HOKKAIDO UNIVERSITY

Title	Studies on Highly Localized Excitation of PbS Quantum Dots on Metal Nanostructures [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第12477号
Issue Date	2016-09-26
Doc URL	https://hdl.handle.net/2115/63398
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	doctoral thesis
File Information	Li_Xiaowei_abstract.pdf, 論文内容の要旨

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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士 (理学)　氏名　李　笑瑋

学 位 論 文 題 名

Studies on Highly Localized Excitation of PbS Quantum Dots on Metal Nanostructures

(金属ナノ構造上における PbS 量子ドットの局在励起に関する研究)

Photoelectrochemistry, the conversion of sustainable sunlight to electrical or chemical energy, is believed to be a promising technology to feasibly solve the energy problem. However, photoelectric conversion efficiency of traditional single-junction semiconductors is limited by factors such as the bandgap of the semiconductor, dissipation as heat and electron-hole recombination, resulting in theoretical limit of 34% under sunlight illumination. Novel nano-materials that advance efficient photoelectric conversion has attracted tremendous interest. One approach is to utilize semiconductor quantum dots (QDs) of which bandgap absorption is expanded than bulk semiconductors by simply tuning the size less than Bohr radius based on quantum confinement. Lead sulfide (PbS), compared with other semiconductors, has remarkable characteristics of utilizing the solar spectrum from infrared to a whole visible light because of a rather large Bohr radius. Another way to promisingly promote the conversion efficiency over the present limit is multiple exciton generation (MEG) of QDs, a process that a photon with high energy exceeding the bandgap excites more than two pairs of electrons or holes instead of wasting the excess energy as heat. MEG has been observed for PbS QDs, but is limited in UV. Further solution is the combination of localized surface plasmonic resonance (LSPR) of noble metal nanostructures to enhance photon trapping and also to suppress electron-hole recombination in QDs. Photoelectric conversion efficiency can be improved by a PbS QDs-Au nanoparticles system, but unfortunately, the improvement is limited in near infrared (NIR). In this thesis, aiming to enhance photoelectric conversion efficiency in an expanded resonance region not only in NIR but in visible, strong electromagnetic field of Au nanostructures were applied to couple with size-controlled PbS QDs in photo-electrochemistry environment.

Chapter 1 is a general introduction of semiconductor QDs based on quantum confinement, the surface plasmon resonance and surface-enhanced Raman scattering of PbS QDs.

In Chapter 2, the size-dependent optical and electronic properties of PbS QDs were determined by absorption and fluorescence spectra; electron-hole pair separation and recombination in PbS QDs was characterized by in-situ electrochemical photoluminescence and photocurrent measurements.

PbS QDs is able to enhance the electromagnetic field generated by LSPR owing to the metallic resonance because semimetal PbS has relatively small bandgap and small effective mass of both electron and hole; therefore, a PbS QD-LSPR coupled system credibly facilitate molecule detection by surface-enhanced Raman scattering (SERS). In Chapter 3, a SERS substrate of Au nanodimers was sensitized by PbS QDs, resulting in modified spectrum of oleic acid (OA) which is the capping ligand of PbS QDs. Such spectral modification confirmed that PbS QDs was coupled with Au nanodimers and the strong electromagnetic field was confined between their gaps.

In Chapter 4, PbS QDs sensitized TiO_2/Au/TiO_2 working electrode was fabricated, and sulfide (S^{2-}) in the electrolyte was used as the donor in order to stabilize photoexcited PbS QDs. Photochemical

reaction between excited PbS QDs and sulfide redox couple (S^{2-}/S_n^{2-}) was revealed by in-situ electrochemical surface-enhanced Raman scattering and photoelectric response measurement. Increasing Raman intensity of polysulfur (S_n^{2-}) vibrations as the potential polarized positively revealed that the hole generated in photoexcited PbS QDs oxidize sulfide to form polysulfur.

In Chapter 5, enhanced photoelectric conversion efficiency of PbS QDs sensitized $TiO_2/Au/TiO_2$ electrode was obtained across an expanded visible light region. Capping ligands of PbS QDs was exchanged from long-chain molecules OA into short-chain molecules of 3-mercaptopropionic acid (MPA), resulting in a reduced core size of QDs (named MP-537). Compared to previous results, appreciably enhanced photocurrent conversion efficiency was obtained by the small MPA-capped PbS QDs sensitized plasmonic electrode both in the long wavelength range (red area, Figure 1) as well as in short wavelength range (blue area), owning to both the strong quantum confinement as well as the metallic resonance of the PbS QDs-Au NPs coupled system.

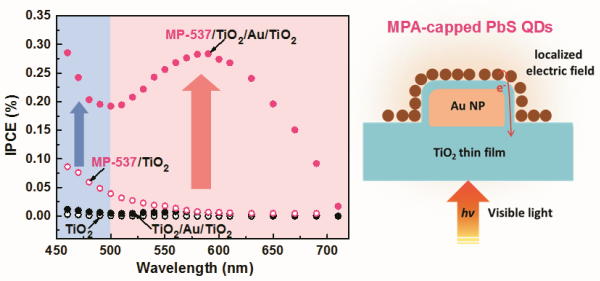

Figure 1. Enhanced photoelectric conversion efficiency not only in long wavelength range (red area) but also in short wavelength range (blue area) by coupling PbS QDs (MP-537) with Au NPs.

In Chapter 6, size-controlled PbS QDs with bandgap energy in NIR and presenting MEG in visible region were utilized to couple with the LSPR of Au NPs, resulting in enhanced photoelectrical conversion efficiency across a wide visible light range. Although the largest QDs (OP-1344, marked in red, Figure 2) presents the weakest quantum confinement with almost equal conduction band position compared with that of TiO_2 thus result in a low output power density (*W*, red hollow diamond-dashed line), this largest QDs created distinct output power density by coupling with Au NPs (red solid line) than the other two sizes of PbS QDs (grey area). The remarkable enhancement by OP-1344 is ascribed to factors including suppressed charge recombination in strongly enhanced electromagnetic field, promoted excitation of MEG by LSPR, and LSPR-modified absorption.

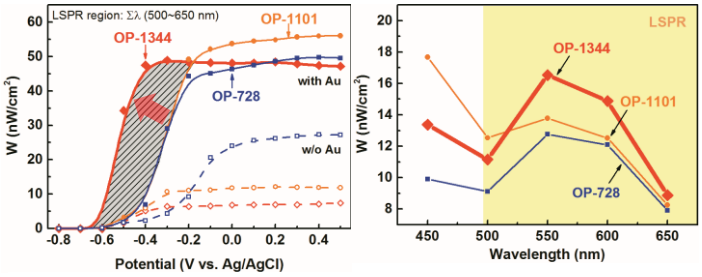

Figure 2. The output power density of the electrodes by coupling size-controlled PbS QDs with LSPR in the visible light range.

In Chapter 7, further study was focused on the formation of strong coupling between PbS QDs and size and shape-controlled Au nano-bowties by dark-field scattering spectrum. Hybridized states characterized as Rabi splitting was observed when the LSPR approximate to the exciton of PbS QDs, demonstrating that the interaction between PbS QDs and Au NPs is in the strong coupling regime.

In summary, this thesis demonstrates the validity of integrating PbS QDs and Au nanostructures to control the interaction between photons and electrons. The enhanced photoelectric response by the designed specific coupling system that combines MEG with LSPR to generate high-density excitation confined in ultra-small spaces could provide insights in further developments of the charge separation and manipulation of QDs-sensitized photoenergy cells to exceed the present photoenergy conversion efficiency limit.