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Facile preparation of Fe_2O_3 thin film with photoelectrochemical properties†

Hyun Gil Cha, Jieun Song, Hyun Sung Kim,* Woonsup Shin, Kyung Byung Yoon and Young Soo Kang*

We report a simple approach for preparing undoped and Pt-doped Fe_2O_3 thin films with excellent photoactivity *via* facile hydrothermal growth. The photocurrent densities of undoped and Pt-doped Fe_2O_3 thin films were recorded up to 1.2 and 1.38 mA cm^{-2} at 0.23 V Ag/AgCl under 1 sun illumination, respectively.

Among various metal oxides, α-Fe_2O_3 (hematite) has attracted great attention as a key material in photoelectrochemical electrodes for water oxidation. It displays superior optical properties with broad absorption in the visible range (band gap, E_g = ~2.0 eV), appropriate valence band position for water oxidation, stability against photodegradation and it has abundance as an element.[1]

Many conventional vacuum techniques for Fe_2O_3 film growth, including atmospheric pressure chemical vapor deposition,[2] electron-beam evaporator,[3] pulse laser deposition,[4] atomic layer deposition,[5] reactive DC magnetron sputtering,[6] metal organic decomposition,[7] *etc.* have been widely reported due to their straightforward control of chemical composition, deposition parameters, and excellent reproducibility. However, the practical applications of these growth techniques have been restricted because of the high cost of the manufacturing equipment and the limitations in achieving a large surface area and uniform coating. In contrast, solution-based film growth can offer large surface area with economical equipment and easy precise compositional control during the deposition procedure with superior photoproperties. For instance, the Grätzel group recently demonstrated the formation of Fe_2O_3 film using a nanoparticle suspension by the doctor-blade method which had excellent photocurrent generation properties.[8] Also Mohapatra *et al.* introduced the preparation of ultrathin Fe_2O_3 nanotube arrays by using by a sonoelectrochemical anodization method and obtained photoactivity up to 1.41 mA cm^{-2} at 0.5 V *vs.* Ag/AgCl after annealing under hydrogen conditions.[9] Although these methods look

Korea Center for Artificial Photosynthesis, Center for Nanomaterials, Department of Chemistry, and Interdisciplinary Program of Integrated Biotechnology, Sogang University, Seoul, Korea.
E-mail: yskang@sogang.ac.kr; Fax: (+82)-2-701-0967
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promising, the simple hydrothermal preparation of Fe_2O_3 film enables more efficient large area film growth on the various metal oxide substrates and can contribute to the improvements in material-processing and the enhancement of photocurrent generation. In this report, we introduce a new facile preparation method of Fe_2O_3 thin film through hydrothermal reaction using a simple gel solution and demonstrate a superior photoactive property.

The Fe_2O_3 film precursor solution was readily prepared by dissolving $FeCl_3$ in an aqueous solution of sodium hydroxide (see Fig. S1, ESI†). In this method, the substrate of the fluorine-doped tin oxide (FTO) glass was directly submerged into the Fe_2O_3 precursor gel and the Fe_2O_3 film was formed *in situ* on the FTO glass during hydrothermal crystallization at various temperatures (130, 150, and 170 °C). After some experimentation, the optimal $FeCl_3$ and NaOH concentrations were determined by XRD monitoring of the film crystallization during the growth.

The thickness and coverage of pristine Fe_2O_3 films as a function of growth time were estimated by scanning electron microscopy (SEM) images in Fig. 1. The thickness had increased up to 470 nm after 5 h reaction time at 170 °C and simultaneously coverage was also increased. It took about 5 h to fully cover the FTO glass with Fe_2O_3 at 170 °C.
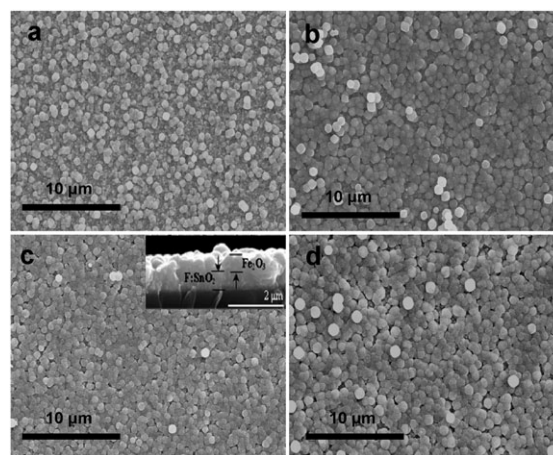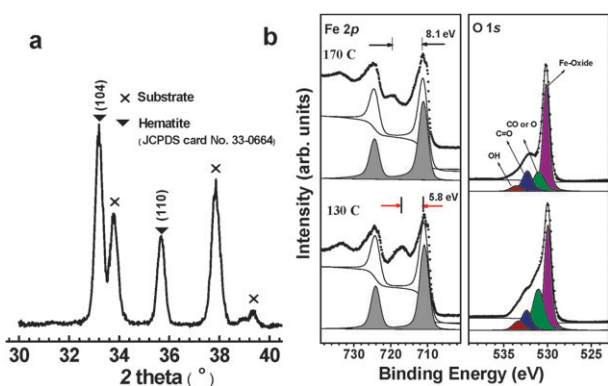

Fig. 1 SEM images of Fe_2O_3 film grown on the FTO glass formed at 170 °C at different reaction times; (a) 1 h, (b) 3 h, (c) 5 h (inset is the image of cross-sectional view) and (d) 7 h.

Fig. 2 (a) GIXRD patterns of Fe_2O_3 films grown on FTO glass at 170 °C, and (b) XPS spectra for the Fe 2p and O 1s signals of Fe_2O_3 films grown at 170 and 130 °C, respectively.

The structure of this film was verified by grazing incidence XRD (GIXRD) analysis (Fig. 2(a)), confirming that it is one phase hematite with the rhombohedral symmetry of Fe_2O_3 (space group: $R3c$(167), $a = 0.5035$, $b = 0.5035$, $c = 1.3748$ nm; JCPDS card No. 33-0664).[10,11] Also the grain of the film was determined as a single crystal by the analysis of the TEM electron diffraction pattern as shown (Fig. S2, ESI†).

XPS spectra of Fe_2O_3 film grown at 130 and 170 °C revealed that the peaks corresponding to Fe 2p and O 1s are in the binding energy range of 705–740 eV and 528–540 eV (Fig. 2(b)). The difference in energy between the Fe 2p 3/2 binding energy of 710.8 eV and the corresponding satellite peak, 718.9 eV, is 8.1 eV. This results in indisputable proof of the presence of Fe^{3+} ions from the Fe_2O_3 film hydrothermally grown at 170 °C. In contrast, the difference in energy as mentioned above was 6.8 eV, which is attributed to the existence of a metastable phase in the case of the Fe_2O_3 film prepared at 130 °C.[12] The metal hydroxide and oxy-hydroxide oxygen are generally observed at ~531.9 eV. Fe_2O_3 film grown at 170 °C has much lower peak area corresponding to metal hydroxide/oxy-hydroxide than does the film grown at 130 °C. Based on these obtained XPS analysis data, we reasoned that the Fe_2O_3 film can be hydrothermally synthesized with a pure phase at a temperature above 170 °C. The purity of the Fe_2O_3 film will have a great effect on the photoactivity. The optical bandgap of Fe_2O_3 film can be estimated by calculating the intercept of the extrapolated linear fit to the experimental data of a plot of $(\alpha h\upsilon)^2$ *versus* incident photon energy ($h\upsilon$) near the absorption edge where α is the absorption coefficient of the film.[13] A $(\alpha h\upsilon)^2$ *vs.* $h\upsilon$ plot for Fe_2O_3 electrode is shown in Fig. S3 in ESI†. The determined indirect bandgap value is 2.09 eV, which closely matches the value reported in the literature.[14]

Fe_2O_3 films grown *via* hydrothermal reaction were shown to have strong adhesion to the substrate using the scotch tape peeling method, *i.e.*, tape is adhered to the grown Fe_2O_3 film and then peeled off. Before photocurrent measurement, pristine Fe_2O_3 film was annealed at 500 °C under air for improved photoactivity. Indeed, only negligible photoactivity was observed from Fe_2O_3 film without the annealing process. Because there should be an electron trap site such as a metal hydroxide between the grown Fe_2O_3 film and the conducting

FTO electrode, this trap site can be a suppression factor for the electron transfer from a photoexcited electron in the Fe_2O_3 conduction band to the conduction band of FTO. By means of the annealing process at 500 °C, any electron trap site such as a metal hydroxide should be eliminated by the hydrolysis reaction. Removing the electron trap site dramatically improves photoactivity of the Fe_2O_3 film.

All photoelectrochemical parameters were investigated in a three electrode system using 1 M KOH solution as the electrolyte, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. Photocurrent density was evaluated as a function of applied voltage under 1 sun (100 mW cm^{-2}) AM1.5 at a scan rate of 50 mV s^{-1}. Fig. 2(a) shows the I–V curve of Fe_2O_3 film photoanode prepared at the indicated temperatures under dark and light illumination on the front-side. The dark response is negligible up to about 0.6 V *vs.* Ag/AgCl ($< \sim 1.00$ µA cm^{-2}). The photocurrent rises steeply between −0.2 and 0.2 V and has a plateau with an onset voltage of $\sim$ −0.3 V Fe_2O_3 film for improved photocurrent. Interestingly, the photoresponse is enhanced by increasing synthetic temperature between 130 °C and 170 °C. The photoanode prepared at 170 °C displays the optimal photocurrent for water oxidation by sunlight. At 0.23 V, the photocurrent density is 1.2 mA cm^{-2} (Fig. 3(c)). This is the largest photocurrent value ever as compared to pure Fe_2O_3 film from other methods. In the case
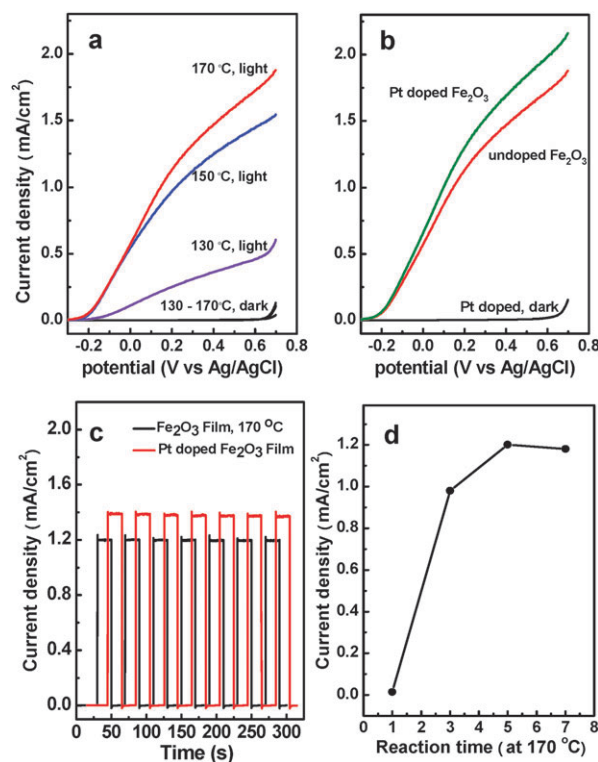

Fig. 3 Photoelectrochemical performances of Fe_2O_3 thin films. (a) Current–voltage curves of undoped Fe_2O_3 thin films prepared at the indicated reaction temperatures for 5 h, (b) of Pt-doped Fe_2O_3 thin film in comparison to the undoped one at 170 °C for 5 h, (c) photoresponse at 0.23 V$_{Ag/AgCl}$ of undoped and Pt-doped Fe_2O_3 thin film (170 °C, 5 h), and (d) photocurrent density for different reaction times in darkness and under AM1.5 G, 1 sun.

of Fe_2O_3 film prepared over 170 °C, photocurrent density value is slightly decreased or saturated. Also Fig. 3(d) shows the photocurrent density of Fe_2O_3 films as a function of reaction time at 170 °C. Note that there is an optimal reaction time of Fe_2O_3 film (5 h) where both coverage and photocurrent density are large. As a result, the superior qualities of the Fe_2O_3 film such as coverage and purity strongly influence the photoactivity.

A Mott–Schottky plot shows the flat-band potential determined from the fitted space charger layer capacitance values at each potential for Fe_2O_3 film (Fig. S4, ESI†). The plot obtained from the Fe_2O_3 film shows n-type behavior due to the positive slope of the linear plot. The flat-band potential (V_{fb}) values can be determined as -0.78 $V_{Ag/AgCl}$ by extrapolation to C = 0 and charge carrier concentration (N_D), calculated from the slope as 1.1×10^{21} cm^{-3} at the AC frequency of 3000 Hz. The higher carrier concentration of the hydrothermally synthesized Fe_2O_3 film may be responsible for higher photocurrent density because they reduced the resistivity of the film.[15]

Generally various doped elements such as Si, Sn, Pt, Ge, Ti, Ta,[1a–d,11,16] etc. lead to improved photocurrent activity in the Fe_2O_3 photoanode. For any element-doped metal oxide film which is grown via hydrothermal reaction, it is a simple and economical process to prepare precursor solutions with the desired doping element by simply dissolving the doping element sources in precursor solution. Doped Pt in Fe_2O_3 improves the photoinduced conductivity and enhances charge transfer by suppressing a carrier recombination due to the substitution of Fe^{3+} by Pt^{4+} as electron donor in Fe_2O_3 electrode.[11] Consequently, we obtained 1.38 mA cm^{-2} at 0.23 V vs. Ag/AgCl with Pt-doped (0.06 at%) Fe_2O_3 films synthesized from precursor solution containing platinum dissolved in hydrochloric acid as the Pt source (Fig. S5, ESI†). We are presently investigating the photoactivity effect of various doping elements.

In conclusion, these results demonstrate that Fe_2O_3 film grown via simple hydrothermal reaction has shown excellent photoelectrochemical performance. In particular, this simple method can be applied to obtain various element-doped Fe_2O_3 films such as Si, Sn, Pt, Ge, Ti, Ta, etc. with the goal of improving photocatalytic properties.

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