

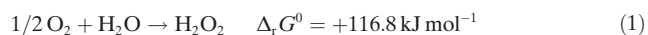
Gold-Nanoparticle-Loaded Carbonate-Modified Titanium(IV) Oxide Surface: Visible-Light-Driven Formation of Hydrogen Peroxide from Oxygen

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Abstract: Gold nanoparticle-loaded rutile TiO_2 with a bimodal size distribution around 10.6 nm and 2.3 nm (BM-Au/ TiO_2) was prepared by the deposition precipitation and chemical reduction (DP-CR) technique. Visible-light irradiation ($\lambda > 430$ nm) of the BM-Au/ TiO_2 plasmonic photocatalyst yields $35 \mu\text{M}$ H_2O_2 in aerated pure water at irradiation time (t_p) = 1 h, and the H_2O_2 concentration increases to $640 \pm 60 \mu\text{M}$ by the addition of 4% HCOOH as a sacrificing electron donor. Further, a carbonate-modified surface BM-Au/ TiO_2 (BM-Au/ $\text{TiO}_2\text{-CO}_3^{2-}$) generates a millimolar level of H_2O_2 at t_p = 1 h with a quantum efficiency (Φ) of 5.4 % at λ = 530 nm under the same conditions. The recycle experiments confirmed the stable performance of BM-Au/ TiO_2 .

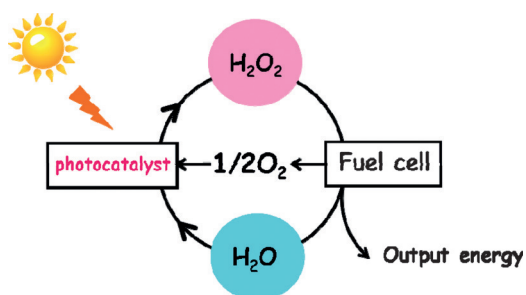
Hydrogen peroxide (H_2O_2) has attracted much interest as not only a “green” oxidant for organic synthesis^[1] but also the source for a new fuel cell.^[2] Presently, most H_2O_2 is produced by the anthraquinone oxidation process through the many steps needing large amounts of input energy and organic solvent.^[3] As alternative, various chemical and physical methods have recently been studied.^[4] If H_2O_2 can be produced from O_2 and water, a sustainable energy cycle is completed by combining with the H_2O_2 -based fuel cell (Scheme 1). For this endergonic reaction to proceed, the effective use of sunlight with a broad energy peak locating

from 500 nm to 650 nm is desirable as an energy source [Eq. (1)].



UV-light irradiation of TiO_2 in water yields H_2O_2 , but the H_2O_2 concentration is only limited to micromolar levels.^[5] We have reported that a millimolar level of H_2O_2 can be produced from O_2 by UV-light irradiation of gold nanoparticle (NP)-loaded TiO_2 (Au/ TiO_2) in an aqueous solution of ethanol.^[6] The photocatalytic synthesis of H_2O_2 has been intensively studied to increase its steady-state concentration by using heterogeneous photocatalysts such as Au-Ag/ TiO_2 ,^[7] graphene oxide- TiO_2 ,^[8] and silicon nanowire- TiO_2 -Au.^[9] A coming challenge is to use the visible light as the energy source for the effective sunlight utilization. So far, several reports on the H_2O_2 synthesis from O_2 using visible-light photocatalysts including graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)-based photocatalysts^[10,11] have been published. Particularly, a high Φ value of about 10 % has been achieved at λ = 420 nm in the $\text{g-C}_3\text{N}_4$ system; however, it is inactive at $\lambda > 500$ nm.^[11] On the other hand, the plasmonic photocatalysts represented by Au/ TiO_2 have appeared as a new class of photocatalysts.^[12] By using the Au/ TiO_2 plasmonic photocatalyst, various oxidative transformations including alcohol to carbonyl compounds,^[13,14] thiol to disulfide,^[15] benzene to phenol,^[16] and amine to imine^[17] have been developed. A bimodal (BM)-Au/ TiO_2 plasmonic photocatalyst has been shown to have a potential for the application to the reductive transformation.^[18] So far, the BM-Au/ TiO_2 plasmonic photocatalyzed reaction is only limited to the reduction of nitrobenzene analogs to the corresponding azobenzenes.

Herein we report the visible-light-driven reduction of O_2 to H_2O_2 in pure water by the BM-Au/ TiO_2 plasmonic photocatalyst, further showing that carbonate-surface modified BM-Au/ TiO_2 (BM-Au/ $\text{TiO}_2\text{-CO}_3^{2-}$) yields a millimolar level of H_2O_2 in the presence of formic acid (HCOOH). BM-Au/ TiO_2 was prepared by the DP-CR technique.^[18] The visible-light activity of Au/ TiO_2 depends on the crystal form of TiO_2 , and rutile is superior to anatase^[14] in contrast to the UV-light activity of TiO_2 for most photocatalytic reactions.^[19] At the first step, large Au NPs were loaded on rutile TiO_2 (L-Au/ TiO_2) by the DP method.^[20] At the second step, $[\text{Au}(\text{OH})_3\text{Cl}]^-$ complex ions were adsorbed on the TiO_2 surface of L-Au/ TiO_2 , and then, they were reduced by NaBH_4 to yield small Au NPs. For comparison, the second CR procedure was applied to unmodified TiO_2 to produce small Au NP-loaded TiO_2 (S-Au/ TiO_2). The Au 4f X-ray photoelectron spectra of Au/ TiO_2 have two signals at 87.0 and 83.3 eV due to the



Scheme 1. Solar oxygen cycle using the H_2O_2 -based fuel cell.

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Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201606734>.

emissions from the Au 4f 5/2 and Au 4f 7/2 orbitals for metallic Au, respectively.^[21] Evidently, the Au^{III} complex adsorbed on TiO₂ is reduced to metallic Au by NaBH₄ at the second step.

Transmission electron microscopy (TEM) images (see Figure S1 in the Supporting Information) and the Au particle size distribution for L-Au/TiO₂ show that Au particles with a mean size (*d*) of 9.7 nm (standard deviation $\sigma = 1.6$ nm) are highly dispersed on the TiO₂ surface. In BM-Au/TiO₂, L- and S-Au particles with *d* values of 10.6 nm ($\sigma = 4.0$ nm) and 2.3 nm ($\sigma = 1.3$ nm), respectively, are separately formed on TiO₂. For S-Au/TiO₂, the *d* value was 2.3 nm ($\sigma = 1.0$ nm). The Au loading amounts were determined to be 0.52 wt% for S-Au/TiO₂, 0.49 wt% for L-Au/TiO₂, and 0.88 wt% for BM-Au/TiO₂ by inductively coupled plasma spectroscopy.

Further, CO₃²⁻ ions were adsorbed on the BM-Au/TiO₂ surface from a 100 mM Na₂CO₃ aqueous solution (BM-Au/TiO₂-CO₃²⁻). Figure 1A shows diffuse reflectance Fourier

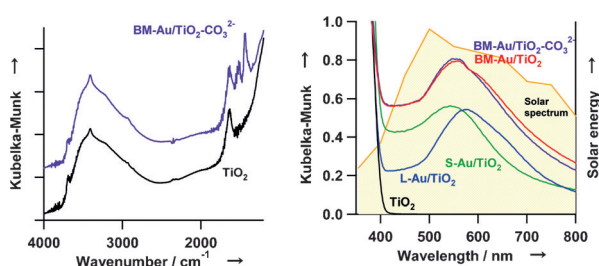


Figure 1. A) DRIFT spectra for CO₃²⁻ ion-adsorbed BM-Au/TiO₂ and TiO₂ for comparison. B) UV/Vis absorption spectra for the unmodified TiO₂ and Au/TiO₂ samples and the solar spectrum.

transform infrared (DRIFT) spectra for BM-Au/TiO₂-CO₃²⁻ and TiO₂ for comparison. In the spectrum of TiO₂, a signal assignable to the stretching vibration of the surface Ti-OH groups [$\nu(\text{Ti}_s\text{-OH})$] is observed at 3695 cm⁻¹, while in the 1200–1800 cm⁻¹ region, a signal due to the deformation vibration of adsorbed water [$\delta(\text{H}_2\text{O})$] is situated at 1637 cm⁻¹. The spectrum of BM-Au/TiO₂-CO₃²⁻ has additional two characteristic signals at 1520 and 1448 cm⁻¹, which can be assigned to the antisymmetric [$\nu_a(\text{OCO})$] and symmetric [$\nu_s(\text{OCO})$] stretching vibrations for the CO₃²⁻ ions adsorbed on the TiO₂ surface with a bidentate structure.^[22] Also, the $\nu(\text{Ti}_s\text{-OH})$ signal significantly weakens with the adsorption of CO₃²⁻ ions. Evidently, CO₃²⁻ ions are adsorbed on the Ti_s-OH sites of BM-Au/TiO₂-CO₃²⁻ through chelation. Figure 1B shows UV/Vis absorption spectra of TiO₂ and Au/TiO₂, and the solar spectrum. While rutile TiO₂ only has absorption at $\lambda < 410$ nm, the Au NP loading induces strong and broad absorption due to the localized surface plasmon resonance (LSPR) in the visible region. The LSPR peaks for S-Au/TiO₂ and L-Au/TiO₂ are located around 550 nm and 580 nm, respectively. The spectrum of BM-Au/TiO₂ is likely the sum of the absorptions of S-Au/TiO₂ and L-Au/TiO₂ with an apparent LSPR peak at 566 nm, well matching with the solar spectrum. The spectrum hardly changes with the CO₃²⁻ adsorption, which also supports the conclusion that CO₃²⁻ ions are selectively adsorbed on the TiO₂ surface of BM-Au/

TiO₂-CO₃²⁻. The larger Au loading amount is responsible for the stronger absorption intensity.

We examined the photocatalytic activity of BM-Au/TiO₂ for the O₂ reduction reaction (ORR) to H₂O₂ without and with sacrificing electron donors (4% C₂H₅OH or HCOOH), and that of BM-Au/TiO₂-CO₃²⁻ in the presence of 4% HCOOH. Catalyst was added in an aerated aqueous solution (10 mL), and H₂O₂ generated under irradiation of visible light ($\lambda > 430$ nm) at 298 K was quantified by the iodometric titration. To evaluate the activity at the comparable Au amount, 20 mg of S- and L-Au/TiO₂ was added in each run, while 10 mg of BM-Au/TiO₂ and BM-Au/TiO₂-CO₃²⁻ were used. Figure 2A shows time courses for the H₂O₂ generation

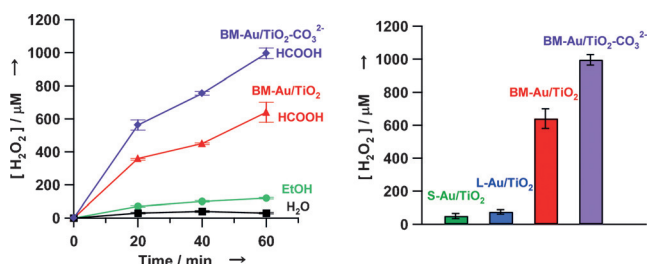


Figure 2. A) Time courses for the BM-Au/TiO₂-photocatalyzed H₂O₂ generation in the absence (black) and presence of 4% C₂H₅OH (green) and 4% HCOOH (red), and for the BM-Au/TiO₂-CO₃²⁻-photocatalyzed H₂O₂ generation with 4% HCOOH (purple) under irradiation of visible light ($\lambda > 430$ nm, light intensity integrated from 420 to 485 nm = 4.0 mW/cm²) at 298 K. B) Photocatalytic activity of S-Au/TiO₂, L-Au/TiO₂, BM-Au/TiO₂, and BM-Au/TiO₂-CO₃²⁻ for the reduction of O₂ to H₂O₂ in an aqueous solution containing 4% HCOOH (pH 1.7) in the dark and under irradiation of visible light ($\lambda > 430$ nm, light intensity integrated from 420 to 485 nm = 4.0 mW/cm²) at 298 K.

in the BM-Au/TiO₂ system. No H₂O₂ was generated in the dark. Visible-light irradiation of BM-Au/TiO₂ in pure water yields $35 \pm 5 \mu\text{M}$ H₂O₂ at $t_p = 20$ minutes. Since the Au/TiO₂ plasmonic photocatalyst oxidizes water under visible-light irradiation,^[23,24] the total reaction is expressed by Equation (1). The addition of the electron donors greatly enhances the reaction, and the H₂O₂ concentration increases with increasing t_p . In the HCOOH-added system, the H₂O₂ concentration reaches $640 \pm 60 \mu\text{M}$ at $t_p = 1$ h. We have recently reported that a decreasing pH of the reaction solution accelerates the Au/TiO₂ photocatalytic ORR to H₂O₂ under UV-light irradiation.^[25] The pH values of the C₂H₅OH- and HCOOH-added solutions were 7.2 and 1.7, respectively. Thus, HCOOH works as not only a good electron donor but also as a pH-regulating agent. Gas chromatography confirmed the formation of CO₂ during the reaction (Figure S2). The total reaction is exergonic, and written by Equation (2).



Surprisingly, BM-Au/TiO₂-CO₃²⁻ exhibits much higher activity than BM-Au/TiO₂ under the same conditions, and the H₂O₂ concentration increases with an increase in t_p . Since the

pH of the solution remained at 1.7, the possibility can be excluded that the carbonate effect is due to a pH change.

The photocatalytic activities of the Au/TiO₂ samples were examined in the presence of 4% HCOOH. Figure 2B compares the concentration of H₂O₂ generated at $t_p = 1$ h. The H₂O₂ concentration in the BM-Au/TiO₂ system ($640 \pm 60 \mu\text{M}$) far exceeds the sum of the H₂O₂ concentrations in S-Au/TiO₂ ($50 \mu\text{M}$) and L-Au/TiO₂ ($75 \mu\text{M}$). Further, in the BM-Au/TiO₂-CO₃²⁻ system, the H₂O₂ concentration reaches about 1 mM. Further, the reaction was performed in the BM-Au/TiO₂-CO₃²⁻ system using a green light emitting diode as a light source, and a quantum efficiency was calculated from the equation of $\Phi = 2 \times (\text{molecule number of H}_2\text{O}_2 \text{ formed}) / (\text{incident photon number})$ to be 5.4% at $\lambda = 530$ nm.

The life time as well as the activity is the key factor for the catalysts. To examine the stability of the BM-Au/TiO₂ photocatalyst, recycle experiments were carried out (Figure S3). When the catalyst was not washed after the reaction, the activity gradually decreased with an increase in the recycle number (N). Then, the catalyst was reused by washing with water after each run. Unexpectedly, the photocatalytic activity increases at $N=2$ to be maintained at least $N \leq 5$. These intriguing results are discussed in more detail later in connection with the action mechanism of the present plasmonic photocatalyst.

Mesoporous TiO₂ nanocrystalline films were formed on fluorine-doped tin oxide electrodes (TiO₂/FTO) by the doctor blade method (see the Supporting Information), and CO₃²⁻ ions were chemisorbed on the surface (CO₃²⁻-TiO₂/FTO). To gain information about the surface modification effect by CO₃²⁻ ions, electrochemical (EC) measurements were carried out for a three-electrode EC cell containing the TiO₂/FTO structure with and without carbonate surface modification (working electrode) | Ag/AgCl (reference electrode) | aerated 0.1 M NaClO₄ aqueous solution with and without 1 mM H₂O₂ | glassy carbon (counter electrode). Figure 3A shows linear sweep voltammograms for the TiO₂/FTO and CO₃²⁻-TiO₂/FTO electrodes in the absence and presence of O₂ and H₂O₂. In the unmodified TiO₂/FTO electrode system, the current

onset potential (E_{on}) is located at -0.1 V without O₂ and H₂O₂, at 0 V with O₂ and without H₂O₂, and at $+0.2$ V without O₂ and H₂O₂. The E_{on} with O₂ and H₂O₂ remains $+0.2$ V. These results indicate that the reductions start for H₂O₂ at $+0.2$ V [$E_{\text{on}}(\text{H}_2\text{O}_2)$], for O₂ at $+0$ V [$E_{\text{on}}(\text{O}_2)$], and for TiO₂ at -0.1 V [$E_{\text{on}}(\text{TiO}_2)$]. In the CO₃²⁻-TiO₂/FTO electrode system, the current with O₂ and H₂O₂ significantly decreases, and the E_{on} is almost in agreement with the $E_{\text{on}}(\text{O}_2)$. Also, the value with O₂ and without H₂O₂ is rather close to the $E_{\text{on}}(\text{TiO}_2)$. Clearly, the surface modification with CO₃²⁻ ions effectively suppresses the reductions of H₂O₂ by the TiO₂/FTO electrode.

Further to clarify which of S- and L-Au NPs acts as the oxidation site in BM-Au/TiO₂, we carried out photoelectrochemical (PEC) measurements by using S- and L-Au/TiO₂ nanocrystalline films formed on FTO (Au/TiO₂/FTO) as the photoanode (see the Supporting Information). A three-electrode PEC cell with the structure of photoanode | Ag/AgCl (reference electrode) | 0.1 M NaClO₄ electrolyte solution containing 4% HCOOH | glassy carbon (cathode) was fabricated. In the photocurrent time curves for the S- and L-Au/TiO₂/FTO photoanode cells at the rest potential in the dark, irradiation of visible light ($\lambda > 430$ nm) causes anodic photocurrent in each system (Figure S4). A much larger photocurrent is observed for the S-Au/TiO₂/FTO system than the L-Au/TiO₂/FTO system. As suggested by the results on the particulate system, HCOOH should be oxidized on the surface of Au NPs of the Au/TiO₂/FTO photoanode, while O₂ is reduced at the cathode in this PEC cell. The action spectrum is also important for elucidating the reaction mechanism. The action spectra of the incident photon-to-current efficiency (IPCE) for the Au/TiO₂/FTO photoanode cells were measured using optical filters with varying cut-off wavelength.^[26] Figure 3B shows the action spectra of IPCE for the present PEC cells, and the absorption spectra of the photoanodes for comparison. The IPCE value for the S-Au/TiO₂/FTO system is significantly larger than that for the L-Au/TiO₂/FTO system in the 475–660 nm range. The IPCE in each system increases with decreasing wavelength of incident light with only a weak shoulder near the LSPR peak, whereas a peak is observed near the LSPR-peak wavelength in the action spectra for several Au/MO-plasmonic photocatalytic reactions.^[14,15,17,27] A similar action spectrum has recently been reported for the water oxidation by a PEC cell employing Au/SrTiO₃ as the photoanode.^[28] The absorption intensity of the interband transition monotonically increases with decreasing wavelength, and thus, the reaction may be triggered by the excitation of the 5d-6sp transition of Au NP in addition to its LSPR. These results are consistent with the previous conclusion that the excited electrons are transferred from S-Au NPs to L-Au NPs by way of TiO₂.^[18] As a result of the decrease in d from 10.6 to 2.3 nm, the density of states (DOS) of Au NPs greatly lowers.^[29] While in the small Au NPs, the small DOS increases the entropic driving force for the forward electron transfer from Au NP to TiO₂ with that for the back electron transfer simultaneously decreased, the opposite situation is valid for L-Au NPs.^[30] The difference in the entropic driving force for the electron transfer at the S-Au NP/TiO₂ and the L-Au NP/TiO₂ interfaces rationalizes the

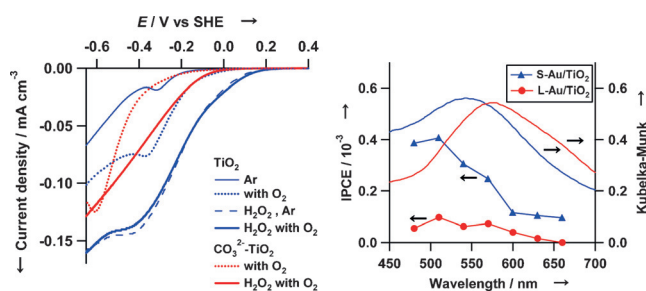
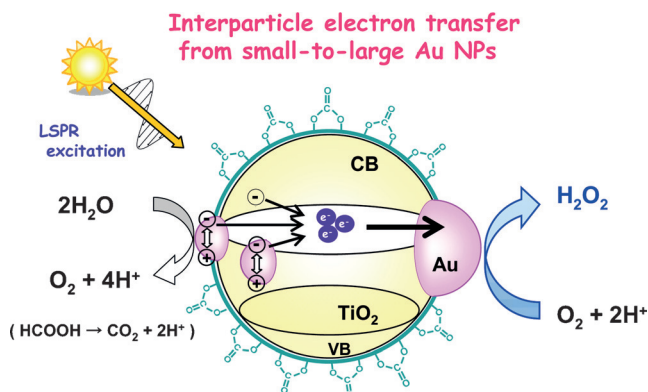


Figure 3. A) Dark current–potential (E/V vs. standard hydrogen electrode, SHE) curves for TiO₂/FTO electrodes without and with the carbonate surface modification in 0.1 M NaClO₄ aqueous solution in the absence and presence of O₂ and 1 mM H₂O₂ (pH \approx 6.2). B) IPCE action spectra for the three-electrode PEC cells with a structure of S-Au/TiO₂/FTO and L-Au/TiO₂/FTO (photoanode) | Ag/AgCl (reference electrode) | 0.1 M NaClO₄ electrolyte solution containing 4% formic acid | glassy carbon (cathode), and the absorption spectra for the photoanodes for comparison.

electron transport from S-Au NPs to L-Au NPs through TiO_2 in BM-Au/ TiO_2 .

On the basis of these results above, the mechanism of the BM-Au/ TiO_2 plasmonic photocatalyzed-reduction of O_2 to H_2O_2 is proposed (Scheme 2). Visible-light irradiation of BM-Au/ TiO_2 gives rise to the interfacial electron transfer from small-to-large Au NP through the conduction band (CB) of



Scheme 2. A mechanism proposed for the BM-Au/ TiO_2 - CO_3^{2-} plasmonic photocatalyzed-reduction of O_2 to H_2O_2 .

TiO_2 .^[18] The Fermi energy (E_F) of S-Au NPs lowers, while the E_F of L-Au NPs rises up. As a result, the oxidizing and reducing abilities are induced on S- and L-Au NPs, respectively. In pure water, H_2O is oxidized to O_2 and H^+ on the S-Au NP surface of Au/ TiO_2 , of which visible-light activity steeply increases at the Au mean particle size < 4 nm.^[30] In the presence of HCOOH , it is preferentially oxidized to CO_2 and H^+ on the S-Au NP surface. On the other hand, the ORR proceeds on the L-Au NP surface. Thermodynamically, the potential of the electrons in the CB of rutile TiO_2 (flat-band potential, $E_{fb} = +0.04$ V at pH 1.0 vs. SHE)^[31] is insufficient for the one-electron ORR ($E^0(\text{O}_2/\text{HO}_2) = -0.046$ V vs. SHE)^[32] to proceed, but is sufficient for the two-electron ORR ($E^0(\text{O}_2/\text{H}_2\text{O}_2) = +0.695$ V vs. SHE).^[32] In this system, due to the electron pool effect^[33] and electrocatalysis for the two-electron ORR of the L-Au NP,^[34] O_2 would be effectively reduced to H_2O_2 on the surface. Similar effects have been suggested for the Cu^{II} ions in a visible-light-responsive Cu^{II} -grafted rutile TiO_2 system.^[35] Eventually, in the BM-Au/ TiO_2 system, S-Au NPs highly dispersed on TiO_2 work as an antenna for the incident light to inject electrons into TiO_2 , and the collected electrons in L-Au NPs are effectively used for the two-electron ORR because the Au/ TiO_2 -catalyzed H_2O_2 decomposition is significantly suppressed at $d < 3$ nm and $d > 8$ nm.^[6] The much higher photocatalytic activity of BM-Au/ TiO_2 than S-Au/ TiO_2 and L-Au/ TiO_2 can be mainly attributed to the long-range charge separation by the visible-light-induced vectorial interfacial electron transfer (S-Au \rightarrow CB- TiO_2) \rightarrow L-Au). However, H_2O_2 once produced undergoes degradation via the reduction of the surface peroxide species ($\text{Ti}_s\text{-OOH}$), resulting from the reaction of H_2O_2 with the surface Ti-OH ($\text{Ti}_s\text{-OH}$) groups, by the CB-electrons in TiO_2 .^[36] CO_3^{2-} ions chemisorbed on TiO_2 suppress the $\text{Ti}_s\text{-}$

OH-mediated reductive degradation pathway. Consequently, the extremely high visible-light activity of BM-Au/ TiO_2 - CO_3^{2-} would stem from the compatibility of the effective charge separation in the BM-Au/ TiO_2 heterostructure and the suppression of the TiO_2 surface-mediated H_2O_2 decomposition by the surface modification with CO_3^{2-} ions. The reaction in the presence of HCOOH yields CO_2 [Eq. (2)], which could partly be adsorbed on the TiO_2 surface during the reaction. These considerations explain the increase in the activity at $N \geq 2$ (Figure S3). The surface-fluorination of TiO_2 was previously reported to be effective in increasing the H_2O_2 concentration under irradiation of UV light.^[37,38]

In summary, this study has shown that irradiation of visible light ($\lambda > 430$ nm) of BM-Au/ TiO_2 in aerated pure water yields $35 \mu\text{M}$ H_2O_2 , and the generation of a millimolar level of H_2O_2 with a Φ value of 5.4 % at $\lambda = 530$ nm has been achieved in the BM-Au/ TiO_2 - CO_3^{2-} -system with HCOOH as an electron donor. We anticipate that this study presents the useful information about the design of the photocatalyst for the solar H_2O_2 synthesis.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (C) (grant number 15K05654) and MEXT-Supported Program for the Strategic Research Foundation at Private Universities.

Keywords: hydrogen peroxide · oxygen reduction reaction · plasmonics · photocatalysis · solar chemical transformations

How to cite: *Angew. Chem. Int. Ed.* **2016**, 55, 12773–12777
Angew. Chem. **2016**, 128, 12965–12969

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Received: July 11, 2016

Revised: August 2, 2016

Published online: September 8, 2016