Research Article

Enhanced Water Splitting by Fe$_2$O$_3$-TiO$_2$-FTO Photoanode with Modified Energy Band Structure

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The effect of TiO$_2$ layer applied to the conventional Fe$_2$O$_3$/FTO photoanode to improve the photoelectrochemical performance was assessed from the viewpoint of the microstructure and energy band structure. Regardless of the location of the TiO$_2$ layer in the photoanodes, that is, Fe$_2$O$_3$/TiO$_2$/FTO or TiO$_2$/Fe$_2$O$_3$/FTO, high performance was obtained when $\alpha$-Fe$_2$O$_3$ and H-TiNT/anatase-TiO$_2$ phases existed in the constituent Fe$_2$O$_3$ and TiO$_2$ layers after optimized heat treatments. The presence of the Fe$_2$O$_3$ nanoparticles with high uniformity in the each layer of the Fe$_2$O$_3$/TiO$_2$/FTO photoanode achieved by a simple dipping process seemed to positively affect the performance improvement by modifying the energy band structure to a more favorable one for efficient electrons transfer. Our current study suggests that the application of the TiO$_2$ interlayer, together with $\alpha$-Fe$_2$O$_3$ nanoparticles present in the each constituent layers, could significantly contribute to the performance improvement of the conventional Fe$_2$O$_3$ photoanode.

1. Introduction

Green energy sources have been extensively investigated to replace the fossil fuels due to their inherent problems of pollution and limited resources [1]. Among them, hydrogen (H$_2$) gas was one of the most actively studied energy sources owing to its abundance, high specific energy capacity, and environmentally friendliness [2–4]. Hydrogen can be produced by using hydrocarbons such as fossil fuels, natural gas, and water. Production of hydrogen gas by electrolysis of water has been known to be the most efficient way [5–7]. Energy required to generate hydrogen and oxygen by electrolysis of water can be supplied through sun light. For the sun light to be effectively utilized, electrodes having functions of photoabsorbent and catalyst need to be employed for electrolysis of water. Photoelectrochemical (PEC) system is an efficient approach to produce hydrogen gas from water by utilizing an unlimited resource of the sun light without generating environmentally deleterious byproducts. With the development of PEC system, much attention has been paid to the fabrication of high efficient photoelectrode for water splitting [4, 8–10]. Among other things, materials extensively studied for the photoelectrode were Co [11, 12], Co-Pi [13, 14], IrO$_2$ [15], TiO$_2$ [16–18], CuO [19], WO$_3$ [20], Fe$_2$O$_3$ [21], and so forth.

In particular, more interest has been drawn to Fe$_2$O$_3$ material which could harvest visible part of solar spectrum [21–23]. However, Fe$_2$O$_3$ has some critical issues to be resolved for the application to the PEC system as photoelectrode such as electron-hole recombination. Several approaches have been taken to reduce the recombination; application of nanostructured materials, doping with appropriate materials, and so forth. Photocurrent density generated with the Fe$_2$O$_3$ nanorods and nanowires was reported to have 1.3 mA/cm$^2$ [21] and 0.54 mA/cm$^2$ at 1.23 (V versus RHE) [22], respectively. On the other hand, Fe$_2$O$_3$ photoanode doped with Ti and Si showed a little better performance of 1.83 mA/cm$^2$ [24] and 2.2 mA/cm$^2$ at 1.23 (V versus RHE) [25], respectively. However, the photocurrent density...
of Fe₂O₃ photoanode modified with the nanostructures and doping was found to be still far below the theoretical value of 12.6 mA/cm² at 1.23 (V versus RHE). From our previous work, we reported a high photocurrent density of 1.32 mA/cm² at 1.23 (V versus RHE) with Fe₂O₃/FTO photoanode without any doping [26], synthesized by a simple process of dip coating and short-time heat treatment at 500 °C of nanosized Fe₂O₃ on the FTO substrate. Our results confirmed the importance of microstructure of Fe₂O₃ to the reduction of electron-hole recombination, which could be modified and optimized by the coating amount of Fe₂O₃ and following heat treatment conditions [27]. Taking advantage of photocatalytic effect of TiO₂, Fe₂O₃/TiO₂/FTO photoanode was also fabricated in another study. From the energy band structure viewpoint of the photoanode, the electrons transfer in the photoanode.

2. Experimental Details

FTO glasses (Asahi Glass Co.) as a conducting substrate of Fe₂O₃ photoanode film for water splitting was at first etched for 20 min using Piranha solution (7:3 = 70% conc. H₂SO₄:30% H₂O₂) to make them have fresh surface and then were dipped simply to make H-TiNT (hydrogen titanate nanotube) particles supported in aqueous Fe(NO₃)₃ solution (corresponding to Fe₂O₃ precursor) or H-TiNT particle dispersed solution (corresponding to TiO₂ precursor particles). In this study, various photoanode arrangements such as Fe(NO₃)₃/FTO, Fe(NO₃)₃/H-TiNT/FTO, and H-TiNT/Fe(NO₃)₃/FTO were prepared. Coated Fe(NO₃)₃ and H-TiNT particles were transformed into Fe₂O₃ and TiO₂ phases, respectively, with heat treatments at 500 °C for 10 min in air. In other words, for the performance improvement of Fe₂O₃ film, the arrangements with H-TiNT interlayer incorporated in between Fe(NO₃)₃ and FTO and with H-TiNT top layer on the Fe(NO₃)₃/FTO were tried. All aqueous solutions in this experiment were prepared using distilled water with 1.8 MΩ.

To make H-TiNT interlayer (finally Fe₂O₃/TiO₂/FTO arrangement), the FTO glass after having been surface-treated for 20 min in 0.2 M polyethyleneimine (PEI, Aldrich Co.) aqueous solution containing positively charged ions was used as a transparent conductive substrate. First, the surface-pretreated FTO glass was immersed for 20 min in an aqueous 10 g/L H-TiNT particle solution dispersed together with 0.2 M tetrabutylammonium hydroxide (TBAOH, Aldrich Co.) to produce negatively charged ions. Afterwards, using the same method, an H-TiNT-treated film was subsequently immersed in 0.2 M polydiallyldimethylammonium chloride (PDMA, Aldrich Co.) aqueous solution, which contained positively charged ions. The obtained H-TiNT/FTO glass was dried under UV-Vis light irradiation (Hg-Xe 200 W lamp, Super-cure, SAN-EI Electric) to remove water and all surfactants, such as PEI, TBAOH, and PDMA using photocatalytic removal reaction occurred by H-TiNT particles with optical energy bandgap of 3.5 eV [24], without any sintering. Then, for the Fe(NO₃)₃ nanoparticle coating process, the dried H-TiNT/FTO substrates were dipped in an aqueous 1.0 M Fe(NO₃)₃ solution with dipping times of 12 hrs. For formations of H-TiNT top layer on Fe(NO₃)₃/FTO films (finally TiO₂/Fe(NO₃)₃/FTO arrangement), the precursor solution of Fe₂O₃ film supported was made of 1.0 M Fe(NO₃)₃, 9H₂O and 0.2 M TBAOH (tetrabutylammonium hydroxide, Aldrich) for dipping fresh FTO substrate for 12 hrs. After that, obtained Fe(NO₃)₃/FTO were dried at 80°C for 12 hrs. For formation of H-TiNT/Fe(NO₃)₃/FTO films, repetitive self-assembling of oppositely charged ions in an aqueous solution was applied to coat directly the H-TiNT particles using the same process explained above. All dipping process was carried out at room temperature in air.

All heat treatment was done inside a box furnace with heating rate of 500°C/sec to produce the final photoanode thin film with α-Fe₂O₃ phase for the water splitting process, where the rapid heating rate was accomplished by plunging the samples into the hot zone of the furnace maintained at the setting temperatures of 420–550°C. Repetition of this process yielded an H-TiNT particle thin film coated on the FTO or Fe₂O₃ film with approximately 700–1000 nm thickness as previously reported in our researches [30]. After the heat treatment at various conditions, the surface microstructure of the Fe₂O₃ thin films was observed with scanning electron microscope (SEM; S-4700, Hitachi) and their crystallinity was analyzed using X-ray diffractometer (XRD; D/MAX 2500, Rigaku), Raman spectroscopy (Renishaw, inVia Raman microscope), UV-Vis spectroscopy (S-3100, Sinco). To measure the I-V and C-V electrochemical properties using μAutolab type III potentiostat (Metrohm Autolab), a calomel electrode and a Pt wire were used as the reference and counter electrodes, respectively, when the as-prepared, heat-treated coated Fe₂O₃/H-TiNT composite films with various arrangements were used as the working electrode in an aqueous 1.0 M NaOH deaerated solution under irradiation of 100 mW/cm² UV-Vis spectrum (Hg-Xe 200 W lamp, Super-cure, SAN-EI Electric). The measured potentials versus calomel were converted to the reversible hydrogen electrode (RHE) scale in all I-V graphs.

3. Results and Discussions

Figure 1 shows I-V photoelectrochemical data and surface morphology of the Fe₂O₃ precursor/(H-TiNT)/FTO samples, which had been heat treated at the predetermined temperatures of 420–550°C for 10 min. The amount of Fe₂O₃ in the samples was 65.48 wt% for the Fe₂O₃/H-TiNT/FTO and about 30 wt% for the Fe₂O₃/FTO, which was determined based on the I-V photoelectrochemical performance as
reported in our previous study [29]. All the samples were measured in the 1.0 M NaOH solution under 100 mW/cm² of UV-Vis light illumination, and the linear sweep voltammetry was in the range of 0.0−+2.0 (V versus RHE). The photocurrent densities were obtained by eliminating the “dark” fraction from “illumination” data, where dark data was measured in the dark room without UV light illumination. For the comparison, sample (e) without TiO₂ interlayer was adopted from our previous work [26].

Regardless of the heat treatment temperatures, the performance improvement was observed in the samples with TiO₂ interlayer incorporated in between Fe₂O₃ and FTO. In particular, sample (c) prepared under the same condition as sample (e) other than the presence of TiO₂ interlayer film showed about 3 times increase of photocurrent density at 1.23 (V versus RHE) and the reduction of the onset voltage to about 0.75 V. These results suggest that the TiO₂ interlayer can play a significant role in the efficient collection and conversion of photoenergy. The extent of performance improvement was found to be affected by the heat treatment temperature; it showed a gradual improvement with the heat treatment temperature of up to 500°C, above which it rather deteriorated. A similar result was observed with the Fe₂O₃/FTO samples without TiO₂ interlayer film in our previous work [26].

Morphology of the Fe₂O₃/FTO sample after heat treatment at 500°C for 10 min was shown in Figure 1(e). The Fe₂O₃ particles were observed to form a film conformal to the FTO substrate, indicating a very thin and uniform film as noted by Oh et al. [31]. Microstructure changes of the Fe₂O₃ precursor/H-TiNT/FTO samples were also monitored as a function of heat treatment temperature of 420−550°C. The as-coated porous and rough H-TiNT particles with fibrous morphology as reported in our previous work [27] were broken into spherical particles through the heat treatments. It is noteworthy that the Fe₂O₃ particles in the Fe₂O₃/H-TiNT/FTO samples were relatively smaller than those in the Fe₂O₃/FTO sample, suggesting that the growth of the Fe₂O₃ particles was restrained by H-TiNT during the heat treatments. However, no noticeable microstructural differences were observed among the Fe₂O₃/H-TiNT/FTO samples which could explain the performance variation occurred in the samples.

The contribution of the TiO₂ interlayer placed in between Fe₂O₃ and FTO on the photocurrent density improvement at 1.23 (V versus RHE) as a function of heat treatment temperature was quantitatively expressed in Figure 2. The data for the Fe₂O₃/FTO samples were taken as a reference from our previous work [26]. The effect of the TiO₂ interlayer on the performance improvement was substantially increased with the temperature to the highest at 500°C, above which it rather declined.

Phase changes of the constituent materials in the samples with the heat treatments were observed in our previous work [30]. It was observed that Fe₂O₃ precursor was gradually transformed into α-Fe₂O₃ phase with the increase of heat treatment temperature from 420 to 550°C. However, peaks corresponding to α-Fe₂O₃ phase became weaker above 500°C. On the other hand, H-TiNT was transformed gradually but not fully into anatase-TiO₂ phase due to the short heat treatment time of 10 min. Therefore, from the phase and photocurrent density changes of the samples, the performance improvement is considered to be closely associated with
the phases present in the samples: the best performance could be obtained when H-TiNT and anatase-TiO\(_2\) phases coexisted with the well-developed \(\alpha\)-Fe\(_2\)O\(_3\) phase in the sample.

Effect of the coating layers arrangement in the Fe\(_2\)O\(_3\)/TiO\(_2\)/FTO samples was investigated in terms of the performance in Figure 3, in which the photocurrent densities were obtained by eliminating the “dark” fraction from “illumination” data. All the samples except sample (d) were obtained by eliminating the “dark” fraction from “illumination” data. All the samples except sample (d) were heat treated once at 500°C for 10 min in the air following synthesis of the multilayered electrodes. Sample (d) was heat treated twice under the same condition mentioned above: once after TiNT coating on the FTO, then repeated after Fe\(_2\)O\(_3\) coating on the heat-treated TiO\(_2\)/FTO layer. Regardless of the location of TiO\(_2\) layer, above or below Fe\(_2\)O\(_3\) layer (Fe\(_2\)O\(_3\)/TiO\(_2\)/FTO (Figures 3(b) and 3(d)) or TiO\(_2\)/Fe\(_2\)O\(_3\)/FTO (Figure 3(c))), samples containing TiO\(_2\) layer (Figures 3(b), 3(c), and 3(d)) showed much better performance compared to that (Figure 3(a)) without TiO\(_2\) layer, increased photocurrent density as well as reduced onset voltage.

Microstructure observed in Figure 4 suggested that film uniformity along with the controlled particles size could play an important role for the performance improvement, Fe\(_2\)O\(_3\)/TiO\(_2\)/FTO sample (Figure 4(b)) with the best performance consisted of smaller particles with high uniformity than sample (c) of TiO\(_2\)/Fe\(_2\)O\(_3\)/FTO. Double heat-treated sample (d) of Fe\(_2\)O\(_3\)/TiO\(_2\)/FTO showed an inferior performance to the corresponding sample (b) with the same layer structure, which was annealed only one time. This result also confirmed the importance of microstructure to the performance; the poor microstructure with agglomerated particles and cracked surface after the double heat treatment as shown in sample (d) adversely affected the performance of the sample. On the other hand, Figure 4(a) shows the Fe\(_2\)O\(_3\) precursor powders becoming much larger when heat treated at 500°C for 10 min, compared to the Fe\(_2\)O\(_3\) particles existing together with the TiO\(_2\) in the case of Figures 4(b)–4(d). These observations are consistent with the results of Figure 1, which showed the restrained growth of the Fe\(_2\)O\(_3\) particles by H-TiNT during the heat treatment.

It is noteworthy that among the samples with TiO\(_2\) layer, the sample (Figures 4(b) and 4(d)) with the TiO\(_2\) layer in between Fe\(_2\)O\(_3\) and FTO layer showed better result than the sample (Figure 4(c)) having the TiO\(_2\) layer above Fe\(_2\)O\(_3\) layer. These results were discussed in terms of energy band structure and microstructure. Energy band diagrams of the Fe\(_2\)O\(_3\)/TiO\(_2\)/FTO and TiO\(_2\)/Fe\(_2\)O\(_3\)/FTO samples without UV-Vis light irradiation were schematically drawn in Figures 5(a) and 5(b), respectively. It was proposed by Wang et al. that a photoelectrode with TiO\(_2\) based film such as SrTiO\(_3\) located above Fe\(_2\)O\(_3\) film was a favorable structure for electrons transfer from the energy band diagram consideration [32]. Their claim seems to be reasonable from the comparison of the energy band diagrams when being not under UV-Vis light. However, our results showed that the electrons generated on the Fe\(_2\)O\(_3\) layer in the Fe\(_2\)O\(_3\)/TiO\(_2\)/FTO photoanode could be transferred to the TiO\(_2\)/FTO when being under the UV-Vis light irradiation by overcoming the discontinuity of the conduction bands.

On the other hand, the microstructure of the Fe\(_2\)O\(_3\)/TiO\(_2\)/Fe\(_2\)O\(_3\) sample synthesized for the current work was also carefully considered. While synthesizing the Fe\(_2\)O\(_3\)/TiO\(_2\)/FTO sample, some of the Fe\(_2\)O\(_3\) nanoparticles could be
Figure 4: SEM photos of (a) Fe(NO₃)₃ powders heat treated at 500°C for 10 min, and (b), (c), (d) correspond to Figures 3(b), 3(c), and 3(d), respectively.

Figure 5: Energy band diagrams of (a) Fe₂O₃/TiO₂/FTO and (b) TiO₂/Fe₂O₃/FTO photoanode and (c) schematic microstructure of Fe₂O₃-TiO₂-FTO.
infiltrated to the bottom FTO substrate through TiO$_2$ particles when TiNT/FTO was placed in the precursor solution of Fe$_2$O$_3$. As a result, Fe$_2$O$_3$ nanoparticles could also be present in the middle TiO$_2$ and the bottom FTO layer as depicted in Figure 5(c). Thus, our sample of Fe$_2$O$_3$/TiO$_2$/FTO seemed actually to have an energy band diagram combining both of Figures 5(a) and 5(b), indicating that the photoanode with Fe$_2$O$_3$ nanoparticles present even in the middle and bottom substrate is preferable for the performance enhancement.

Oxidation-reduction reactions for the selected photoanode samples were observed by using cyclic voltammetry (CV) to investigate the effect of the coating sequence of constituent films and heat treatment condition on the photoelectrode performance. CV data for the samples of FTO glass, TiO$_2$/FTO, and Fe$_2$O$_3$/FTO were obtained as a reference in Figures 6(A)-(a), 6(A)-(b), and 6(A)-(c), respectively. As expected the sample including Fe2O3 showed active reactions with the applied potential. According to the data (Figure 6(B)) from the Fe$_2$O$_3$/TiO$_2$/FTO samples heat treated at the various temperature of 420 – 550°C for 10 min, the sample heat treated at 500°C showed multiple oxidation-reduction peaks, contributing to higher photocurrent density. These results were found to be consistent with $I$-$V$ data of the samples described in Figure 1 where the sample heat-treated at 500°C showed best performance. The sample of Fe$_2$O$_3$/TiO$_2$/FTO which showed best result after heat treatment at 500°C was then compared with TiO$_2$/Fe$_2$O$_3$/FTO sample to see the effect of the location of TiO$_2$ layer placed in the photoanode, which was also heat treated under the same condition. These samples showed a clear contrast in the results as shown in Figures 6(C)-(a) and 6(C)-(b), respectively: Fe$_2$O$_3$/TiO$_2$/FTO sample produced more and clear oxidation-reduction peaks. On the other hand, the sample of Fe$_2$O$_3$/TiO$_2$/FTO, which was heat treated twice after each coating of TiO$_2$ and Fe$_2$O$_3$
layers, showed an intermediate performance (Figure 6(C)-
(c)). These results were all well consistent with the $I-V$
data in Figure 3 where the sample of Fe$_2$O$_3$/TiO$_2$/FTO heat
treated once (Figure 3(b)) at 500°C showed best performance
followed by the sample double heat treated (Figure 3(d)) and
TiO$_2$/Fe$_2$O$_3$/FTO sample (Figure 3(c)).

4. Conclusions

Fe$_2$O$_3$-TiO$_2$ based photoanodes for water splitting were syn-
thetized on the FTO substrate and their performance results
were understood from the microstructure and energy band
aspects. Comparatively, the photoanode (Fe$_2$O$_3$/TiO$_2$/FTO)
comprising top layer of α-Fe$_2$O$_3$ nanoparticles along with
the interlayer having mixed phases of H-TiNT/anatase-TiO$_2$
showed best performance. The nanoscaled Fe$_2$O$_3$ particles
with high uniformity were observed to contribute to the
performance enhancement. In addition, the presence of the
Fe$_2$O$_3$ nanoparticles in the middle and bottom layers caused
by the infiltration of the precursor solution of Fe$_2$O$_3$ during
synthesis seemed to modify the energy band structure to
more favorable one for efficient electrons transfer. Our cur-
cent results suggest that the application of the TiO$_2$ interlayer,
together with optimized amount of α-Fe$_2$O$_3$ nanoparticles
present in the constituent layers, could significantly con-
tribute to the performance improvement of the conventional
Fe$_2$O$_3$ photoanode.

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