# Development of a Highly Efficient Hydrogen Generation System by Plasmon-Induced Charge Separation Using Sunlight as an Energy Source

TAKAHASHI Yukina

Although the total amount of sunlight is large, the energy density per unit area is small and the supply is unstable. Therefore, it is important in practical use to devise some means to store and increase the energy density.  The localized surface plasmon resonance (LSPR) of metal nanoparticles increases the density of solar energy, and the phenomenon of plasmon-induced charge separation (PICS), which occurs when metal nanoparticles are combined with semiconductors, can be used to convert light energy into electrochemical energy, which can be used to generate hydrogen from solar energy. This paper describes a research plan to develop a highly efficient hydrogen generation system using solar energy.

## Introduction

A stable supply of renewable energy that does not rely on fossil resources such as oil and coal is essential to the realization of a sustainable society. Among the energy sources such as solar, wind, hydro, geothermal, tidal, and biomass, which can always be supplied from nature, solar is a particularly promising energy source.  This is because the energy is obtained from outside the closed system of the earth, where the law of conservation of energy holds. The sun generates enormous amounts of energy through nuclear fusion. Only a small fraction of that energy reaches the Earth's surface. The energy reaching the surface of the earth and the sea is approximately 3 x $10^{24}$ J $y^{-1}$.[1] This value is approximately 5000 times as large as world energy consumption.[2] However, although an enormous amount of light energy falls on the earth in total, it has the disadvantage of having a small energy density per unit area. In addition, since it is dependent on nature, the supply is unstable because it is greatly affected by the seasons and weather, with the exception of some regions such as the Sahara Desert. In other words, it is an important issue in the implementation of the system to store a large amount of energy when it is supplied in large quantities, to downsize the system to produce only the necessary amount in small quantities when needed on site, and to devise ways to increase the energy density. Among them, we are focusing on ways to increase energy density.

## Photoenergy harvesting in order to increase the energy density

One of the solutions is by using metal nanoparticles in order to dense the light energy. When metals are nanosized from several nanometers to a hundred nanometers in diameter, they have the effect of trapping the photoenergy of incident light in the nanospace beyond the diffraction limit of the particle surface (Figure 1). This effect is based on a phenomenon called localized surface plasmon resonance (LSPR), and the resonance wavelength can be controlled from the UV to the near-infrared, depending on the metal species, particle size, shape, aggregation state, and refractive index of the surrounding medium. This property has been applied to sensors using the shift of plasmon peak wavelengths, and is also known to enhance both photoexcitation and emission processes of photoactive materials, such as dyes and quantum dots, on the surface of nanoparticles, which can be used for surface enhanced Raman scattering (SERS),[3] photocurrent enhancement of solar cells,[4-8] and luminescence enhancement of fluorescent dyes.[9] Theoretically, the light energy harvesting effect by LSPR is calculated to be tens to millions of times larger than that of incident light. The light energy harvesting effect of LSPR can overcome the disadvantage of sunlight, which has a low energy density per unit area.

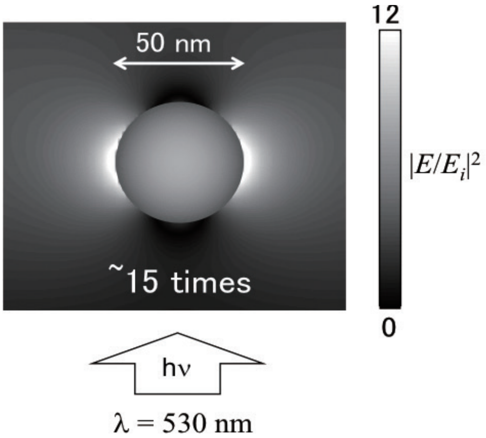

Figure 1 Photo-harvesting effect of a gold nanoparticle with the diameter of 50 nm based on LSPR (calculation).

## Photoenergy conversion to other energy

There is also a method of directly utilizing light energy captured by metal nanoparticles without the use of dyes or other means. When plasmonic metal nanoparticles are combined with a semiconductor such as titanium dioxide, electrons in the metal nanoparticles transfer into the conduction band of the semiconductor under light irradiation at resonance wavelengths, a phenomenon called plasmon-induced charge separation (PICS) (Figure 2).[10] This leads to a reduction reaction on the semiconductor and an oxidation reaction on the metal nanoparticles, and is expected to be applied to sensors,[11] photoelectric conversion devices,[10,12] and visible-light-responsive photocatalysts.[10,13] In this system, light irradiation causes charge transfer to proceed directly without the use of dyes. Therefore, energy loss can be eliminated by constructing a simple system, and high conversion efficiency can be expected. This can be used in the hydrogen generation reaction by water reduction and hydrocarbon generation reaction by carbon dioxide reduction to convert light energy into chemical energy that can be stored, thereby overcoming the disadvantages of sunlight, which is unstable in supply.

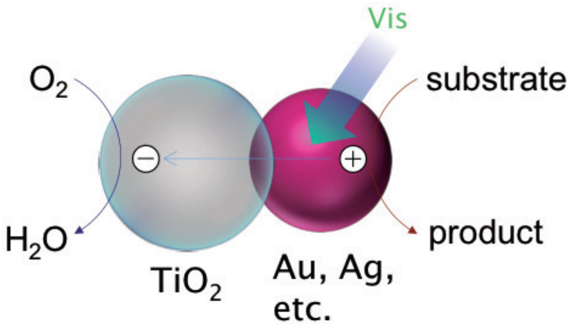

Figure 2 Schematic illustration of the conventional PICS.

## Problems with conventional PICS system

However, conventional PICS has several problems due to the use of n-type semiconductors. One is the low stability of metal nanoparticles. Since oxidation reactions occur on the metal nanoparticles, it may cause the metal nanoparticles themselves to dissolve, even silver nanoparticles, which are known to be relatively stable. We have been studied to solve the problem. We succeeded in improving the thermal stability of spherical silver nanoparticles, by introducing an $Al_2O_3$ nanomask as a template of the nanoparticles, and the chemical stabilities by coating with a thin and dense titanium dioxide film.[14] In same way, by coating with titanium dioxide film, we improved stabilities of gold nanorods,[15] and silver nanoplates,[16] which are effective for the use of near-infrared light due to their shape anisotropy but are easily deformed into a spherical shape. However, the use of cheaper and less unstable metals was desired.

Second is the low efficiency of the charge separation. The photoelectric conversion efficiency ($\eta$) of the conventional PICS was approximately 1%.[10] In titanium dioxide photocatalysts, metal nanoparticles supported on the photocatalyst function as an electron pool that suppresses recombination of excited electrons and holes, as evidenced by their use as reduction sites.[17] Therefore, electrons transferred to the semiconductor after charge separation by conventional PICS are likely to undergo reverse electron transfer to the metal nanoparticles (recombination in the broad sense). It was supported by the reports that charge separation lifetime improved from picoseconds to microseconds by changing the semiconductor combined with the metal nanoparticles from n-type to p-type.[18]

## Highly efficient hydrogen generation via PICS system with a p-type semiconductor

We therefore propose that the above problem can be solved by using a p-type semiconductor, which reverses the charge transfer, because the reduction reaction can proceed on the metal nanoparticles used in PICS (Figure 3).[19] The catalytic effect of the metal nanoparticles in the reduction reaction can also be expected. As a result, the selectivity of the reaction products can be improved. For example, copper is known to be able to reduce carbon dioxide to C2 compounds such as ethanol and ethylene when used as an electrode in electrochemical reactions.[20] Therefore, it is expected that by controlling the type of metal and crystal planes that make up the nanoparticles, arbitrary chemical reactions can be promoted, such as the generation of hydrogen and the generation of specific hydrocarbons through the reduction of carbon dioxide. In same way, as the p-type semiconductor, for example, iridium oxide is a proven material as an electrode for the electrochemical oxidation of water,[21] and is expected to water splitting into oxygen and hydrogen. The proposed system is theoretically expected to be dramatically more efficient than conventional systems.

It was noted above that conventional PICS system can be applied to sensing devices. The proposed system can also work as a sensor with higher sensitivity than conventional one. It may be possible to simultaneously detect the hydrogen generation reaction as an electrical signal in the novel system. It will be able to detect not only hydrogen generation reactions, but also the progress of beneficial chemical reactions. This sensing system will be useful in a variety of systems in the future.

## Conclusion

We have described the possibility of a novel, highly efficient hydrogen generation system using PICS with a p-type semiconductor. The proposed novel system is expected to realize high-sensitivity sensing at the same time. We believe that the realization of this system, which is expected to be able to effectively harvest and utilize energy of sunlight, will contribute to solving energy problems of the world.

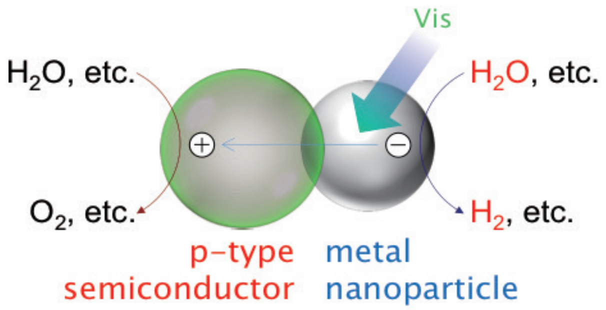

Figure 3 Schematic illustration of the PICS with p-type semiconductor.

## References

[1] Solar Energy Perspectives, OECD/IEA, 2011.

[2] bp Statistical Review of World Energy 2020.

[3] M. Fleischman, P. J. Hendra, A. J. McQuillan, *Chem. Phys. Lett.*, 26, 163 (1974).

[4] C. Wen, K. Ishikawa, M. Kishima, K. Yamada, *Sol. Energy Mater. Sol. Cells*, 61, 339 (2000).

[5] S. D. Standridge, G. C. Schats, T. Hupp, *J. Am. Chem. Soc.*, 131, 8407 (2009).

[6] K. R. Catchpole, S. Pillai, J. *Luminescence*, 121, 315 (2006).

[7] D. Derkacs, S. H. Lim, P. Matheu, W. Mar, E. T. Yu, *Appl. Phys. Lett.*, 89, 093103 (2006).

[8] K. Nakayama, K. Tanabe, H. A. Atwater, *Appl. Phys. Lett.*, 93, 121904 (2008).

[9] P. Anger, P. Bharadwaj, L. Novotny, *Phys. Rev. Lett.*, 96, 113002 (2006).

[10] Y. Tian, T. Tatsuma, *J. Am. Chem. Soc.*, 127, 7632 (2005).

[11] T. Tatsuma, Y. Katagiri, S. Watanabe, K. Akiyoshi, T. Kawawaki, H. Nishi, E. Kazuma, *Chem. Commun.*, 51, 6100 (2015).

[12] Y. Takahashi, T. Tatsuma, *Appl. Phys. Lett.*, 99, 182110 (2011).

[13] E. Kowalska, R. Abe, B. Ohtani, *Chem. Commun.*, 241 (2009).

[14] Y. Takahashi, T. Tatsuma, *Nanoscale*, 2, 1494 (2010).

[15] Y. Takahashi, N. Miyahara, S. Yamada, *Anal. Sci.*, 29, 101 (2013).

[16] Y. Takahashi, K. Suga, T. Ishida, S. Yamada, *Anal. Sci.*, 32, 275 (2016).

[17] W. Kubo, T. Tatsuma, *J. Mater. Chem.*, 15, 3104 (2005).

[18] Z. Lian, M. Sakamoto, H. Matsunaga, J. J. M. Vequizo, A. Yamakata, M. Haruta, H. Kurata, W. Ota, T. Sato, T. Teranishi, *Nat. Commun.*, 9, 2314 (2018).

[19] Y. Takahashi, Y. Yamadori, T. Murayama, S. Shingo, S. Yamada, in preparation.

[20] Y. Hori, R. Takahashi, Y. Yoshinami, A. Murata, *J. Phys. Chem. B*, 101, 7075 (1997).

[21] Y. Takahashi, T. Tatsuma, *Electrochemistry*, 82, 749 (2014).

---

**Dr. TAKAHASHI Yukina**

Associate Professor,
International Institute for Carbon-Neutral Energy Research (I$^2$CNER),
Kyushu University