Tin and Indium Sulfide by Plasma-Enhanced Atomic Layer Deposition for CO_2 Electroreduction

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The increase in concentration of CO_2 in the atmosphere continues to be an alarming environmental concern. Electrocatalytic reduction of CO_2 (CO_2RR) is a promising strategy that uses electrical energy to convert CO_2 to a range of carbon-based useful chemical products. Formate (HCOOH) is one of those products with great potential as a hydrogen carrier and as a precursor to produce industrially-relevant chemicals. In the quest to replace noble metal Pd electrocatalysts for formate production, researchers have identified In, Sn and Bi compounds as promising alternative candidates.[1] It is known that material properties such as crystallinity, surface chemical composition and surface morphology greatly impact electrocatalytic performance. Here, we explored thermal and plasma-enhanced atomic layer deposition (PE-ALD) to control these properties of SnS_2 and In_2S_3 films and evaluate their impact on CO_2RR.

Thin films of tin sulfide and indium sulfide have been deposited via thermal ALD using H_2S in combination with tetrakis(dimethylamido)tin (TDMASn) and indium acetylacetonate (In(acac)$_3$) respectively.[2][3] Inspired by several reports illustrating the significant influence of using plasma on the ALD growth characteristics and material properties of sulfides,[4][5] we employed H_2S plasma as the reactant in this work. The PE-ALD process for In_2S_3 using In(acac)$_3$ and H_2S plasma exhibits a growth per cycle of 0.36-0.14 Å/cycle in the temperature range of 145-260 °C. X-ray diffraction analysis reveals a tetragonal In_2S_3 phase in the whole temperature range. (Fig. 1) The surface morphology of the In_2S_3 films is identified to be rough with continuous crystallite structures. (Fig. 2)

The PE-ALD process for SnS_2 exhibits steady growth with a growth per cycle of 1.07-0.9 Å/cycle after a short incubation period in a temperature range of 80-180 °C. (Fig. 3) In comparison to the thermal ALD process which deposits amorphous SnS_2 thin films at 80°C and a mixture of SnS and SnS_2 phases at 180°C, the PE-ALD process deposits crystalline SnS_2 with strong c-axis oriented growth and most of the basal planes aligned parallel to the substrate in the temperature range of 80-180°C. (Fig. 4) Additionally, a transition in morphology from grain-like structures (30-50 nm) to out-of-plane oriented structures is found for SnS_2 deposited by PE-ALD at 80°C and 180°C, respectively.

To evaluate the sulfide thin films for CO_2RR, electrodes are prepared by applying thermal or PE-ALD directly on carbon gas diffusion electrodes (GDEs). Also on this substrate, the different ALD process conditions lead to differences in surface morphology, where the PE-ALD deposition of SnS_2 yields out-of-plane oriented structures at 180°C and continuous grains at 80°C whereas the thermal ALD process deposits amorphous SnS_2 films at 80°C. (Fig. 5(a-c)) The electrodes are evaluated in a flow-by reactor at 100 mA cm^{-2} with 0.5 M $KHCO_3$ as catholyte and 2.0 M KOH as anolyte. While CO_2RR experiments with In_2S_3 are ongoing, a comparison of the SnS_2 electrodes reveals that SnS_2 with out-of-plane oriented structures outperforms the other two SnS_2 morphologies in terms of its lower overpotential (i.e. 260 mV less negative) and maintaining structural stability even though its initial faradaic efficiency towards formate is lower (i.e. 64% vs. 80%). (Fig. 6,7) This result confirms the importance of optimizing the surface morphology for CO_2RR electrocatalysts.

References

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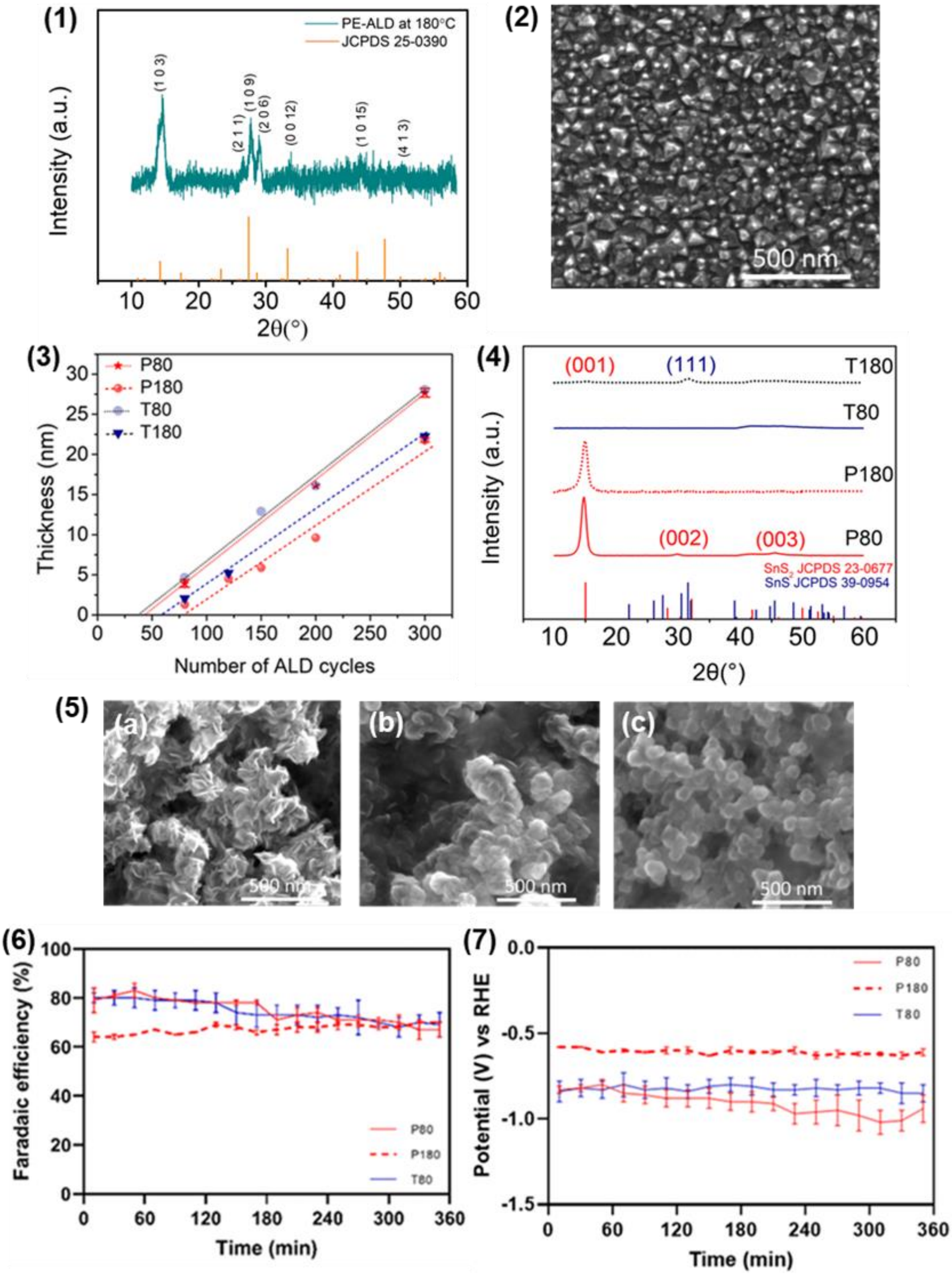

Fig. (1) XRD patterns of the In_2S_3 films grown by the PE-ALD process at 180 °C. Fig. (2) Top-view SEM image of In_2S_3 film deposited by the PE-ALD process at 180 °C. Fig. (3) Thickness against the number of ALD cycles for the PE-ALD process and the thermal ALD process at 80 °C and 180 °C. Fig. (4) XRD patterns of the SnS_x films grown by the PE-ALD and thermal ALD processes at 80 °C and 180 °C. Fig (5) Top-view SEM image of SnS_2 film deposited on gas diffusion electrode by the (a) PE-ALD process at 180 °C (b) PE-ALD process at 80°C , and (c) thermal ALD process at 80°C. CO_2RR results for SnS_2 films showing Faradaic efficiencies for formate [Fig. (6)] while measuring potentials [Fig. (7)] over six hours.