

Preparation of Au nanorod/TiO₂ composites and evaluation of their performance as plasmonic photocatalyst

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Titanium dioxide (TiO₂) is one of the most important photocatalysts because TiO₂ is cheap, nontoxic and chemically stable. However, TiO₂ (band gap = 3.2 eV) can only absorb ultraviolet (UV) light due to the wide band-gap. UV light accounts for only about 5% of the total solar energy. Therefore, development of visible light-responding photocatalysts is an important topic for efficient utilization of solar energy. Recently, visible light-responding photocatalysts utilizing surface plasmon resonance (SPR) of gold (Au) nanoparticles have been reported^[1-7]. Au nanoparticles exhibit absorption at around 550 nm. We focused on Au nanorods (Au NRs) to utilize light of longer wavelength. Au NRs which are anisotropic nanoparticles have short axis and long axis, and especially long axis show strong absorption at near infrared region. In this study, we synthesized Au NRs/TiO₂ composites and evaluated the performance as a plasmonic photocatalyst.

Figure 1 shows TEM images of Au NRs/TiO₂ samples. Au NRs were successfully deposited on the surface of TiO₂ with keeping the shape of rods by using a method of colloid photodeposition operated in the presence of a hole scavenger (CPH)^[7].

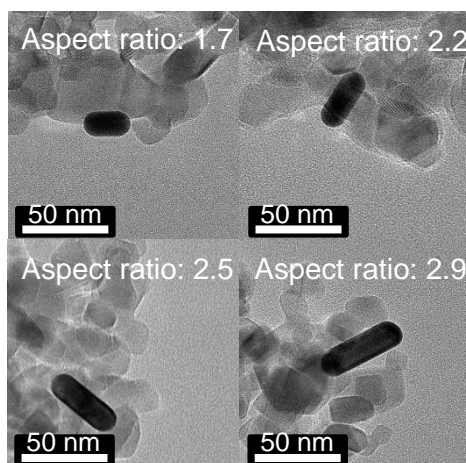


Figure 1 TEM images of Au NRs/TiO₂.

Figure 2(a) shows absorption spectra of Au NRs/TiO₂ composites. In the spectra of Au NRs/TiO₂, photoabsorption was observed at around $\lambda = 530$ nm and $\lambda > 600$ nm. The wavelength of photoabsorption at around $\lambda = 530$ nm and longer than $\lambda = 600$ nm which were attributed to transverse and longitudinal SPR mode (T- λ_{top} and L- λ_{top}) of Au NRs,

respectively. The $L\text{-}\lambda_{\text{top}}$ gradually shifted to longer wavelength with increasing value of aspect ratio (AR) of Au NRs and reached 850 nm at AR = 3.4.

To examine the effect of the value of AR of Au NRs on their photocatalytic performance, the Au NRs/TiO₂ composites shown in Figure 2(a) were used for acetone formation from 2-propanol under irradiation of visible light from Xe lamp with R60 cut-filter, and the amounts of acetone formed for 20 h are shown in Figure 2(b). The amount of acetone decreased almost linearly with the increase in AR of Au NRs. Figure 2(b) also shows the effect of the value of AR on the energy of photoabsorption at top wavelength due to $L\text{-}\lambda_{\text{top}}$ of Au NRs. The energy of photoabsorption at $L\text{-}\lambda_{\text{top}}$ decreased with increasing AR. The AR dependency of the oxidation activity was similar to that of the energy of photoabsorption at $L\text{-}\lambda_{\text{top}}$, suggesting that SPR photoabsorption by Au NRs was one of the important factors determining the activity of plasmonic photocatalysis.

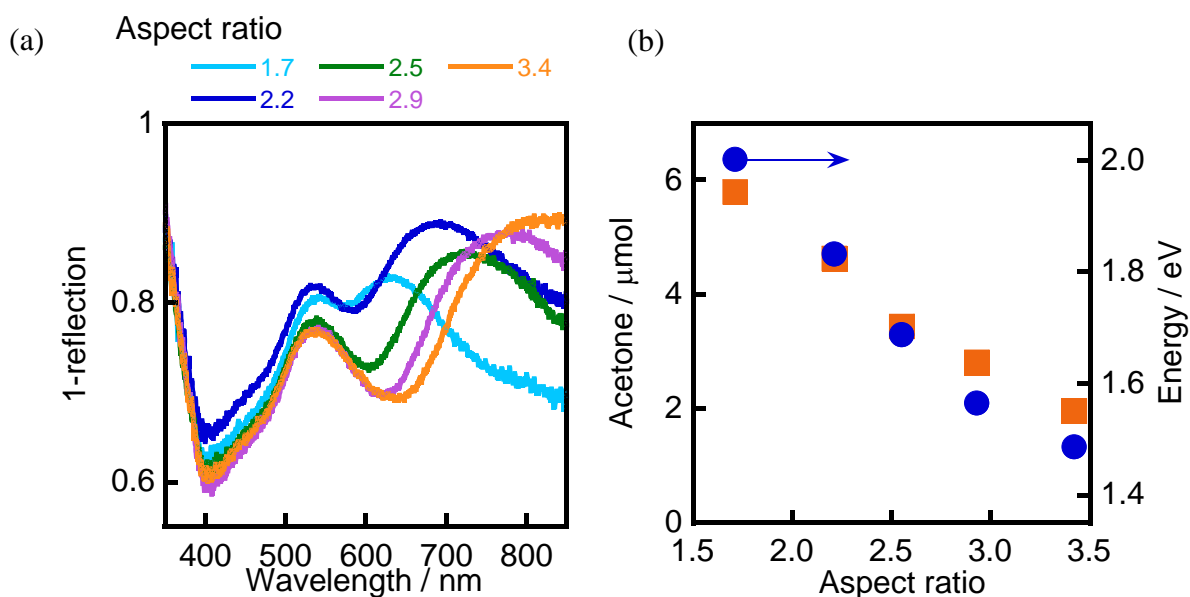


Figure 2 (a) Absorption spectra of Au NRs/TiO₂ and (b) effect of aspect ratio of Au NRs on formation of acetone over Au NRs/TiO₂ under irradiation of visible light from Xe lamp with R60 at 20°C for 20 h and energy of light due to SPR absorption.

References:

- [1] Y. Tian and T. Tatsuma, *J. Am. Chem. Soc.*, **2005**, 127, 7632.
- [2] E. Kowalska, O. O. P. Mahaney, R. Abe, and B. Ohtani, *Phys. Chem. Phys. Phys.*, **2010**, 12, 2344.
- [3] Y. Zhong, K. Ueno, Y. Mori, X. Shi, T. Oshikiri, K. Murakoshi, H. Inoue, H. Misawa, *Angew. Chem. Int. Ed.*, **2014**, 53, 10350.
- [4] A. Tanaka, S. Sakaguchi, K. Hashimoto and H. Kominami, *Catal. Sci. Technol.*, **2014**, 4, 1931.
- [5] A. Tanaka, K. Hashimoto, H. Kominami, *J. Am. Chem. Soc.*, **2012**, 134, 14526.
- [6] A. Tanaka, K. Hashimoto, H. Kominami, *J. Am. Chem. Soc.*, **2014**, 136, 586.
- [7] A. Tanaka, A. Ogino, M. Iwaki, K. Hashimoto, A. Ohnuma, F. Amano, B. Ohtani and H. Kominami, *Langmuir*, **2012**, 28, 13105.