Young Researcher Award of The Electrochemical Society of Japan (Sano Award)

Metal and Metal Oxide Nanoparticles for Photoelectrochemical Materials and Devices

Yukina TAKAHASHI,^{a,b,*} Sunao YAMADA,^a and Tetsu TATSUMA^b

^a Department of Applied Chemistry, Faculty of Engineering, Kyushu University,
744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

^b Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

* Corresponding author: yukina@mail.cstm.kyushu-u.ac.jp

ABSTRACT

We have developed three types of photoelectrochemical nanomaterials and devices based on metal and/or semiconducting metal oxide nanoparticles for effective use of light energy. Photocatalysts with oxidative energy storage abilities were developed by coupling a photocatalyst with a rechargeable metal oxide or metal hydroxide nanomaterial to address an issue that TiO₂ photocatalyst does not function after dark. Plasmonic metal nanoparticle ensembles were thermally and/or chemically stabilized by using a metal oxide nanomask or ultrathin metal oxide coating and applied to localized surface plasmon resonance sensors and photovoltaic cells based on the plasmon-induced charge separation. Organic and organic-inorganic hybrid photoelectrodes were also developed to give photocurrents enhanced by optimally arranged plasmonic metal nanoantennas.

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Keywords : Photocatalyst, Localized Surface Plasmon Resonance, Plasmon-induced Charge Separation, Nano-particle

1. Introduction

Effective utilization of light energy by using solar cells and photocatalysts is of great significance in view of energy strategies for the future. In particular, efficient light harvesting is an important issue, because ambient photon flux density is low in general. With this in mind, we have developed the following three new classes of nanomaterials and photoelectrochemical devices based on the nanomaterials: (1) photocatalysts with energy storage abilities,^{1–8} which can store energy derived from light and continue redox reactions even in the night, (2) plasmonic metal nanoparticle ensembles stabilized by metal oxide nanomasks and ultrathin metal oxide coatings,^{9,10} as well as solid-state photovoltaic cells¹¹ and plasmon resonance sensors^{9,10,12} based on the ensembles, and (3) organic^{13–18} or organic-inorganic hybrid^{19–21} photoelectrodes with optimally arranged plasmonic metal nanoantennas. The former one stores surplus energy during the day and uses it in the night, while the latter two trap photons efficiently taking advantage of the large absorption cross-section of plasmonic metal nanoparticles.

2. Photocatalysts with Oxidative Energy Storage Abilities

TiO₂ photocatalyst has been developed on the basis of Honda-Fujishima effect,²² and it is now practically used for removal of harmful and fouling organic compounds and sterilization.²³ Electrons in the TiO₂ valence band are excited by UV light to its conduction band, and accordingly positive holes are generated in the valence band. The excited electrons and holes cause reductive and oxidative reactions, respectively. However, photocatalysts work only under illumination. So as to retain some photocatalytic effects even after dark, Tatsuma et al. developed photocatalysts with energy storage abilities.^{24–29} Surplus energy from a photocatalyst is stored during the daytime, and it allows continuing some photocatalytic reactions during the night. In the early stage of the development, a

Figure 1. (Color online) Mechanisms of photocatalysts with oxidative energy storage abilities.

photocatalyst, TiO₂^{7,24–28} or SrTiO₃,²⁹ was coupled with a redox-active n-type semiconductor, WO₃,^{24–27,29} MoO₃,⁷ or H₃PW₁₂O₄₀ (PWA).²⁸ The latter, a rechargeable material, is reduced by the photoexcited electrons from the photocatalyst under illumination, and the reduced material exhibits anti-bacterial²⁷ and anti-corrosion²⁴ effects on the basis of reductive reactions after dark. However, in general, oxidative reactions are more important for most photocatalytic effects than reductive reactions.

Therefore, Takahashi and Tatsuma developed photocatalysts with oxidative energy storage abilities (Fig. 1) by employing a rechargeable material Ni(OH)₂, which behaves as a p-type semiconductor.¹ The Ni(OH)₂-TiO₂ composite film turns from colorless to brown under UV light, indicating that Ni(OH)₂ is partially oxidized to NiOOH.¹ The NiOOH can drive a variety of reactions in turn, for instance oxidative mineralization of methanol and formaldehyde to CO₂ [Fig. 2(a)].³ Volatile organic compounds (VOCs) such as phenol can also be oxidized and removed by NiOOH.¹ NiOOH is reduced to Ni(OH)₂ as a result of those chemical reactions as well as electrochemical reduction [Fig. 2(b)].

Figure 2. (Color online) (a) Chemical discharging reactions and (b) electrochemical discharging curves of the charged Ni(OH)_2 film. Reprinted with permission from Ref. 1. Copyright 2005 American Chemical Society.

Remote energy storage by a photocatalyst apart from the rechargeable material is also possible.² In this case, Ni(OH)_2 is oxidized to NiOOH typically by hydroxyl radical on the basis of photocatalytic remote oxidation;³⁰ oxygen is reduced photocatalytically to hydrogen peroxide, which diffuses in the gas phase and photocleaved into hydroxyl radicals.³¹ As an energy storage material, other redox-active p-type semiconductors, such as NiO and Co(OH)_2 , are also available.⁶ Oxidative reactions can be driven

at more positive potentials when Ir or Ru oxide is used as a rechargeable material.⁶ Although TiO_2 photocatalyst does not function after dark and it is excited only by UV light, these two major limitations can be removed simultaneously by combining a rechargeable material with a visible light-driven photocatalyst,^{4,5,8} such as Pt nanoparticle-loaded WO_3 developed by Ohtani et al.,³² Cu-loaded WO_3 ³³ or Fe-loaded TiO_2 ³⁴ developed by Hashimoto et al., or Au nanoparticle (AuNP)-loaded TiO_2 .³⁵

3. Stabilization of Plasmonic Metal Nanoparticles

Noble metal nanoparticles exhibit localized surface plasmon resonance (LSPR) in the UV, visible, and near-IR ranges and their light absorption cross-section is generally much larger than those of dye molecules. The resonant wavelength and intensity can be controlled by changing the composition, size, and shape of nanoparticle. The plasmonic nanoparticles are therefore promising materials for effective utilization of light energy particularly in far-red and near-IR regions. However, nanoparticles melt at lower temperatures than does the bulk metal and fuse into larger, non-plasmonic particles. In addition, nanoparticles of less noble metal like silver nanoparticles (AgNPs) could be chemically oxidized and dissolved. Even gold nanoparticles (AuNPs), which are more stable than AgNPs, are corroded by iodine, so that AuNPs are difficult to be coupled with a dye-sensitized solar cell. Therefore, we have improved thermal and chemical stabilities of AuNPs and AgNPs by a simple method so as to apply the nanoparticles to photovoltaic cells and sensors.

Takahashi and Tatsuma fabricated monodisperse AuNP and AgNP ensembles by electrodeposition through a thin Al_2O_3 nanomask [Fig. 3(a)].⁹ The nanomask functions as a template for nanoparticles and prevents the fusion of nanoparticles even at 500°C [Fig. 3(b)]. The improved thermal stability allows coating of the metal nanoparticles with an ultrathin TiO_2 film and annealing, so that the ensembles can be protected by a compact and chemically stable TiO_2 film.⁹ The stabilized ensembles were applied to both wet [Fig. 4(a)]⁹ and all solid-state [Fig. 4(b)]¹¹ photovoltaic cells based on the plasmon-induced charge separation (PICS), which was first reported by Tatsuma et al.^{35,36} The TiO_2 -coated plasmonic nanoparticle electrode exhibited cathodic photocurrents in the wet

Figure 3. (Color online) (a) Electrodeposition of a plasmonic AuNP ensemble through a thin Al_2O_3 nanomask and (b) thermal stabilities of plasmonic AgNP ensembles with and without a thin Al_2O_3 nanomask. AFM images were reproduced from Ref. 9 by permission of The Royal Society of Chemistry.

Figure 4. (Color online) Band diagrams of (a) the cathodic photoelectrode and (b) the solid-state photovoltaic cell based on PICS.

Figure 5. (Color online) Thermal stabilities of AuNR ensembles with and without an ultrathin TiO_2 coating. Reproduced from Ref. 11 by permission of The Japan Society for Analytical Chemistry.

system.^{9,37} In contrast, anodic photocurrents flow when nanoparticles are deposited on a TiO_2 electrode.^{35,38} These results indicate that PICS is based on electron transfer³⁹ from the plasmonic nanoparticle to TiO_2 . PICS attracts much attention, because of its wide range of applications.^{35–42} In particular, many research groups apply PICS to photovoltaics and photocatalysis.^{36,43} However, in most of those applications, AuNPs are used because of their thermal and chemical stability. The present technique opens a route to the use of less noble metal nanoparticles for those photoelectrochemical applications.

Takahashi and Yamada improved thermal stability of gold nanorods (AuNRs), which are rod-shaped nanoparticles.^{10,12} Although AuNRs absorb and make effective use of light at longer wavelengths than spherical AuNPs, AuNRs are thermodynamically less stable than spherical AuNPs. AuNRs turn to spherical nanoparticles easily by irradiating high intensity light or heating and lose their unique optical properties. The thermal stability of AuNRs was therefore improved by coating with a thin TiO_2 film.

The TiO_2 -coated AuNRs exhibit only small morphological changes even after annealing at 300°C , at which AuNRs without the TiO_2 coating loses their anisotropy completely (Fig. 5).¹⁰ AuNRs are used for chemical sensors and biosensors because their LSPR peaks show red-shifts sensitively as the local refractive index increases.⁴⁴ The TiO_2 coating is thin enough to observe peak shifts in response to refractive index changes. In addition, photocatalytic activity of the TiO_2 coating allows self-cleaning of its surface and repeated use of the TiO_2 -coated AuNR ensemble as a sensing device.

4. Arrangement Optimization of Plasmonic Metal Nanoantenna and Organic Dyes

Plasmonic metal nanoparticles are known to enhance photocurrents of photovoltaic devices such as dye-sensitized solar cells⁴⁵ and organic thin film solar cells⁴⁶ on the basis of LSPR-based optical near field. However, they could also quench the excited states of organic dyes. Since these positive and negative effects should have different dependencies on parameters such as the dye-nanoparticle spacing, particle size, and particle density, investigation of these dependencies is very important for designing devices with maximum enhancement and suppressed quenching. We therefore examined the dependencies systematically.^{13–21}

Takahashi, Tatsuma, and co-workers fabricated dye-sensitized photoanodes based on the TiO_2 -coated AuNP ensemble described above. The ultrathin TiO_2 coating protects AuNPs from corrosion by iodine contained in the electrolyte solution. In addition, the spacing between Ru-complex dye and AuNP can be controlled by changing the TiO_2 thickness (e.g. 3–40 nm).^{19–21} The optimum spacing in terms of the photocurrent enhancement was found to be about 10 nm.¹⁹ It was revealed for the first time that the dye-sensitized photocurrents are deteriorated by a further decrease of the spacing. On the other hand, an increase of the particle density causes a decrease of the interparticle spacing and allows photocurrent enhancement at longer wavelengths due to a plasmon coupling effect.²⁰ The optimum AuNP size is 100 nm in the presence of the coupling effect, whereas it is 40 nm in the absence of the effect.

Takahashi, Yamada, and co-workers studied interaction between plasmonic metal nanoparticles and polythiophene, which is frequently used as a polymer dye for organic thin film solar cells.^{13–18} In a system of polythiophene with AgNPs, both photocurrents and fluorescence are enhanced by AgNPs, indicating that the photocurrent enhancement is due to enhancement of dye excitation.¹³ The thickness of the polymer layer thus can be optimized.¹⁴ In addition, it was verified that the larger AgNPs and the more anisotropic particles such as silver nanocubes exhibited the greater plasmonic enhancement.^{16,17}

A correlation between photocurrents of polythiophene and the density of electrostatically adsorbed¹⁵ or electrodeposited¹⁸ AuNP (~ 20 nm) was also investigated with a constant amount of polythiophene, which was controlled by degree of electropolymerization. The maximum photocurrent enhancement is reached when the interparticle spacing estimated from the particle density is approximately twice as large as the particle diameter (Fig. 6). Further introduction of AuNPs would not improve the plasmonic enhancement, because the decay distance of the optical near field around the particle surface is almost the same as the diameter of the AuNP.⁴⁷ In contrast, the quenching effect would still intensify with increasing particle density because quenching takes place at a shorter distance from the particle surface. Alternatively, shorter interparticle spacing would give rise to plasmon coupling, which causes red-shift of the resonant wavelength of AuNPs, resulting in disagreement with the absorption band of dye. These results are in line with recent reports by Yamada et al. on photocurrents and fluorescence of porphyrin enhanced by AgNPs, which are saturated even if the particle density is lower than that for the closely packed layer.^{48,49}

Figure 6. (Color online) Photocurrent enhancement effects of density-controlled AuNPs on electropolymerized polythiophene photoelectrodes. Reprinted with permission from Ref. 15. Copyright 2012 American Chemical Society.

5. Conclusions

Functional nanomaterials for effective use of light energy were developed and applied to photocatalysts with oxidative energy storage abilities, stabilized LSPR sensors and photovoltaic devices based on PICS, and organic photoelectrodes with plasmonic metal nanoantennas. The nanomaterials and related techniques developed in the series of works would contribute to further improvements in light harvesting efficiency and development of new devices.

Acknowledgments

The authors are grateful to Dr. P. Ngaotrakanwivat, Dr. F. Yang, Dr. N. Sakai, Mr. T. Kawawaki, and Dr. A. Kogo, Dr. J. You, Dr. K. Leonard, Prof. H. Yonemura, and Dr. H. Tahara for valuable discussion and encouragement. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 25870510) from JSPS, research grants from Hayashi Memorial Foundation for Female Natural Scientists, and the Asahi Glass Foundation.

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