

## Investigation of Isotopic Selectivity on Plasmon-Induced Photoconversion System

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Illumination of visible light onto metal nanoparticles with a several tens or hundreds nanometer scales can induce a collective oscillation of free electrons, which is called as the localized surface plasmon resonance. The combination of metal nanoparticles and wide gap semiconductor recognized as the plasmonic photoconversion system enables to convert the visible to near-infrared light energy into the chemical energy.<sup>1</sup> Up to date, the plasmonic cathode electrodes have been established by the introduction of plasmonic nanostructures on the p-type semiconductor electrodes.<sup>2</sup> In our previous study, we have observed the unique pH dependent on the plasmon-induced hydrogen evolution reaction (HER).<sup>3</sup> In the present study, we have investigated the isotopic selectivity on plasmon-induced HER process for the clarification of the unique molecular behavior at the plasmonic structure surface. Through the investigations, we have observed the characteristic isotopic selectivity at the plasmonic field.

The metal nanostructures prepared by the nanosphere lithography method were prepared on p-type GaP electrode. The extinction spectrum of nanostructures shows the resonance peak at around 800 nm. The photocurrent measurements using the plasmonic cathode electrode in both H<sub>2</sub>O and D<sub>2</sub>O solutions. In the general isotopic effect on HER, the photocurrent values decrease as increasing the content of D<sub>2</sub>O in the electrolyte solution. By contrast, interestingly, we have observed the inverse isotope effect on the plasmon-induced HER system as shown in Fig. In addition, the photocurrent increments depending on the contents of D<sub>2</sub>O were also observed. Numerical kinetic equation analyses were performed to discuss the molecular behavior. As the results, it was found that the surface adsorption process of D atoms was selectively accelerated in the plasmonic field as compared with the non-plasmonic HER system. Additionally, a wavelength dependence also clarified the contribution of the plasmon to the phenomena. From above results, the surface molecular process in the plasmon induced proton coupled electron transfer reaction has been proposed.

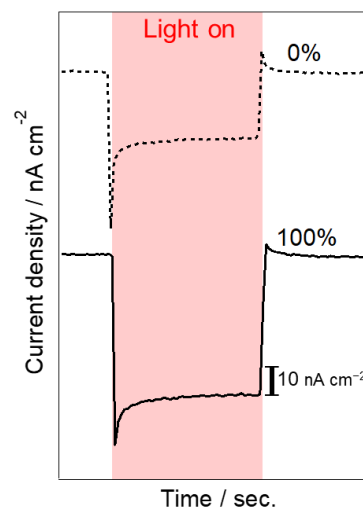


Fig. Photocurrents for GaP/Au electrode obtained under visible light illumination ( $1000\text{ nm} > \lambda > 640\text{ nm}$ ). The electrolyte solutions were 0.5 M NaClO<sub>4</sub>aq. Percentages indicate the content of D<sub>2</sub>O in solution. The electrochemical potential of the electrode was  $-0.3\text{ V vs. Ag/AgCl}$ .

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