Plasmon-induced Photocurrent Generation on Ga_2O_3 Loaded with Gold Nanoparticles

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Ga_2O_3 is a promising photocatalyst with the more negative conduction band compared with commonly used TiO_2 due to its much more negative conduction band position which is beneficial to improving efficient water splitting. However, the wide bandgap makes it inactive in the visible light region [1]. In our proposal, gold nanoparticles (Au-NPs) are utilized to increase the photocatalytic activities in the visible light region due to the localized surface plasmon resonance. And the separation of plasmonically excited electron-hole pairs is achieved by the Schottky junction constructed at the interface between Au and semiconductor [2,3]. The electrons on the conduction band of Ga_2O_3 could take part in the reduction of water to produce H_2. Meanwhile, the oxidation process is conducted by holes to achieve the evolution of O_2. Therefore, the interface between Au-NPs and Ga_2O_3 plays important role for efficient energy conversion. In this work, the size effect of Au-NPs and the effect of interface modification on the performance of the plasmonic Ga_2O_3 photoelectrode are investigated.

Different sizes of Au-NPs were obtained from Au film with various thicknesses deposited onto Ga_2O_3 (Sn-doped, (-201)) upon annealing process under 800°C in N_2 for 1h (Au-NPs/Ga_2O_3). The average particle size of Au-NPs increased from 10 to 135 nm as the thickness of Au film increased from 2 to 10 nm, and the samples with Au-NPs size of 13 nm showed the best photocurrent and the incident photon to current conversion efficiency (IPCE) of 0.1% at a peak wavelength measured under the conventional three-electrode photoelectrochemical measurement system with a saturated calomel electrode as reference electrode, a Pt wire as a counter electrode and an aqueous electrolyte solution of $KClO_4$ (0.1 M).

To further improve the oxidation process in the water splitting, a thin TiO_2 layer with several nanometers was deposited on the Au-NPs/Ga_2O_3 by atomic layer deposition (ALD). The IPCE and absorption calculated by Δ (1-T-R) of the Au-NPs/Ga_2O_3 system showed an increment compared with samples without the interface modification, indicating that the interface modification by TiO_2 layer has a positive effect. Also, the onset potential shifted to positive with modification by TiO_2 on Au-NPs/Ga_2O_3, indicating the positive shift of the flat-band potential of the photoelectrode. Although the mechanism of the photocurrent enhancement by TiO_2 modification on Au-NPs/Ga_2O_3 is still unclear, it is speculated that the absorption enhancement due to the refractive index increment of surrounding medium of Au-NP, and flat-band potential change could affect the hot-electron induced photocurrent generation.

References

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