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博士の専攻分野の名称 博士（情報科学） 氏名 鐘 玉磬

学 位 論 文 題 名

Plasmon-Induced Water Splitting under Visible Light Irradiation using Gold Nanostructured Strontium Titanate Single Crystal Substrate

（金ナノ構造担持チタン酸ストロンチウムを用いた可視光照射下でのプラズモン誘起水分解）

As a potential solution to the energy crisis, H_2 production from water via solar irradiation has attracted global attention over the last few decades, because the chemical energy in H_2 can be stored for long periods. Numerous attempts have been made since the photoelectrochemical (PEC) water splitting based on an n-type TiO_2 photoanode was discovered. However, because of the wide band gap of the semiconductor materials adopted, only UV light can be used to directly drive the water splitting reaction. The UV irradiation merely accounts for 5% of the solar spectrum. Visible and infrared light, which take the major part, are still underutilized. Therefore, it is of significance to extend the light-energy conversion to longer wavelengths, especially to the visible and infrared regions. Common materials used for water splitting are particulate. They are undesired because extra energy is required to separate H_2 and O_2 , which evolved in the same reaction chamber. In addition, an external electric bias is necessary in PEC water splitting. To overcome these problems, a plasmon-induced water splitting system under visible light irradiation using gold nanostructured strontium titanate ($SrTiO_3$) single crystal is presented in this study. Gold nanoparticles (Au-NPs) with particle size of several tens of nanometer were employed for $SrTiO_3$ surface decoration, which enhanced the $SrTiO_3$ photoresponse in visible wavelength region due to the localized surface plasmon resonance. It is proposed that the simultaneous evolution of H_2 and O_2 can be realized without an electric wire connecting the anode and the cathode and with space conserved for light irradiation on the anode side through the use of two sides of the same semiconductor substrate.

In order to fabricate Au-NPs, a 3-nm Au thin film was sputtered on $SrTiO_3$ surface and annealed in nitrogen atmosphere at 800°C. After annealing, the gold films transformed to a discontinuous nanoparticle structure. The Au-NPs exhibited characteristic plasmon resonance band with a peak at ca. 630 nm. Numerical simulation shows that the electromagnetic field intensity is greatly enhanced around the interface between gold and $SrTiO_3$ substrate. The stoichiometric evolution of H_2 and O_2 was clearly demonstrated. The efficiency action spectrum closely corresponds to the plasmon resonance spectrum, indicating that the

plasmon-induced charge separation at the Au/SrTiO₃ interface promotes water oxidation and the subsequent reduction of a proton on the backside of the SrTiO₃ substrate. The photo energy derived from visible light irradiation is successfully converted to chemical energy, which is stored as the form of H₂ gas. As a substitution of the conventional external electric bias, the chemical bias used to promote water splitting is significantly reduced to 0.23 V by plasmonic effects (Chapter 2).

The co-catalyst effect on hydrogen evolution in the plasmon-induced water splitting is discussed in detail. A Pt board was stick on the SrTiO₃ substrate via In-Ga alloy to obtain ohmic contact. The water spitting yield with this SrTiO₃/Pt composite substrate was remarkably enhanced. Subsequently, the Pt board was decorated with a noble metal or metal oxide as a co-catalyst for H₂ evolution. Enhanced evolution of H₂ and O₂ with stoichiometric ratio was demonstrated with all kinds of co-catalysts. Rhodium thin layer exhibited relatively high performance as a 3-fold increment compared with the absence of any co-catalyst. The separate evolution of H₂ and O₂ was successfully realized, so as to suppress the undesirable reverse reactions of water splitting. A rational evaluation method of the co-catalyst is thus developed based on the elimination Schottky barrier (Chapter 3).

A facile plasmon-enhanced water splitting system using gold nanostructured semiconductor heterojunction is described. With a larger potential gradient in the energy band, the electron transfer can be facilitated by using semiconductors with different band positions. The substrate composed of single crystal SrTiO₃ with the rutile TiO₂ thin film heterojunction exhibited enhanced water spitting activity compared with the absence of TiO₂ thin film because the back electron transfer reaction might be prevented due to the synergistic effect. The effect on the H₂ evolution efficiency of the thickness of the Pt co-catalyst film was also explored (Chapter 4).

Herein, the plasmon-enhanced water splitting was demonstrated in visible wavelength with gold nanoparticles loaded SrTiO₃. The H₂ and O₂ generation efficiency is highly dependent on the pH values of the solution environments. It is expected that the plasmon resonant wavelength of Au nanostructures can be tuned by simply changing their shape and/or size to cover a large part of the solar spectrum. It indicates the possibility of constructing an artificial photosynthesis system with low energy consumption. The results of these studies warrant future research to evaluate the mechanism of plasmon-enhanced water splitting and provide a facility approach for further design of the plasmon-enhanced solar energy conversion devices.