Based on the CV results, a series of experiments were carried out to observe the effect of deposition potential on the growth of CuSe nanosheets. Figure 2a-e show the SEM images of the deposits obtained at different deposition potential. The as-prepared nanosheets cross each other and almost perpendicular to the substrate. It is found that the deposition potential has a remarkable influence on the as-prepared products. When the deposition potential is -0.02 V, the CuSe nanosheets are unevenly sized. Some of them can reach 5 \(\mu\)m while others only several hundred nanometers. With increasing the deposition potential, the deposited products trend uniformed gradually. For the deposition potential of -0.15 V, the nanosheets are uniformed with the average size about 700 nm. However, when changing the deposition potential to -0.20 V, the size of the nanosheets increases. The specific statistical distribution is shown in Figure 2f. At more negative cathodic deposition potentials, some bubbles will come out from the cathodic substrate, which corresponds to the formation of H\(_2\)Se. Since the bubbles would block the growth of the nanosheets, only a few nanoparticles were found on the substrate.

Figure 2. SEM images of the CuSe nanosheets obtained at different deposition potential. a) -0.02 V; b) -0.05 V; c) -0.10 V; d) -0.15 V; e) -0.20 V. f) The statistical distribution of the nanosheets. The deposition time was 30 min and deposition temperature was 60 \(^\circ\)C. The scale bar is 5 \(\mu\)m.
Figure 3. Schematic illustration of the growth of CuSe nanosheet. Left hand is the unit cell of the klockmannite CuSe. (a-d) Atomic models of CuSe nanosheet at different growth stage.

CuSe nanosheets were synthesized during the electrodeposition under a wide range experiment condition, which indicated that the morphology of the product is affect by its special crystal structure. To understand the growth mechanism of CuSe nanosheets, a series atomic model were proposed as illustrated in Figure 3. The left-hand side is the unit cell of the klockmannite CuSe, where the green atoms are copper and brown atoms are selenium. The Cu atoms are in two different environment, CuSe$_3$ (triangular planes) and CuSe$_4$ (tetrahedron). The unit cell can be seen as slabs connected by Se–Se bonds. The tetrahedral units are linked by vortex through triangular layers. The Cu$_1$–Se bond at triangular planes is 2.275 Å, while the Cu$_2$–Se bonds at tetrahedron are 2.408 Å and 2.375 Å respectively. It is worth noting that the Cu$_1$–Se bonds are striking shorter than Cu$_2$–Se bonds, which suggests Cu$_1$–Se bonds strength is much larger than Cu$_2$–Se bonds. The Se–Se bond length at connect layer is 2.378 Å and combined with covalent chemical bond. [11]

When the deposition potential is lower than +0.13V, Se atoms are formed on the cathodic substrate by the redox of Se$^{4+}$ ion. At the same time, Cu$^{2+}$ ion turns into Cu$^+$ ions at the same potential. The deposited Se atoms combine with Cu$^+$ by sacrifice electrons supplied by the cathode, and form CuSe dipoles through ionic bonding as illustrated in Figure 3a. The main reason is that the Cu$_1$–Se bond length is much smaller than the other bond, which makes them combined more easily. The feature makes them grow fast in the Cu$_1$–Se triangular plane. When the slab is extend to a certain degree, scattered Cu$^+$ will be combined with Se out of the plane to reduce its surface energy (Figure 3b), meanwhile, the dangling bonds of Cu will be the site adsorbing Se to form the Cu$_4$Se tetrahedron layer. In this layer, Cu$_2$–Se bonds are no longer in-plane, but zigzag form as shown in Figure 3c. Once the Cu$_2$–Se bonds form, the Cu$_4$Se tetrahedron layer will grow fast due to the polarization of the positive and negative ionic charges on the Cu$^{2+}$ and Se$^{2+}$ terminated surfaces. According to its atomic model, Se atoms will combine with Se atoms to form Se–Se in the following growth process. Because the binding ability of Se–Se is much lower than Cu–Se, the growth rate of Se–Se layer is much slower than Cu–Se layer, which leads to the formation anisotropic 2D CuSe nanosheets. When the electrolyte temperature is low, Cu$^+$ is difficult to combine with Se$^{2+}$ to enter its lattices on the viewpoint of thermodynamic.
4. Conclusions

In summary, 2D cupper selenide nanosheets films were synthesized on Au coated PET substrate by the simple electrodeposition. CV was used to study its growth process. It demonstrated that copper selenium is formed by an induced co-deposition mechanism, where selenium is deposited first and then the reduction of Cu$^+$ is induced, and finally the formation of copper selenide nanostructures is finished.

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References

[1] Seo, Y.-H.; Lee, B.-S.; Jo, Y.; Kim, H.-G.; Choi, Y.; Ahn, S.; Yoon, K.; Woo, K.; Moon, J.; Ryu, B.-H.; Jeong, S. 2013 J. Phys. Chem. C 117 9529-9536.
[2] Xu, J.; Zhang, W.; Yang, Z.; Ding, S.; Zeng, C.; Chen, L.; Wang, Q.; Yang, 2009 S Adv. Funct. Mater. 19 1759-1766.
[3] Seo, Y.-H.; Lee, B.-S.; Jo, Y.; Kim, H.-G.; Woo, K.; Moon, J.; Choi, Y.; Ryu, B.-H.; Jeong, S. 2013 Acs App. Mater. Inter. 5 6930-6936.
[4] Wu, YM; Korolkov, I; Qiao, X; Zhang, XH; Fan, J; 2016 J. Solid State Chem. 238 279-283
[5] Wu, XJ; Huang, X; Liu, JQ; Li, H; Yang, J; Li, B; Huang, W; Zhang, H 2014 Angew. Chem. Int. Edit 53 5083-5087
[6] Gu, YJ; Su, YJ; Chen, D; Geng, HJ; Li, ZL; Zhang, LY; Zhang, YF 2014 Crystengcomm 16 9185-9190
[7] Dhanam, M.; Manj, P. K.; Prabhu, R. R. 2005 J. Cryst. Growth 280, 425-435.
[8] Kemell, M.; Ritala, M.; Salonieri, H.; Leskela, M.; Saajavaara, T.; Rauhala, E. 2000 J. Electrochem. Soc. 147, 1080-1087.
[9] Kemell, M.; Salonieri, H.; Ritala, M.; Leskela, M 2000 Electrochim. Acta, 45, 3737-3748.
[10] Sebastian, P.; Valles, E.; Gomez, E 2014 Electrochim. Acta, 123, 285-295.
[11] Morales-Garcia, A.; Soares, A. L., Jr.; Dos Santos, E. C.; de Abreu, H. A.; Duarte, H. 2014 A J.Phys. Chem. A 118, 5823-5831.