Construction of visible responsive broadband absorber utilizing strong coupling between plasmon and nanocavity modes and its application to light energy conversions

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Nanoparticles colloidal solutions of metals such as gold (Au) and silver (Ag) show very intense color due to localized surface plasmon resonances (LSPRs). LSPRs which are collective oscillations of conduction electrons give rise to the enhancement of electromagnetic field in the vicinity of nanoparticles and are expected as a light harvesting optical antenna for light energy conversion devices based on their spectrum tunability. We have successfully developed the plasmon-induced energy conversions such as water splitting and ammonia synthesis systems as well as solid-state plasmonic solar cells based on the principle of plasmon-induced hot electron transfer from gold nanoparticles (Au-NPs) to the semiconductor electrode.[1-5] In these days, the plasmon-induced hot electron transfer has received considerable attention as a novel strategy for the solar energy conversion.[6,7] However, the insufficient absorption limited its solar energy conversion efficiency for the monolayer of Au-NPs only dispersed on the semiconductor electrode. In the present study, we apply the principle of modal strong coupling to visible responsive broadband absorber for plasmonic water splitting using Au-NPs/titanium dioxide (TiO_2)/Au-film electrode.

Strong coupling between the Fabry–Pérot nanocavity mode of TiO_2/Au-film and LSPR of Au-NPs is induced when both bands of these two modes overlap each other. A key feature of this strong coupling is partially inlaying of Au-NPs into the TiO_2 nanocavity by several nanometers to increase the coupling strength. From the absorption spectrum of Au-NPs/TiO_2/Au-film structure, it was shown that the absorption spectrum is splitted into two peaks due to the formation of hybrid modes and more than 98% of photons are absorbed at the maximum wavelengths of the hybrid modes. A dispersion curve obtained by plotting the splitting energy to the cavity resonant wavenumber indicates an anti-crossing behavior which is characteristics to the strong coupling. Photocurrent was measured using a three-electrode system with a saturated calomel electrode (SCE) as a reference electrode, Pt wire as a counter electrode and this Au-NPs/TiO_2/Au-film electrode as a working electrode in an aqueous electrolyte solution of potassium hydroxide (KOH). We found that the incident photon-to-current conversion efficiency (IPCE) action spectrum exhibited two bands, which almost corresponds to the absorption spectrum of the electrode. Most importantly, in this strong coupling system, the internal quantum efficiency (IQE) of the photocurrent generation is also enhanced at the strong coupling wavelengths. We also explored the plasmon-induced water splitting under strong coupling conditions using a two-electrode system, and a stochiometric evolution of hydrogen (H_2) and oxygen (O_2) has been successfully confirmed. The action spectrum of H_2 evolution almost corresponds to its absorption spectrum. We concluded that the strong coupling between Fabry–Pérot nanocavity mode of TiO_2/Au-film and LSPR of Au-NPs promoted the plasmon-induced water splitting.[8]

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