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## Sandwich Fe<sub>2</sub>O<sub>3</sub>/Au/Fe<sub>2</sub>O<sub>3</sub> photoanodes for enhanced photoelectrochemical water splitting

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**Abstract** - Solar water splitting has received increasing attentions in recent years as a very promising strategy to produce clean hydrogen fuels. This paper presents a novel design consisting of a sandwich structure of Fe<sub>2</sub>O<sub>3</sub>/Au/Fe<sub>2</sub>O<sub>3</sub> as the photoanode for photoelectrochemical (PEC) water splitting. The tandem layers are constructed by spin-coating of pre-synthesized Fe<sub>2</sub>O<sub>3</sub> nanoparticles and sputtering of the gold intermediate layer. PEC testing shows that the sandwich structure exhibits much higher photocurrent density as compared to the Fe<sub>2</sub>O<sub>3</sub> double-layer anode. Further studies indicate that the Au intermediate layer can contribute in electron transfer as well as light harvesting due to its plasmonic excitation. The mechanism of the photocurrent enhancement is proposed and such sandwich structure may be applied to other semiconductors to improve PEC performance.

**Keywords:** Fe<sub>2</sub>O<sub>3</sub>, Au, sandwich structure, Photoelectrochemical water splitting

### 1. Introduction

Recently, hydrogen gas has been discussed intensively as a promising clean energy with high energy capacity to meet the increasing energy demand in industry. However, current hydrogen sources, such as fossil fuels and biomass, will generate CO<sub>2</sub> in hydrogen production and thus introducing greenhouse effects and environmental problems. In contrast, hydrogen production by splitting water is a clean process without any greenhouse gas evolution (Lewis, 2001). The basic principle of solar water splitting is to utilize the semiconductors to absorb solar energy directly and then convert the energy to clean chemical fuel, hydrogen gas. Photoelectrochemical cell (PEC) water splitting is one approach of solar water splitting and it involves setup of photoelectrolysis cell and illuminated semiconductor electrode. Since the first report of PEC water splitting using TiO<sub>2</sub> in 1972 (Fujishima et al., 1972), researchers have been investigating abundant semiconductors in order to construct a low cost and high efficiency PEC water splitting system. A desirable PEC water splitting photoelectrode is expected to possess: (1) good light absorption, (2) fast carrier-transport properties, (3) proper kinetic properties of the interface favoring water-splitting, (4) corrosion stability, and (5) low cost (Gratzel, 2001).

Among all of the potential semiconductors for PEC water splitting,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, as known as hematite, has been extensively studied since 1980s. It has band gap energy in the range of 1.9~2.3eV, and is one of the most popular materials for visible light harvesting in PEC water splitting (Liang et al., 2006; Wu et al., 2008).  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is highly stable in most electrolytes in both acidic and basic pH. It can hardly be photo-corroded under light irradiation. Moreover, its popularity in PEC water splitting study also attribute to its low cost and abundance (Walter et al., 2008). However,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> alone cannot make a desirable photo-electrode due to several reasons: First of all, the indirect band gap alignment results in low absorption coefficient in capturing solar energy. Secondly, short hole diffusion length gives rise to the charge recombination rate. Thirdly, its slow water-oxidation kinetics

can lead to surface back reactions. Lastly, the poor conductivity suppresses the electron transfer. (Gardner et al., 1963; Dare-Edwards et al., 1983)

In order to solve above problems of the  $\alpha$ - $\text{Fe}_2\text{O}_3$ , we construct a composite photo-electrode with a thin layer of plasmonic Au inserted in between two layers of  $\alpha$ - $\text{Fe}_2\text{O}_3$ . The metallic and plasmonic nature of Au may improve the light energy localization as well as visible light harvesting (Ingram et al., 2011; Liu et al., 2011; Thimsen et al., 2011). In this paper,  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  sandwich structure is constructed to improve the performance of photo-electrode made up of  $\alpha$ - $\text{Fe}_2\text{O}_3$ . Effect of the intermediate Au layer is also studied to explain the significant enhancement of the photo-current.

## 2. Experimental

### 2. 1. Preparation of $\text{Fe}_2\text{O}_3$ nanoparticles

$\text{Fe}_2\text{O}_3$  nanoparticles were synthesized by modifying well-developed hydrothermal method (Liang et al., 2006). 15 mL oleic acid, 1.5g NaOH, 15 mL ethanol and 15 mL DI-water were mixed into a uniform solution, then added in 15 mL 0.01M  $\text{FeCl}_3$  solution. After 30 min stirring, the mixture were transferred to a 100 mL Teflon-lined autoclave, and sealed to heat at  $180^\circ\text{C}$  for 10 h. After cooling down to room temperature, the obtained nanoparticles were washed by ethanol and water repeatedly and dried in vacuum oven.

### 2. 2. Sandwich structure construction

The  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  composite electrode was constructed through easy fabrication process such as spin-coating and sputtering on Indium Tin Oxide coated (ITO) glass substrate, as shown in Fig 1. First of all, a  $\text{Fe}_2\text{O}_3$  layer was prepared by spin-coating on clean ITO glass substrate followed by 40 min Ozone sputtering and annealing at 250 degree in air for 2 h. After that, a second layer of gold with thickness of 30nm was sputtered on the top of the  $\text{Fe}_2\text{O}_3$  layer. Finally, the  $\text{Fe}_2\text{O}_3$  layer was deposited through the same process as the first  $\text{Fe}_2\text{O}_3$  layer.  $\text{Fe}_2\text{O}_3$  double-layer electrode,  $\text{Fe}_2\text{O}_3/\text{ITO}/\text{Fe}_2\text{O}_3$  composite electrode and  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  composite electrodes with different Au intermediate layer thickness were prepared following the similar route.

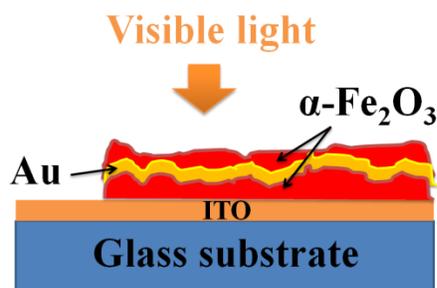


Fig.1 Schematic illustration of sandwich photo-electrode

### 2. 3. Characterization

X-ray diffraction (XRD) measurement was conducted on a Shimadzu XRD-6000 X-ray diffractometer using  $\text{Cu K}\alpha$  source at a scanning rate of  $1^\circ/\text{min}$  with the  $2\theta$  range from  $20$  to  $70^\circ$ . Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100F transmission electron microscope at an accelerate voltage of 200kV. UV-vis diffuse reflectance spectra (DRS) were recorded on a Lambda 750 UV/VIS/NIR spectrophotometer (Perkin-Elmer, USA). The field emission scanning electron microscopy (FESEM) images were performed with a JEOL JSM-7600F scanning electron microscope. A three electrode configuration was used in testing the photo-current by electrochemical workstation (CHI852c). 150W Halogen lamp light source (DOLAN JENNER Model 150 Illuminator) was used to illuminate the samples. Oriel Order Sorting Filter ( $\lambda > 420\text{nm}$ ) was also inserted

into the light source to eliminate the UV light. 0.1M  $\text{KH}_2\text{PO}_4$  solution in deionized (18  $\Omega\text{M}$ ) water with pH adjusted to 7.0 was used as the buffer solution. Ag/AgCl electrode and Pt-wire electrode was employed as the reference and counter electrode (cathode) respectively.

### 3. Results and discussion

#### 3. 1. General results

Fig 2 shows the XRD pattern of the synthesized  $\text{Fe}_2\text{O}_3$  nanoparticle. The XRD pattern can be assigned to the pure phase of hematite with Joint Committee on Powder Diffraction Standards (JCPDS) card number 79-1741 (Hematite, syn). No more peaks other than those belong to hematite can be observed. Inset of Fig 2 shows the morphology of the synthesized  $\text{Fe}_2\text{O}_3$  nanoparticles under TEM imaging. Nano-cubes of  $\text{Fe}_2\text{O}_3$  can be observed with size around 25 to 30 nm. The nanoparticles can be uniformly dispersed in ethanol or chloroform and form reddish-orange-colour colloid.

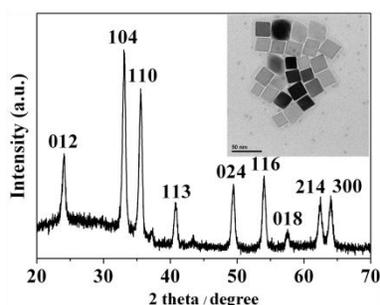


Fig.2 XRD spectra of synthesized  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles. Inset: TEM images of  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles (scale bar = 50nm)

After each layer of coating, photo-electrode is examined by diffuse reflectance and the absorbance was calculated, as shown in Fig 3. Absorption peak around 550nm confirms the visible light range absorption of  $\text{Fe}_2\text{O}_3$  after 1<sup>st</sup> layer deposition. The peak position is coherent to the 2.1eV band gap energy of hematite. After 2<sup>nd</sup> layer construction, the peak position is shifted to 480nm and after 3<sup>rd</sup> layer construction, a significant absorption peak around 480nm and shoulder around 560nm can be observed. After the construction of the sandwich structure, a broad absorption between 420nm to 590nm can be achieved, such confirms the broad visible light absorption of the  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  composite electrode.

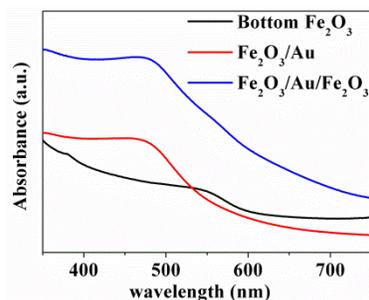


Fig.3 Absorption spectra of the spin-coated films (calculated from diffuse reflectance spectra)

Fig 4 illustrates the surface morphology of the  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  composite electrode under FESEM. Full coverage of the substrate is achieved and only outer-most layer of  $\text{Fe}_2\text{O}_3$  nanocubes can be observed. The surface is not exactly flat since some nanoparticles are stack together. However, single nanoparticles can still be clearly distinguished and no cracks or fusion aggregates is visible.

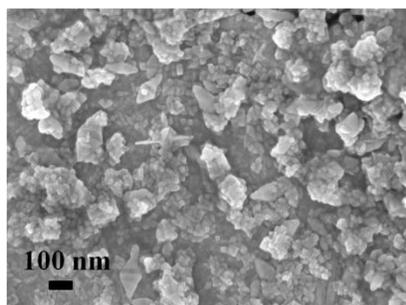


Fig.4 SEM image of sandwich photo-electrode (top view)

### 3. 2. Photoconversion performance

In order to test the improvement of photoconversion performance of the sandwich  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  photo-electrode compared to  $\alpha\text{-Fe}_2\text{O}_3$  double-layer electrode, photo-current with and without illumination (indicated as Dark and Light) is taken and compared in Fig 5. The onset potential of the sandwich electrode is reduced by 0.4V compared to pure  $\text{Fe}_2\text{O}_3$  electrode. At 0.8V, around 0.8mA photocurrent can be observed for sandwich photoelectrode. This suggests the performance is significantly improved by using this sandwich photo-electrode.

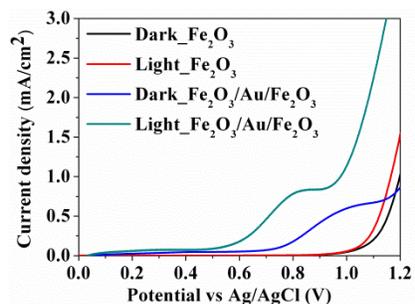


Fig.5 Graphs of current density vs potential showing photo-current comparison of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  photo-electrodes.

### 3. 3. Influence of Au intermediate layer

Coupling plasmonic Au with semiconductor has been reported previously. Thimsen et al. (2011) have suggested that Au may improve the performance of PEC water splitting due to the localized surface plasmonic resonance (LSPR) effects of Au. The energy can be localized at the interface between Au and semiconductor and thus improves the absorption of the light energy by semiconductor. However, the efficient thickness of Au to cause this enhancement is around 5nm and only surface deposited Au has such behavior. Au layer embedded within semiconductor layer does not have such enhancement. Tian et al. (2005) examined the photo-current of Au coupled  $\text{TiO}_2$  and suggested that the enhancement mechanism is due to the visible light absorption of Au layer. He proposed a mechanism in which electrons are excited within Au layer and then transferred to semiconductor. Therefore, experiments were designed to study the effect of the Au intermediate layer in the sandwich structure.

By replacing Au layer with conductive ITO layer with the same thickness, the onset potential is increased by 0.3V; and below 0.8V, the photocurrent is reduced to zero, as shown in Fig 6a. By comparing this result together with the photocurrent of the sandwich  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  photo-electrodes, it can be implied that the role of Au layer is greatly beyond electron transfer.

In order to further investigate the role of the Au layer in light harvesting,  $\text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3$  sandwich photo-electrodes with different thickness of Au were constructed and their photo-current is compared, as shown in Fig 6b. The onset potential remains the same for all three samples; however, the photo-current is gradually increased with thickness of Au at low potential below 0.8V. Since thicker Au layer has larger

light absorption, these results confirm the important contribution of Au layer in light harvesting and photo-excitation.

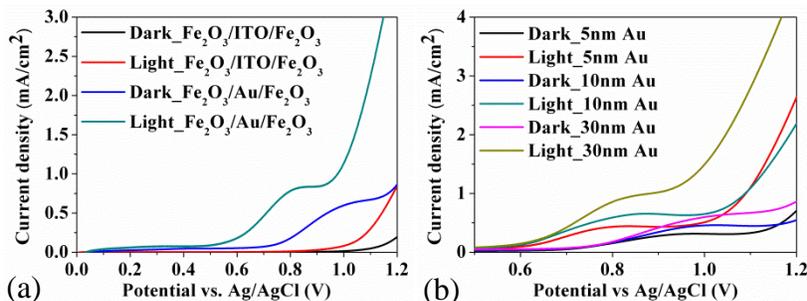


Fig.6 Graphs of current density vs potential showing photo-current comparison of the photoanode of Fe<sub>2</sub>O<sub>3</sub>/Au/Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>/ITO/Fe<sub>2</sub>O<sub>3</sub> (a) and Fe<sub>2</sub>O<sub>3</sub>/Au/Fe<sub>2</sub>O<sub>3</sub> photo-electrodes with different thickness of Au intermediate layer (b).

### 3. 4. Proposed mechanism

Based on the above results, the enhanced PEC performance may be explained by the model as shown in Fig 7. Upon illumination, the electrons can be excited in all three layers, and under the small bias, the excited electrons are directed to be transferred to ITO conductive layer of the photoanode and then further directed to Pt cathode and participate in water reduction at the cathode. The photo-holes left in top Fe<sub>2</sub>O<sub>3</sub> layer are consumed by water and water is thus oxidized to O<sub>2</sub>. The metallic nature of Au may provide a conductive layer for photo-charge migration, and resulted in lower onset potential. All three layers may contribute in light harvesting and photo-excitation. Since Au is embedded in between of two Fe<sub>2</sub>O<sub>3</sub> layers, its localized surface plasmonic resonance (LSPR) effects may be quite limited (Thimsen et al., 2011).

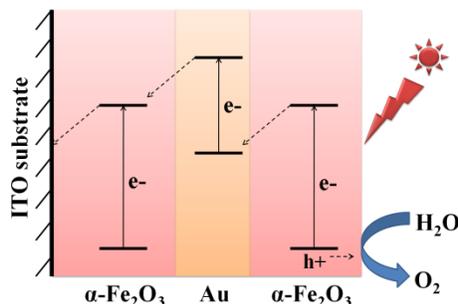


Fig.7 Schematic illustration of band gap energy and electron transfer in the sandwich photoelectrode.

### 4. Conclusion

We constructed a sandwich structure of Fe<sub>2</sub>O<sub>3</sub>/Au/Fe<sub>2</sub>O<sub>3</sub> photo-electrode with the purpose of improving the PEC water splitting performance compared to pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrode. From the photoconversion test, the onset potential and photo-current can be improved by using this sandwich structure. The role of Au intermediate layer can be summarized as follows: (1) The metallic nature of the Au layer allows the electrons and holes to have relative high mobility and thus allows more efficient electron transfer between top and bottom layers. (2) Visible light absorption of Au layer can also generate photo-electrons and transferred to bottom Fe<sub>2</sub>O<sub>3</sub> under small bias. From the experimental results, the second role is dominant over the first role. Such sandwich structure may be applied to other semiconductor as well to improve PEC performance.

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