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Application News

No. S50

Scanning Probe Microscope (SPM) / Atomic Force Microscope (AFM)

Visualization of Photoinduced Charge Distribution of Au Nanoparticle Assembly by SPM

Introduction

Composites of metal nanoparticles and semiconductors are representative heterogeneous photocatalysts which enable a wide range of photochemical conversions. For example, composites of gold (Au) nanoparticles (AuNP) and titanium dioxide (TiO_2) have been widely researched, as they possess promising reactivity as photocatalysts. When TiO_2 absorbs incident light corresponding to its bandgap energy, the excited electrons in its conduction band of the TiO_2 are transferred to AuNP immobilized on its surface, preventing charge recombination in the TiO_2. Visualization of the charge distribution is effective for elucidating this phenomenon. Moreover, visualization is also useful in control of integrated structures which are important in the creation of novel functional bio-devices utilizing metalloproteins involved in electron transfer.

Kelvin probe force microscopy (KPFM) is an analytical technique in which Kelvin's law is applied to the scanning probe microscope (SPM), and makes it possible to measure not only the surface shape of samples, but also their surface potential distribution. Here, visualization of the photoinduced charge distribution (charge separation) on the surface of a hybrid TiO_2 material with an AuNP assembly immobilized on its surface was attempted by KPFM measurements under ultraviolet (UV) irradiation.

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Formation of AuNP Assembly

Samples with and without formation of an AuNP assembly utilizing a biotin-streptavidin interaction were measured. Fig. 1 shows a schematic diagram of the biotin-streptavidin interaction. The SEM images in Fig. 2 (a) and (b) show the case without and with interaction with streptavidin, respectively. From these SEM images, it can be understood that AuNP forms an assembly as a result of the biotin-streptavidin interaction.

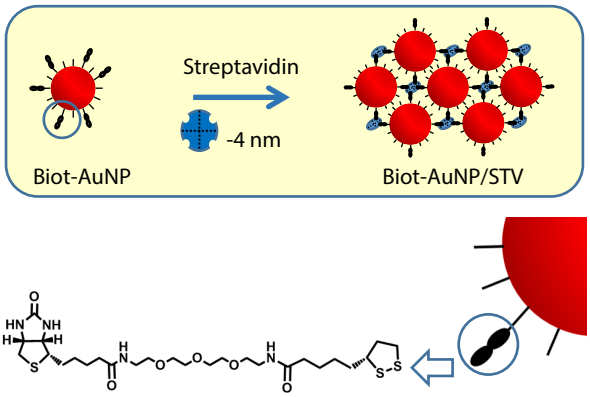


Fig. 1 Schematic Diagram of Biotin-Streptavidin (STV) Interaction

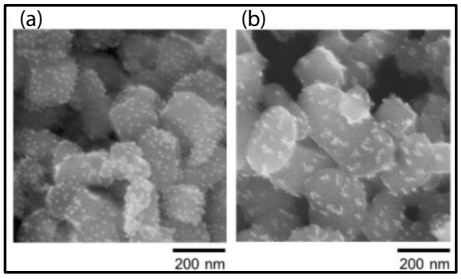


Fig. 2 SEM Images of Hybrid TiO_2 with Immobilized AuNP (a) Without Streptavidin Interaction, (b) With Streptavidin Interaction

KPFM Measurement under UV Irradiation

KPFM measurement makes it possible to measure the surface potential distribution of a sample simultaneously with the surface shape. In this example, as shown in Fig. 3, the surface potential distribution of AuNP immobilized on TiO_2 was measured under conditions without and with UV irradiation in order to visualize the photoinduced charge distribution.

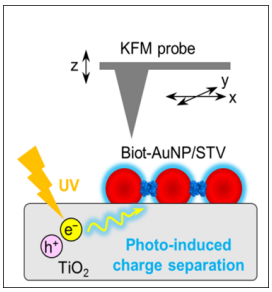
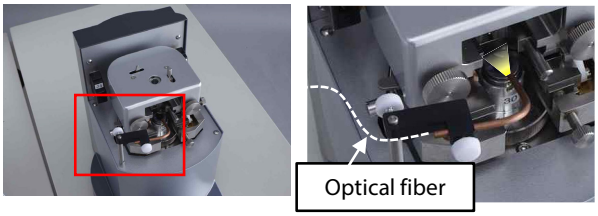


Fig. 3 Image of Measurement of Surface Potential Distribution of Hybrid TiO_2 with Immobilized AuNP

Use of a light irradiation unit makes it possible to measure the sample while irradiating the sample surface with light via an optical fiber. Fig. 4 shows an image of the measurement using a Shimadzu light irradiation unit. In addition to the optical fiber technique, measurement is also possible while irradiating the sample with a fiber light or other suitable device in addition to an optical fiber. In this analysis, an LAX-C100 UVB (240 to 300 nm) (Asahi Spectra Co., Ltd.) was used as the UV light source.



SPM-9700HT light irradiation unit

Image of measurement by light irradiation

Fig. 4 Image of Measurement Using Light Irradiation Unit

Change of Surface Potential Distribution With/Without UV Irradiation of AuNP Immobilized on TiO_2 Surface

Fig. 5 shows the height images (shape images) and surface potential distribution images without UV irradiation (top, under dark condition) and with UV irradiation (bottom, under UV).

(a) shows the case when the AuNP nanoparticles are isolated and dispersed on the TiO_2 surface, that is, without streptavidin interaction, and (b) shows the case when the AuNP has formed an assembly on the TiO_2 as a result of the streptavidin interaction. In both cases, the relative potential of the AuNP is lower than that of the TiO_2 surface under the condition of UV irradiation.

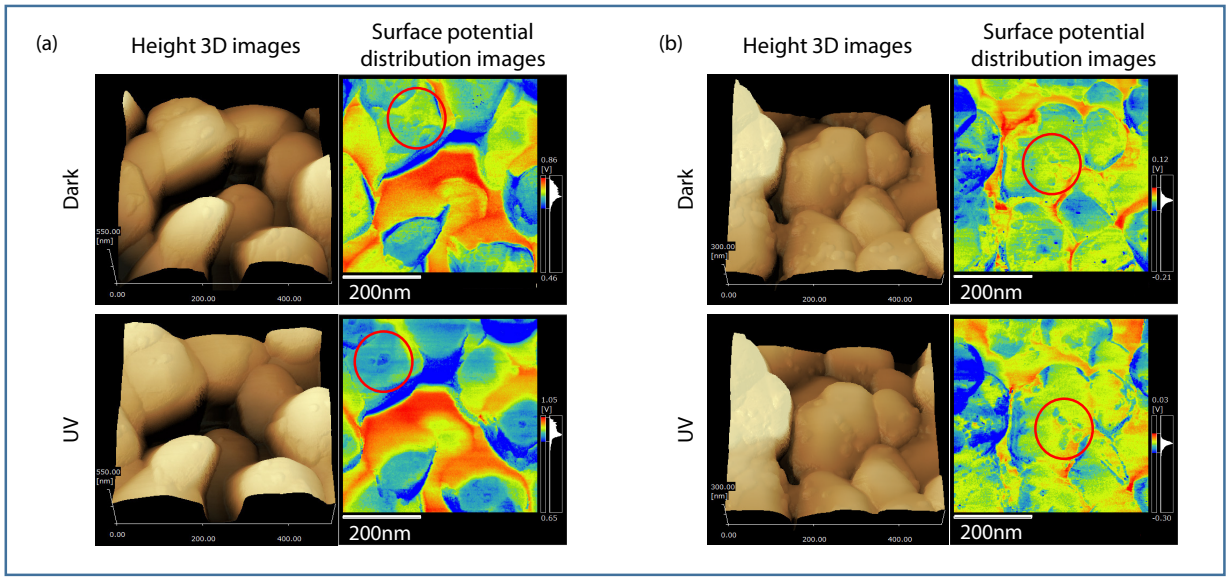


Fig. 5 (Left) Height Images and (Right) Surface Potential Distribution Images
(a) Without Streptavidin Interaction, (b) With Streptavidin Interaction
In comparison with the top row (without UV irradiation), a condition in which the relative potential of the AuNP is lower than that of the TiO_2 surface can be seen in the bottom row (under UV irradiation).

Relative Potential of AuNP to TiO_2 Surface

Fig. 6 shows results of measurements of the relative potential of AuNP to that of the TiO_2 surface for the case of isolated and dispersed AuNP on the TiO_2 surface, that is, without the streptavidin interaction, and the case of a formed AuNP assembly immobilized on the TiO_2 surface by the streptavidin interaction. In the latter case (with streptavidin interaction), a large negative shift in the relative potential of the AuNP was observed as a result of UV irradiation.

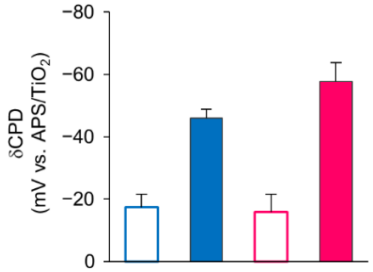


Fig. 6 Relative Potential of AuNP to TiO_2 Surface
(Blue) Without Streptavidin Interaction,
(Red) With Streptavidin Interaction

White indicates without UV irradiation, and color indicates with UV irradiation. The error bars show the median value ±IQR of the measured values of 6-7 particles. When AuNP formed an assembly, the relative potential of the AuNP to that of the TiO_2 surface decreased substantially under UV irradiation.

Conclusion

Visualization of the photoinduced charge distribution of a hybrid of AuNP immobilized on TiO_2 was realized by measuring the surface potential distribution by KPFM under UV irradiation.

This experiment confirmed the effect of the streptavidin interaction in the formation of an AuNP assembly on TiO_2.

In comparison with the sample in which isolated and dispersed AuNP particles existed on the TiO_2 surface, when the AuNP formed an assembly on the TiO_2 as a result of the action of streptavidin, the AuNP displayed a stronger negative shift in relative potential under the condition of UV irradiation. This suggests that AuNP assembly efficiently promotes charge separation.

Samples provided by:
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<References>
Hirofumi Harada, Akira Onoda, Shiho Moriguchi, and Takashi Hayashi, ChemistrySelect 2016, 1, 5666-5670

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