Synthesis and characterization of single phase FeCrAl Oxide Photocathode material for Photoelectrochemical Water Splitting

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Abstract: FeCrAl oxide has been studied as a new photocathode material for hydrogen production with water splitting, but there was phase separation because heterogeneous nucleation took place before other phases formed. When the electrode was pre-heated between layers, single phase of $Fe_{0.84}Cr_{1.0}Al_{0.16}O_3$ could be obtained. It was identified with X-ray diffraction (XRD), Secondary ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS) depth profiling, and X-ray absorption fine structure (XAFS). We could regulate bandgap (1.7 eV) and band position of this material. Prepared electrode showed very high onset potential of ~1.2 V_{RHE}, and its photocurrent density reached 0.3 mA/cm^2 at 0.4 V_{RHE}.

Keywords: Photocathode, Photoelectrochemical cell, Single phase.

1. Introduction

Photoelectrochemical (PEC) water splitting is promising ways among sustainable paths to production of hydrogen, which has been considered an ideal form of renewable energy as non-toxic, non-greenhouse-gas-emitted and powerful sources. In order to realize PEC water splitting with high efficiency, semiconductor materials for photoelectrodes must have small bandgap as a wide range light absorber, suitable band alignment to oxidize water and produce hydrogen, facile charge separation and fast charge transport not to occur recombination, and stable under illumination in aqueous solution. While many photoanode materials have been studied and developed well, still photocathode materials have challenges to meet such requirements for higher onset potential and efficiency. Thus, discovering new materials with proper stoichiometry and material characterizations are important.

$Fe_xCr_yAl_zO_3$ (x+y+z = 2) was first identified as a possible photocathode material through combinatorial discovery.[1,2] After that, nanostructured ternary FeCrAl oxide photocathode was published with highly increased photocurrent density.[3] However, there was phase separation because heterogeneous nucleation took place before other phases formed. Here, we reported single phase $Fe_{0.84}Cr_{1.0}Al_{0.16}O_3$ (FCA) electrode with detailed material characterization for further application.

2. Experimental

The $Fe_{0.84}Cr_{1.0}Al_{0.16}O_3$ photoelectrode was prepared by spin coating method. Well dispersed FCA solution was dropped onto cleaned FTO glass and spin-coated 500rpm for 30s. These cycles were repeated and the FTO glass was pre-heated at 450°C for 20min between each cycle. After several layers deposition, pre-heated electrode was annealed at 525°C for 1.5h ramping up(4°C/min) from room temperature (Fig. 1).

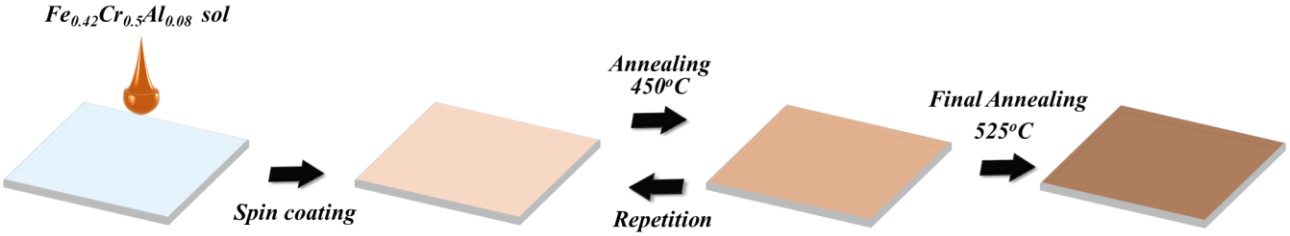

Figure 1. Synthesis of $Fe_{0.84}Cr_{1.0}Al_{0.16}O_3$ Photocathode.

3. Results and discussion

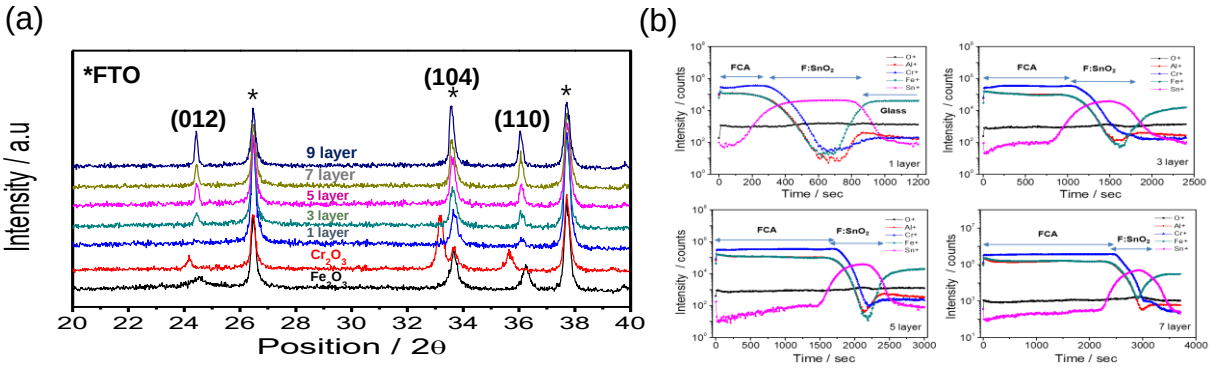

Figure 2. (a) X-ray diffraction patterns of 1, 3, 5, 7, 9 layers of FCA and Cr_2O_3, Fe_2O_3 5 layers electrode. (b) Secondary ion mass spectroscopy depth profiling of 1, 3, 5, 7 layers of FCA electrode.

To determine the crystal structure of FCA electrode, we measured X-ray diffraction (XRD). Figure 2 (a) shows that XRD pattern of FCA 1, 3, 5, 7, 9 layers have same phase and well matched with Corundum structure. Main peaks such as (012), (104), and (110) are slightly shifted when mixed Fe, Cr, and Al elements together compared to Cr_2O_3 and Fe_2O_3. To examine more detail about phase constant with different layer samples, Secondary ion mass spectroscopy (SIMS) depth profiling was conducted on 1, 3, 5, 7 layer treated FCA electrodes. In Figure 2 (b), the intensity of each elements is constant according to the depth. The regions where Fe, Cr, Al decrease and Sn increases are the meeting point of FCA and FTO glass.

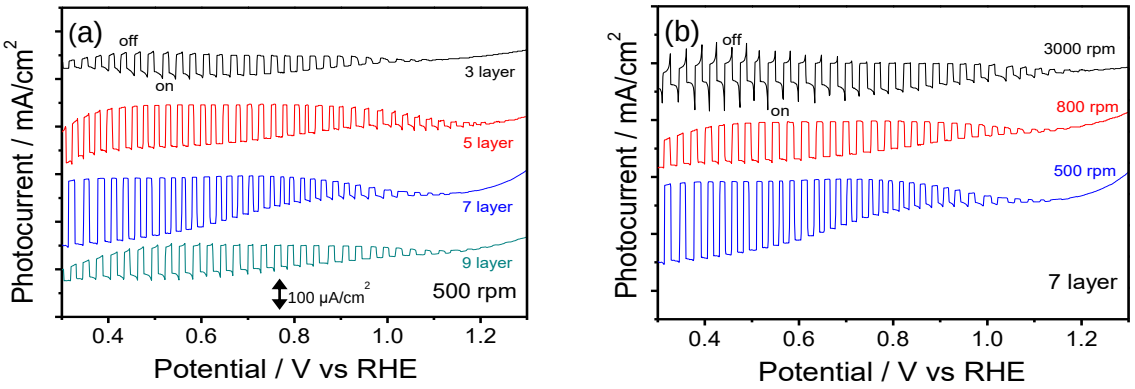

Figure 3. Current (J) – potential (V) curves of (a) 3, 5, 7, 9 layers of FCA electrode with 500rpm, (b) 3000rpm, 800rpm, 500rpm with 7 layers.

The photoelectrochemical performance of FCA electrode is shown in Figure 3. 500 rpm and 7 layer spin coated sample shows the highest performance and onset potential of 0.3 mA/cm^2 at 0.4 V_{RHE} and 1.1 ~ 1.2 V_{RHE} (Fig 3 (a), (b)).

4. Conclusions

We prepared single phase $Fe_{0.84}Cr_{1.0}Al_{0.16}O_3$ material by using pre-heated between layers and final annealing with a simple sol-gel method. FCA was proved as a single phase with X-ray diffraction (XRD), Secondary ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS) depth profiling, and X-ray absorption fine structure (XAFS). Thereby, we could regulate bandgap energy (1.7 eV) and draw band position of FCA with UPS analysis, Mott-Schottky plot.

References

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