

# FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY OF MAGHEMITE NANOPARTICLES LOADED WITH GOLD NANOPARTICLES

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**Abstract.** Photocatalytic water splitting is very useful for solar energy conversion. Iron oxides are attracting a lot of interests due to absorption in the visible region. However, iron oxides have poor conductivity. As one of solutions, the photocatalytic performance may be enhanced with loaded gold nanoparticles (Au-NP) by the characteristic optical absorption and the charge trapping nature. In this study, hybrid material of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and Au-NP (denoted as Au- $\text{Fe}_2\text{O}_3$ ) was prepared and the photo-generated carrier dynamics was revealed by femtosecond transient absorption (TA) spectroscopy. The hybrid material was prepared by mixing maghemite powder into 40 nm Au-NP aqueous solution. TA decay of Au- $\text{Fe}_2\text{O}_3$  indicates faster decay and suggests occurrence of hole transfer from maghemite to Au-NP, which can suppress the charge recombination and may result in enhancement of the photocatalytic reactivity.

**Keywords:** transient absorption spectroscopy, iron oxide, Au nanoparticles, photocatalyst

## 1. Introduction

In recent decades, the energy problem is one of the serious tasks in the world. Photocatalytic water splitting is very useful for solar energy conversion. Iron oxides are attracting a lot of interests as photocatalyst and photoelectrode due to its resource abundance, chemical stability, and strong absorption in the visible region [1,2]. In particular, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) has been studied as a photoanode material for solar water splitting [3-9], whereas only limited reports related to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) were published for photocatalyst [10,11]. One of the reasons that maghemite has not been researched as hematite might be that maghemite usually undergoes a phase transformation into hematite for particles larger than 10 nm [10]. Moreover, several disadvantages of iron oxides limit this ability for photoanodes due to poor conductivity and photocurrent quantum efficiency [2]. Therefore, a practical system has not been constructed even for hematite photoanodes.

The light absorption can be improved for high photocatalytic performance utilizing surface plasmon resonance of combined noble metal nanostructures. Especially, gold nanoparticles (Au-NPs) are considered as suitable candidates because of their good chemical stability and characteristic absorption in the visible wavelength region [12-14]. In addition, Au-NP can be expected as a charge-trapping center, where charges separated at the interface between semiconductor and Au-NP can escape from the charge recombination. We can apply this advantage to various materials. Hybrid materials of hematite and AuNP were reported [15-19]. As another semiconductor, it has been demonstrated the potential hybrid material of BFO ( $\text{BiFeO}_3$ ), decorated Au-NP by utilizing the superficial electrical characteristics of zeta potential [12].

In this paper, we fabricated hybrid material of maghemite and Au-NP and investigated the carrier separation mechanism after photo-excitation at 400 nm. The hybrid material was fabricated by simple method utilizing each superficial electrical characteristic [12,20]. Carrier separation mechanism was investigated by femtosecond transient absorption spectroscopy (fs-TAS) in the visible and NIR region.

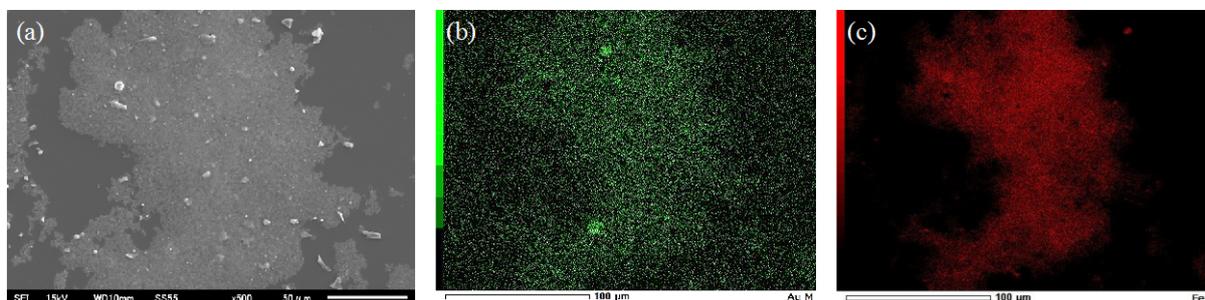
## 2. Experimental

**Synthesis of Hybrid Material.** Au-NP solution was synthesized by boiling 100 mL pure water with adding 0.1 mL of 0.25 M  $\text{HAuCl}_4$  and 1.0 mL of  $3.4 \times 10^{-2}$  M sodium citrate solution. The hybrid material was prepared mixing maghemite powder (mean diameter < 50 nm) into the 40 nm Au-NP aqueous solution, followed by stirring for 1 h and drying in the atmosphere.

**Characterization and Measurement.** The surface of Au- $\text{Fe}_2\text{O}_3$  was examined by a Scanning Electron Microscope (SEM) (JEOL, JSM-6510A) equipped with an X-ray energy-dispersive spectrometer (EDS) (JEOL, EX-54185JMU). Steady state reflectance spectra of the hybrid material and Au-NP colloidal solution were measured with an absorption spectrophotometer (JASCO, V-670). The corresponding optical absorption of powder samples was evaluated by the Kubelka-Munk function. Femtosecond pump-probe TA spectroscopy was carried out with an amplified Ti: sapphire laser (800 nm wavelength, 130 fs fwhm pulse width, 0.8 mJ/pulse intensity, 1 kHz repetition; Spectra Physics, Hurricane). The second harmonic of 400 nm wavelength at a 500 Hz modulation frequency was used for a pump light. On the other hand, the white-light continuum generated by focusing the fundamental beam from Ti: sapphire laser onto a sapphire plate (2 mm thick) was used for a probe light. The probe light was focused at the center of the pump light ( $\sim 0.3$  mm diameter) on the sample, and the diffuse reflected probe light was detected by a Si photodiode after passing through a monochromator (Acton Research, SpectraPro-150).

## 3. Results and Discussion

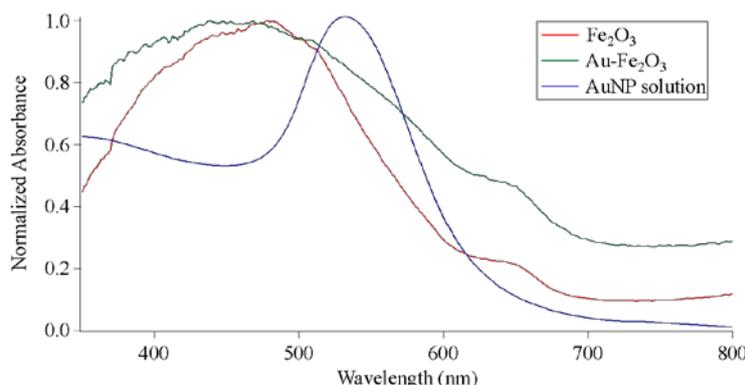
**SEM-EDS Mapping.** Figure 1 (a-c) shows SEM-EDS mapping of fabricated Au- $\text{Fe}_2\text{O}_3$  by the above-mentioned simple method, revealing the distribution of Au and Fe. The similar distributions between these two elements indicate successful fabrication of hybrid material of maghemite and gold nanoparticles. In this study, the pH value of incubation solution was slightly acidic. In this case, maghemite surface is positively charged [20], and Au-NP is negatively charged. As a result, we could assemble them by the superficial electrical interaction between maghemite and Au-NP.



**Fig. 1.** (a) SEM image of Au- $\text{Fe}_2\text{O}_3$ , (b) EDS mapping of Au element, (c) EDS mapping of Fe element

**Steady State Absorption Spectra.** Figure 2 shows steady state absorption spectra of  $\text{Fe}_2\text{O}_3$ , Au- $\text{Fe}_2\text{O}_3$  and Au-NP solution. Steady state absorption spectra of  $\text{Fe}_2\text{O}_3$  and Au- $\text{Fe}_2\text{O}_3$  was evaluated using measured diffuse reflectance spectra by the Kubelka-Munk function and

normalized. Steady state absorption spectra of Au-NP solution was measured by using transmitted light and normalized. For Au-NP solution, we can observe absorption peak at 532 nm due to the surface plasmon resonance, which indicates that the radius of used Au-NP is about 20 nm. The absorption spectrum of Au-Fe<sub>2</sub>O<sub>3</sub> sample indicates a broader band than that of Fe<sub>2</sub>O<sub>3</sub>. This enhancement is induced by interband transition at short wave region from 400 nm to 500 nm and surface plasmon resonance at long wave region from 500 nm to 600 nm. Therefore, we confirmed efficient fabrication of maghemite and AuNP.



**Fig. 2.** Steady state absorption spectra of Fe<sub>2</sub>O<sub>3</sub>, Au-Fe<sub>2</sub>O<sub>3</sub> and Au-NP solution

**Transient Absorption Spectra.** Figure 3 shows TA decays of Fe<sub>2</sub>O<sub>3</sub> and Au-Fe<sub>2</sub>O<sub>3</sub> probed at various wavelengths. Each TA decay of Au-Fe<sub>2</sub>O<sub>3</sub> indicates faster decay than that of bare Fe<sub>2</sub>O<sub>3</sub>. In our previous study, TA signals with a peak around 600 nm are assigned to hole absorption [21]. Especially TA decay probed at 585 nm obviously indicates faster decay (Fig. 3a). Therefore, this decay suggests occurrence of hole transfer from maghemite to Au-NP, which can suppress the charge recombination and may result in enhancement of the photocatalytic reactivity.

The decay was analyzed using a double exponential function (Table 1):

$$A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + C. \quad (1)$$

We focus on the  $\tau_1$ ; this parameter of Au-Fe<sub>2</sub>O<sub>3</sub> is smaller to that of Fe<sub>2</sub>O<sub>3</sub>, while the amplitude of Au-Fe<sub>2</sub>O<sub>3</sub> is larger than that of Fe<sub>2</sub>O<sub>3</sub>. In addition, we can confirm similar trend for  $\tau_2$ . We assume that the rate constant of recombination in the maghemite is  $k_{rec}$  and that the hole transfer from maghemite to Au-NP is  $k_{ht}$ . These parameters satisfy the equations:

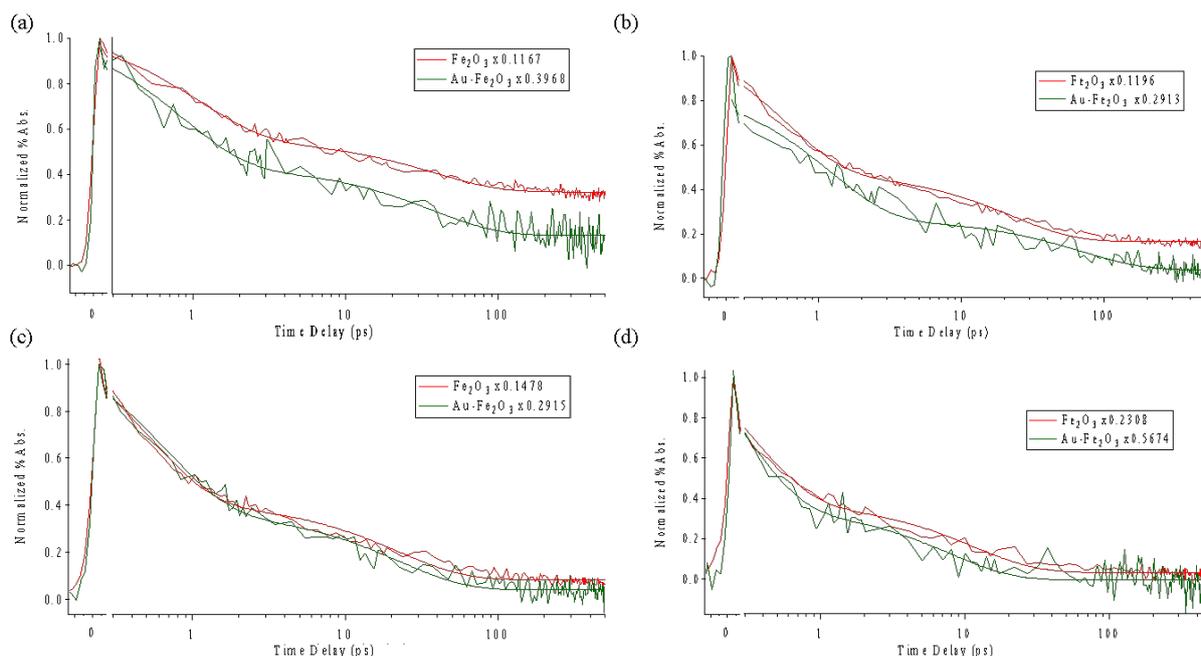
$$\tau_1(\text{Fe}_2\text{O}_3) = 1/k_{rec}; \quad (2)$$

$$\tau_1(\text{Au-Fe}_2\text{O}_3) = 1/(k_{rec} + k_{ht}). \quad (3)$$

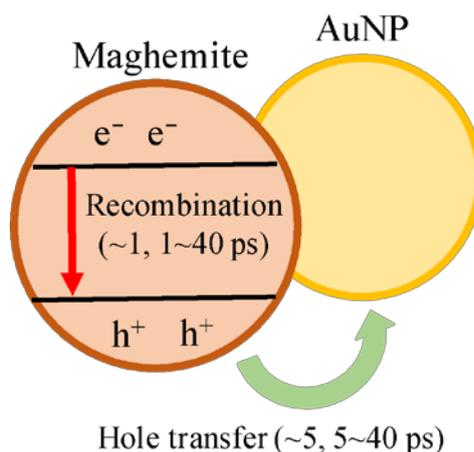
Therefore, we obtain that  $k_{rec}$  and  $k_{ht}$  are  $(1.1 \pm 0.1 \text{ ps})^{-1}$  and  $(3.4 \pm 1.6 \text{ ps})^{-1}$ , respectively. These results indicate fast recombination of photogenerated holes and electrons ( $< 1.1 \text{ ps}$ ), and hole transfer ( $< 5 \text{ ps}$ ), as shown in Fig. 4.

Table 1. Fitting parameters of TA decays of Fe<sub>2</sub>O<sub>3</sub> and Au-Fe<sub>2</sub>O<sub>3</sub> probed at 585 nm

	Fe <sub>2</sub> O <sub>3</sub>	Au-Fe <sub>2</sub> O <sub>3</sub>
A <sub>1</sub>	42.0 ± 1.1 %	52.4 ± 3.6 %
τ <sub>1</sub> (ps)	1.0892 ± 0.0629	0.82545 ± 0.123
A <sub>2</sub>	23.0 ± 0.7 %	29.8 ± 2.0 %
τ <sub>2</sub> (ps)	37.996 ± 2.95	36.799 ± 6.59
Constant	32.4 ± 0.2 %	13.5 ± 0.6 %



**Fig. 3.** Transient absorption decays probed at (a) 585 nm, (b) 650 nm, (c) 750 nm and (d) 920 nm of  $\text{Fe}_2\text{O}_3$  and  $\text{Au-Fe}_2\text{O}_3$



**Fig. 4.** Photogenerated hole transfer kinetic

#### 4. Conclusion

We demonstrated successful fabrication of hybrid material of nanoparticles of maghemite and gold, and revealed charge separation mechanism between them. Hybrid material of gold nanoparticles and maghemite nanoparticles is assembled by the superficial electrical interaction. This fabrication resulted in appearance of broader absorption in a wide visible region due to interband transition and surface plasmon resonance of Au-NPs. Transient absorption indicated hole absorption. Transient absorption decay of  $\text{Au-Fe}_2\text{O}_3$  indicated faster decay. This result suggested that photogenerated holes at iron oxides can escape from fast recombination within 1.0 ps and transfer to gold nanoparticles within 5.0 ps. This charge separation mechanism allows us to expect enhancement of the photocatalytic reactivity by composited gold nanoparticles due to the prolonged carrier lifetime.

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## References

- [1] Tartaj P, Morales MP, Gonzalez-Carreno T, Veintemillas-Verdaguer S, Serna CJ. The iron oxides strike back: from biomedical applications to energy storage devices and photoelectrochemical water splitting. *Adv. Mater.* 2011;23(44): 5243-5249.
- [2] Cherepy NJ, Liston DB, Lovejoy JA, Dong H, Zhang JZ. Ultrafast Studies of Photoexcited Electron Dynamics in  $\gamma$ - and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Semiconductor Nanoparticles. *J. Phys. Chem. B.* 1998;102(5): 770-776.
- [3] Chen YJ, Chen LY. The study of carrier transfer mechanism for nanostructural hematite photoanode for solar water splitting. *Appl. Energy.* 2016;164: 924-933.
- [4] Zhang Z, Hossain FM, Takahashi T. Self-assembled hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanotube arrays for photoelectrocatalytic degradation of azo dye under simulated solar light irradiation. *Appl. Catal. B.* 2010;95(3-4): 423-429.
- [5] Klahr B, Gimenez S, Fabregat-Santiago F, Hamann T, Bisquert J. Water oxidation at hematite photoelectrodes: the role of surface states. *J. Phys. Chem. C.* 2014;118(19): 10393-10399.
- [6] Hiralal P, Saremi-Yarahmadi S, Bayer BC, Wang H, Hofmann S, Wijayantha KGU, Amaratunga GAJ. Nanostructured hematite photoelectrochemical electrodes prepared by the low temperature thermal oxidation of iron. *Sol. Energy Mater. Sol. Cells.* 2011;95(7): 1819-1825.
- [7] Le Formal F, Pendlebury SR, Cornuz M, Tilley SD, Gratzel M, Durrant JR. Back electron-hole recombination in hematite photoanodes for water splitting. *J. Am. Chem. Soc.* 2014;136(6): 2564-2574.
- [8] Pendlebury SR, Wang X, Le Formal F, Cornuz M, Kafizas A, Tilley SD, Gratzel M, Durrant JR. Ultrafast Charge Carrier Recombination and Trapping in Hematite Photoanodes under Applied Bias. *J. Am. Chem. Soc.* 2014;136(28): 9854-9857.
- [9] Barroso M, Pendlebury SR, Cowan AJ, Durrant JR. Charge carrier trapping, recombination and transfer in hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) water splitting photoanodes. *Chem. Sci.* 2013;4: 2724-2734.
- [10] Sharifi T, Kwong WL, Berends HM, Larsen C, Messinger J, Wagberg T. Maghemite nanorods anchored on a 3D nitrogen-doped carbon nanotubes substrate as scalable direct electrode for water oxidation. *Int. J. Hydrog. Energy.* 2016;41(1): 69-78.
- [11] Idris A, Hassan N, Ismail NSM, Misran E, Yusof NM, Ngomsik AF, Bee A. Photocatalytic magnetic separable beads for chromium (VI) reduction. *Water Research.* 2010;44(6): 1683-1688.
- [12] Li S, Zhang J, Kibria MG, Mi Z, Chaker M, Ma D, Nechache R, Rosei F. Remarkably enhanced photocatalytic activity of laser ablated Au nanoparticle decorated BiFeO<sub>3</sub> nanowires under visible-light. *Chem. Commun.* 2013;49(52): 5856-5858.
- [13] Zhang J, Chen G, Chaker M, Rosei F, Ma D. Gold nanoparticle decorated ceria nanotubes with significantly high catalytic activity for the reduction of nitrophenol and mechanism study. *Appl. Catal. B.* 2013;132-133: 107-115.
- [14] Du L, Furube A, Hara K, Katoh R, Tachiya M. Ultrafast plasmon induced electron injection mechanism in gold-TiO<sub>2</sub> nanoparticle system. *J. Photochem. Photobiol. C.* 2013;15: 21-30.
- [15] Shinde PS, Lee SY, Ryu J, Choi SH, Jang JS. Enhanced photoelectrochemical performance of internally porous Au-embedded  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes for water oxidation. *Chem. Commun.* 2017;53(30): 4278-4281.
- [16] Wang L, Hu H, Nguyen NT, Zhang Y, Schmuki P, Bi Y. Plasmon-induced hole-depletion layer on hematite nanoflake photoanodes for highly efficient solar water splitting. *Nano Energy.* 2017;35: 171-178.

- [17] Li Z, Su C, Wu D, Zhang Z. Gold nanoparticles decorated hematite photoelectrode for sensitive and selective photoelectrochemical aptasensing of lysozyme. *Anal. Chem.* 2018;90(1): 961-967.
- [18] Li J, Cushing SK, Zheng P, Meng F, Chu D, Wu N. Plasmon-induced photonic and energy-transfer enhancement of solar water splitting by a hematite nanorod array. *Nat. Commun.* 2013;4: 3651.
- [19] Koren MG, Dotan H, Rothscild A. Nano gold rush: on the origin of the photocurrent enhancement in hematite photoanodes decorated with gold Nanoparticles. *J. Phys. Chem. C.* 2016;120(28): 15042-15051.
- [20] Yu S, Chow GM. Carboxyl group ( $-\text{CO}_2\text{H}$ ) functionalized ferrimagnetic iron oxide nanoparticles for potential bio-applications. *J. Mater. Chem.* 2004;14(18): 2781-2786.
- [21] Okazaki M, Furube A, Chen YJ, Chen LY. Elucidation of carrier separation mechanism of hematite photoanodes by femtosecond transient absorption spectroscopy. In: *Annual Meeting on Photochemistry*. 2017. p.1C10.