The plasmonic nano-grating device for photocatalytic water splitting reaction

S. Jeong, G. Yang, Y. Arashida, K. Akada, Y. Ito, J. Fujita
Institute of Pure and Applied Sciences, University of Tsukuba,
Tsukuba 305-8571, Japan
jeong.samuel.fp@u.tsukuba.ac.jp

Water splitting technology using solar energy in the presence of semiconductor photocatalysts is attracted attention as means of renewable energy production. Titanium dioxide (TiO_2, band gap: 3.2 eV), the most famous photocatalyst, is activated by ultraviolet (UV) light. However, sunlight has a spectrum mainly in the visible (VIS) light range. Therefore, the VIS light utilization on photocatalytic reaction is essential for the effective use of sunlight. We focused on two-photon absorption by VIS light and attempted to enhance the photocatalytic reaction activity. Periodic structures with a pitch size of light wavelength (385-750 nm) induce surface plasmon resonance (SPR) and optical radiation. This high-density photon field can boost two-photon absorption into the photocatalyst. We demonstrated enhanced photocatalytic water splitting reaction with VIS light using nano-grating devices.

We fabricated Au/Ti ring-like nano-grating devices (i.e., SPR devices) using electron beam lithography. Figure 1 shows the structure of our proposed device; we optimized the periodical pitch at which the electric field amplification becomes large in visible light between 385 nm to 750 nm by the finite difference time domain (FDTD) method simulation. We deposited 10 nm Ti and 50 nm Au on the glass substrate, and ZEP520 resist was spin-coated on the top. Then the designed grating pattern was fabricated by electron beam lithography and lift-off process. We optimized the local dose amount to compensate for the reduced pattern processing accuracy due to proximity effects. We measured the optical properties and photocatalytic activity of the SPR device.

Optical measurements confirmed that optical absorption was improved in SPR devices compared to flat patterned devices. Moreover, strong optical radiation was observed in the central hole region of the SPR device, as shown in Figure 2. The optical properties of SPR device indicate the surface plasmons were induced and propagated toward the central hole when the visible light irradiates the SPR device. Then, the TiO_2-photocatalyst was coated on SPR devices, and the photocatalytic activities of SPR device electrode and flat electrode were measured. More than 20 times higher photocurrent was observed in the SPR device electrode compared to the flat electrode (Figure 3). These results suggest that the strong photon field accelerates two-photon absorption into TiO_2, allowing the band gap of TiO_2 to be overcome in visible light. This study shows that the formation of a photoreaction field by nanofabrication is useful for photocatalytic applications.

1. Q. Wang and K. Domen, Chem. Rev. 2020, 120, 2, 919–985

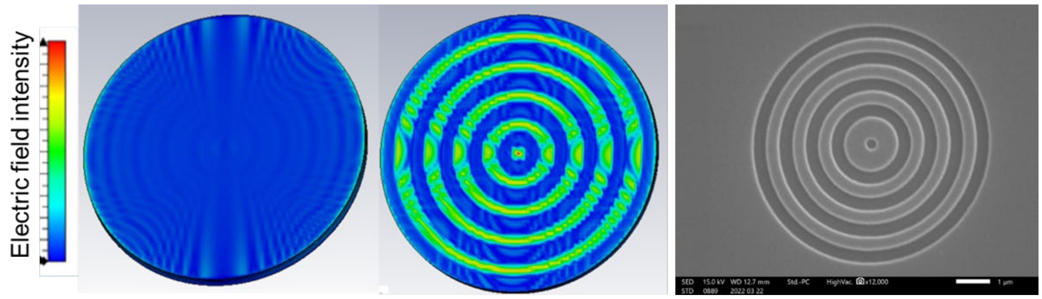

Figure 1. The model of (a) flat pattern and (b) nano-grating pattern. The FDTD simulation suggests nano-grating pattern enhances the electric field intensity on the hole region when VIS light is irradiated. (c) SEM image of fabricated SPR device by electron beam lithography technique

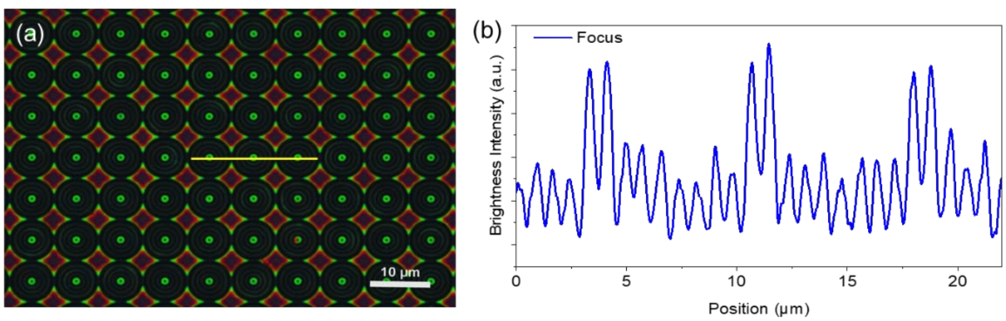

Figure 2 (a) Optical microscope image of the SPR devices when irradiated with VIS light. The yellow line profile is shown in (b). The strong optical radiation field is formed at the center of the SPR device.

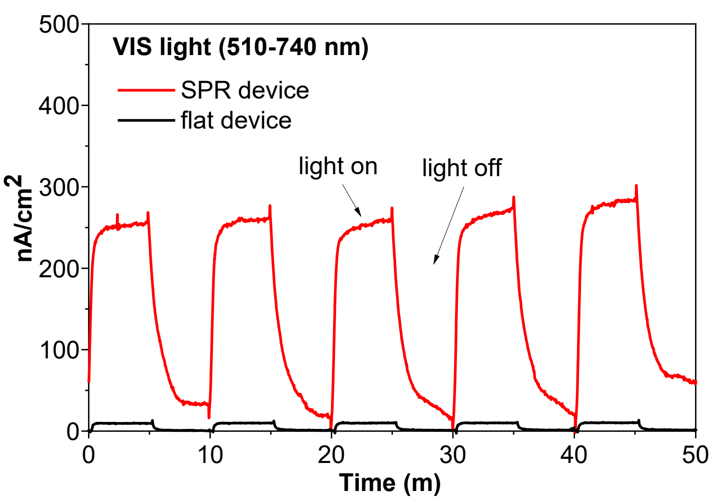

Figure 3 Photocatalytic activities of SPR devices and flat devices. The photocurrent flowed under visible light irradiation was 250 nA/cm^2 for the SPR device and 10 nA/cm^2 for the flat device.