Effect of Cerium Doping on Morphology and Physical Properties of α-Fe_2O_3 films prepared by Hydrothermal Electrodeposition

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Ferric oxide (α-Fe_2O_3, hematite) has become a very desirable material to construct photoelectrochemical cells since its bandgap (E_g=~2.2eV) allows utilization of a considerable portion of solar energy.[1] However, pure phase hematite fails to reach the maximum predicted efficiency (12.9%) for solar water splitting due to its poor charge transfer characteristics and high recombination rate of the photogenerated holes and electrons. To improve the performance of hematite, one attractive strategy is to introduce dopant atoms such as Zr, Cr, Mo, Zn, Cd, Ni, Pt, Ti, Si and Ge.[1] However, there are few reports on rare earth metal doping. Recently, Cerium doped hematite film prepared by a sol-gel route was shown to have improved conductivity.[2] In this study, we report electrochemical growth of Ce-doped α-Fe_2O_3 films with electrodeposition and also present a combined hydrothermal-electrochemical method for the first time to obtain hematite. This technique allows electrodeposition at higher temperatures than it is possible with air-open systems. The effect of temperature, deposition solution and cerium ion amount on the morphology and physical properties of hematite films were characterized.

Potensiostatic electrodepositions were carried out with a conventional 3-electrode cell system where ITO (Indium tin oxide) coated glass was the working electrode at 75°C. The depositions at higher temperature (130°C) were performed in a hydrothermal glass reactor. Both acidic and neutral plating solutions were used for the depositions. Transparent, yellow to orange films were obtained with both solutions. The amorphous films were annealed at 520°C for 30 minutes to obtain the desired crystallinity. The crystal structure and crystallinity of the thin films were analyzed by X- ray diffraction (XRD) analysis. ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM) was used to study the surface morphology of the samples and film composition was examined by X-ray photoelectron spectroscopy (XPS).

FE-SEM study showed that the pristine film prepared from an aqueous bath containing either 0.02M $FeCl_2$ (pH=3.8) or 0.02M $FeCl_2$ and 0.08M $NaCH_3COO$ (pH=6.8) at 75°C were composed of particles with no particular shapes. Upon annealing they were transformed into oval-round particles with diameters ranging between 10-50nm (data not shown). Addition of Ce^{3+} ions (10 %) into acidic solution did not affect this growth behavior under identical deposition conditions (Figure 1a). However, Ce^{3+} addition into the neutral deposition bath resulted in formation of smooth platelets even in the pristine film (Figure 1b) that are a few nanometers thick and around 100nm long. When the depositions were carried out with the same solutions under hydrothermal conditions (130°C), films with distinctive structures were obtained. The undoped film was composed of spherical particles with diameters of ~200nm (data not shown). When Ce^{3+} ions (10 %) were added into the acidic solution, spheres of two different sizes were obtained which were transformed into rhombohedral platelets with 100nm edges upon annealing (Figure 1c). Hydrothermal deposition from Ce^{3+} containing neutral solution gave rise to formation of sheets ~50nm thick and ~200nm wide even in the pristine films (Figure 1d). Photoelectrochemical studies revealed that doping with Ce^{3+} improves the photocurrent produced under illumination (AM1.5 air filter, 100 mW/cm^2).

The effect of Ce^{3+} amount on the growth behavior and physical properties of hematite films were also revealed.

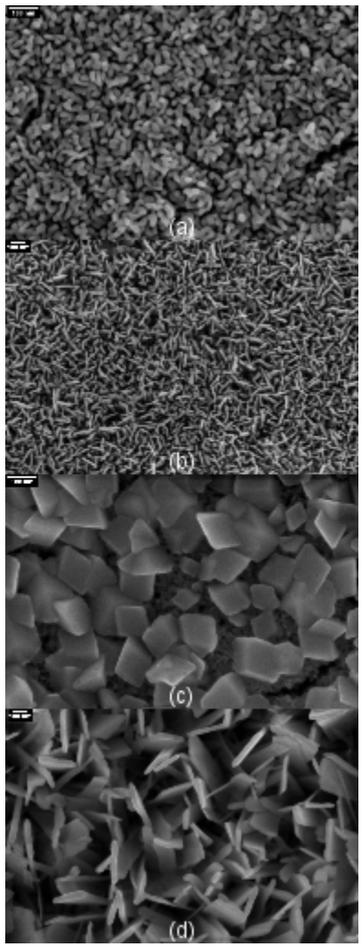

Figure 1. FE-SEM of annealed hematite films electrodeposition from solutions containing 0.02M $Fe^{2+}$and 2mM Ce^{3+} (a) at 75°C (c) at 130°C, and from solutions containing 0.02M Fe^{2+}, 2mM Ce^{3+} and 0.08M $NaCH_3COO$ (b) at 75°C (d) at 130°C. (scale bars:100nm)

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