

Enhancement of Photoelectrochemical Water Splitting and Solar Energy Conversion through Utilization of Plasmonic and Electrocatalytic Noble Metal Nanoparticles

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The aim of the first part of this work has been on improvement of the photoanodic activity of tungsten oxide which exhibits low absorption coefficients near the fundamental band edge somewhat increasing at shorter wavelengths. The long optical pathways of charge carriers within WO_3 correspond to visible wavelengths (400–500 nm), and determine the extent of solar light absorption by the photo-anode material. This issue is also critical for semiconductors, which suffer from inadequate light absorption because the absorption is localised away from the space charge layer. In both cases, given the low overall light absorption and the undesired absorption of photons by the bulk, the use of a plasmon-induced near-field could enhance the incident light absorption and conversion. We demonstrate here utility of gold nanoparticles (modified or stabilized with Keggin-type polyoxometallates, $\text{PMo}_{12}\text{O}_{40}^{3-}$, as capping agents) to enhance photocurrents generated by mesoporous tungsten trioxide, WO_3 , photoanodes irradiated with visible light in aqueous solutions. To generate localized surface plasmons under visible light irradiation, we performed measurements using scanning near-field optical microscope (SNOM). The mechanism for the interaction between the gold plasmons and the semiconductor is complex but sound.

In the second part of this work, our research centers on the improvement of the charge propagation dynamics in the iodine/iodide redox system that, so far, has been the most commonly and most successfully used as a charge relay (mediator) in Dye Sensitized Solar Cells (DSSCs). The semi-liquid or semi-solid iodine/iodide-based system has probably led the most promising results so far in the area of practical DSSCs. More recently, the iodide/triiodide redox couple has been considered together with ionic liquids. But both interfacial and bulk (self-exchange) electron transfers involving the iodine/iodide redox system are somewhat complicated and appear slower than one would expect. Among kinetic limitations there is a need to break the I-I bond in the I_3^- or I_2 molecule; it has also been well-established that platinum (e.g. when deposited on the counter electrode) induces electron transfers within the iodine/iodide redox system. In the present work, we

explore the respective electrocatalytic phenomena on nanostructured platinum (namely Pt nanoparticles that are three-dimensionally distributed in the electrolyte phase), utilize them to enhance iodine/iodide electron transfers, and to develop a new generation of charge relays for DSSC.

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