

Research Article

Cosensitization Properties of Glutathione-Protected Au₂₅ Cluster on Ruthenium Dye-Sensitized TiO₂ Photoelectrode

**Kazuya Nakata,^{1,2} Sho Sugawara,^{1,3} Wataru Kurashige,⁴
Yuichi Negishi,^{2,4} Morio Nagata,⁵ Satoshi Uchida,⁵ Chiaki Terashima,²
Takeshi Kondo,^{2,3} Makoto Yuasa,^{2,3} and Akira Fujishima²**

¹ Department of Applied Biological Science, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

² Research Institute for Science and Technology, Photocatalysis International Research Center, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

³ Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

⁴ Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

⁵ Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

Correspondence should be addressed to Kazuya Nakata; nakata@rs.tus.ac.jp

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Cosensitization by glutathione-protected Au₂₅ clusters on Ru complex, N719-sensitized TiO₂ photoelectrodes is demonstrated. Glutathione-protected Au₂₅ clusters showed no significant changes in properties after adsorption onto TiO₂ particles, as confirmed by optical absorption spectroscopy, transmission electron microscopy, and laser desorption/ionization mass spectrometry. Adsorption property of the glutathione-protected Au₂₅ clusters depends on the pH, which affects the incident photon-to-current conversion efficiency (IPCE) of the TiO₂ photoelectrode containing Au₂₅ clusters. When pH < 5, the IPCE increases with pH. Conversely, the IPCE decreases with pH when pH > 7. The IPCE of a TiO₂ photoelectrode sensitized by both glutathione-protected Au₂₅ clusters and N719 was increased compared with photoelectrodes containing either glutathione-protected Au₂₅ clusters or N719, which suggests that glutathione-protected Au₂₅ clusters act as a coadsorbent for N719 on TiO₂ photoelectrodes. This is also supported by the results that the IPCE of N719-sensitized TiO₂ photoelectrodes increased upon addition of glutathione. Furthermore, cosensitization by glutathione-protected Au₂₅ clusters on N719-sensitized TiO₂ photoelectrodes allows that wavelength of photoelectric conversion was extended to the near infrared (NIR) region. These results suggest that glutathione-protected Au₂₅ clusters act not only as a coadsorbent to increase IPCE but also as an NIR-active sensitizer.

1. Introduction

Dye sensitization of wide bandgap semiconductors such as TiO₂, ZnO, and SnO₂ is an attractive research field with considerable significance for solar energy utilization, including solar cells [1] and water splitting [2]. As wide bandgap semiconductors absorb only ultraviolet (UV) light, by adding dyes which absorb visible (VIS) light, a larger proportion of solar light can be harnessed. To date, a number

of organic dyes, such as phthalocyanines [3–6], perylene bisamides [7–9], xanthenes [10, 11], hemicyanines [12–14], and porphyrins [15–18], have been used as dye sensitizers. One typical sensitizing dye is the ruthenium complex di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), known as N719, which assists in realizing high photoelectric conversion efficiency [19, 20]. There have been many attempts to further increase incident photon-to-current conversion efficiency

(IPCE) in dye-sensitized semiconductor photoelectrodes. One methodology is to use infrared (IR-) active dyes. Generally, dyes absorb UV and VIS light and are able to convert those photons to current. Solar light covers a wide range of wavelengths, including UV (3% of solar light), VIS (42%), and IR regions. Therefore, to improve the overall photoelectric conversion efficiency in semiconductor photoelectrodes, the whole range of solar radiation, including not only UV and VIS but also near infrared (NIR) light, needs to be accessed. Although the photovoltaic performance of semiconductor-based photoelectrodes sensitized by NIR-active dyes has been greatly improved recently, the spectral response of these cells in the NIR region remains insufficient.

The second methodology used to maximize IPCE is coadsorption reagents, which are typically molecules containing carboxylic end-groups such as chenodeoxycholic acid and taurodeoxycholate [21–23], which adsorb together with the dye on the semiconductor surface. The interfacial area of the semiconductor surface favors charge recombination, which should lead to the recapture of injected electrons by the oxidized species of the redox couple present in the electrolyte (e.g., I_3^-), impairing the total light-to-electrical energy conversion efficiency of the device. Coadsorption suppresses this adverse back electron transfer from the semiconductor conduction band to the electrolyte, increasing the IPCE and total energy conversion efficiency. Furthermore, coadsorbents avoid the problems of competitive adsorption and aggregation of dyes that may induce unfavorable charge or energy transfer and quenching of photoexcited states.

The third methodology is cosensitization using multiple dyes. Ogura et al. reported that a DSSC containing two dyes, black dye and D131, showed a high energy conversion of 11.0% [24]. Such high energy conversion was a result of independent contributions of electron transfer from each dye to the TiO_2 electrode. Although many combinations of organic sensitizer dyes have been studied in the context of cosensitization, success has been limited because electron transfer occurs between the dyes, leading to lower total photon energy conversion efficiencies.

In this work, we examine cosensitization on TiO_2 photoelectrodes with N719 and glutathione-protected Au_{25} clusters which act as both adsorbent and sensitizer. Au_{25} clusters with a diameter of less than 2 nm exhibit optical absorptions in the UV, VIS, and NIR regions because of their multiple narrow discrete electronic levels [25, 26]. In particular, thiolate-protected Au_{25} clusters have been studied extensively because of their thermodynamic stability, allowing clarification of their molecular and electronic structures [25–29]. Sakai and Tatsuma reported that glutathione-protected Au clusters adsorbed on TiO_2 electrodes exhibited anodic photocurrent in response to VIS and NIR light ($400 < \lambda < 900$ nm) [30]. This made the electrodes applicable to the conversion of light to electricity. Each photocurrent action spectrum was consistent with the corresponding optical absorption spectrum because photoelectric conversion is based on the electronic transition between the HOMO and LUMO triggered by absorbed light.

Here, we examine the effects of glutathione-protected Au_{25} clusters on cosensitization of TiO_2 photoelectrodes with N719 dye.

2. Experimental Sections

2.1. Preparation of Au_{25} Clusters. Glutathione-protected Au_{25} clusters were synthesized according to a procedure reported in the literature with some modifications [31, 32]. Firstly, Au_{11} clusters were prepared as a precursor of Au_{25} clusters. A mixture of $HAuCl_4 \cdot 4H_2O$ (118 mg, 0.3 mmol), tetraoctylammonium bromide (190 mg, 0.348 mmol), water (5 mL), and toluene (10 mL) was stirred for 15 min. The organic phase was separated and centrifuged to completely remove the water phase. Triphenylphosphine (235 mg, 0.9 mmol) was added to the organic phase, which was then mixed with $NaBH_4$ (34 mg, 0.9 mmol) in ethanol (5 mL) and stirred for 2 h. After evaporation of the solvent, the precipitate was washed with water and hexane to remove excess triphenylphosphine and $NaBH_4$. The precipitate was dissolved in chloroform and evaporated to completely remove water.

To obtain Au_{25} clusters, the Au_{11} clusters (4.7 mg) were dissolved in chloroform (7 mL) and then mixed with glutathione (reduced form, 136 mg, 0.4 mmol) in water (7 mL). The mixture was heated under reflux for 5 h. After cooling, the suspension was evaporated to obtain a powder of Au_{25} clusters. The presence of glutathione was confirmed by FT-IR spectra as shown in Figure S1 available online at <http://dx.doi.org/10.1155/2013/456583>.

2.2. Preparation of Dye-Sensitized TiO_2 Photoelectrodes. TiO_2 photoelectrodes were prepared by screen printing a TiO_2 paste (Ti-Nanoxide T/SP, Solaronix SA) on fluorine-doped tin oxide/glass (FTO) substrates (Solaronix SA). The TiO_2 photoelectrodes were annealed at 200°C for 10 min and then at 500°C for 30 min, resulting in anatase films. Multiple heating steps were performed to avoid cracking of the TiO_2 layer.

For the experiment examining the pH dependence on the IPCE of the glutathione-protected Au_{25} cluster-sensitized TiO_2 photoelectrodes, the above TiO_2 photoelectrode with a thickness of 3.4 μm (confirmed by SEM as shown in Figure S2) was soaked in an aqueous solution (5 mL) of glutathione-protected Au_{25} clusters (1.5 mg) for 24 h, washed with pure water, and then dried under an air flow. The pH of the aqueous solution was adjusted using acetic acid or aqueous NaOH prior to soaking. A 50 μm thick Himilan film was used to assemble the TiO_2 electrode with an Au-sputtered FTO electrode (the thickness of the Au layer was 100 nm). The space between the electrodes was filled with a mixed electrolyte containing hydroquinone (55 mg, 0.5 mmol) and tetrabutylammonium perchlorate (34 mg, 0.1 mmol) in acetonitrile (20 mL).

For the experiment investigating cosensitization with glutathione-protected Au_{25} clusters and N719, the preparation procedures were the same as above, except that 1.7 μm thick TiO_2 photoelectrodes were soaked in solutions containing Au_{25} clusters (in 5 mL of H_2O , 3.0×10^{-4} M)

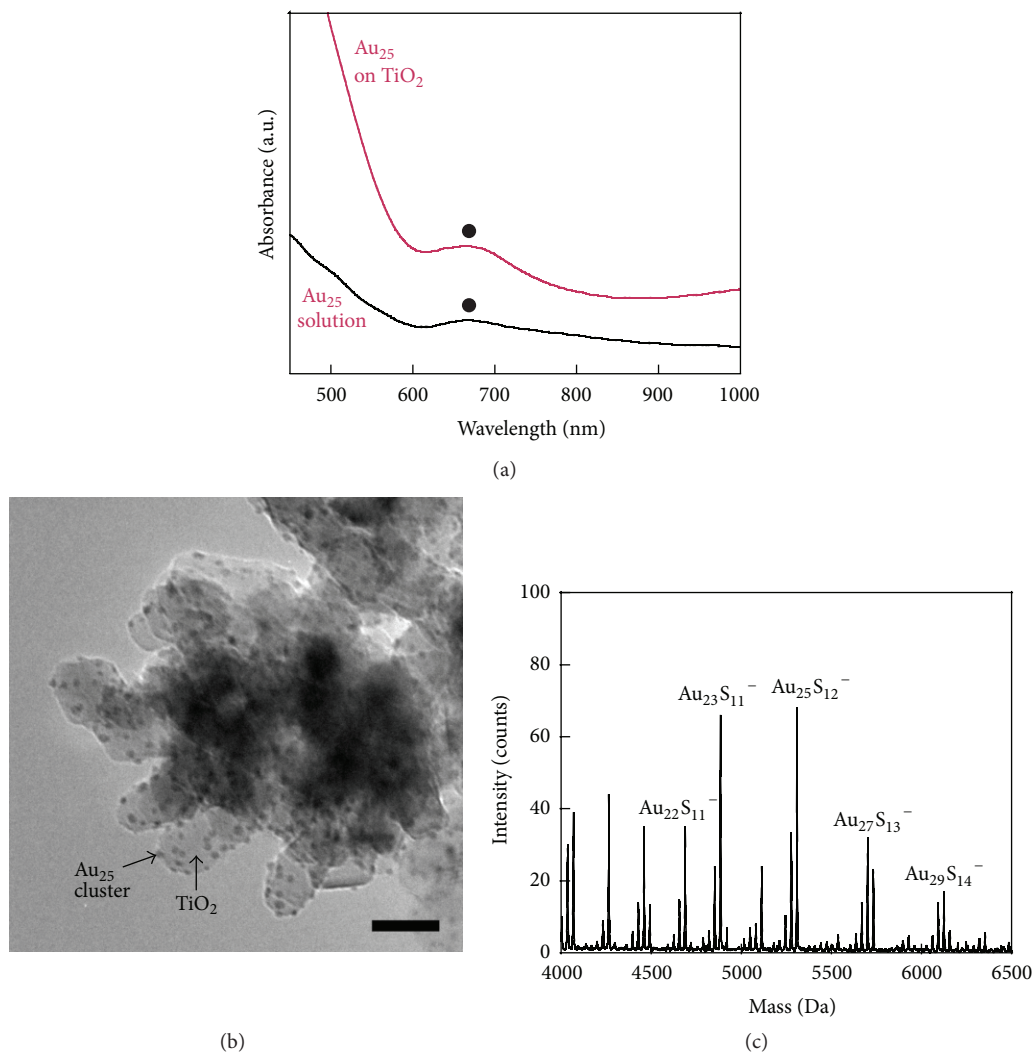


FIGURE 1: (a) Absorption spectrum of Au_{25} clusters in water, (b) TEM image of Au_{25} clusters on TiO_2 particles (scale bar is 20 nm), and (c) LDI-MS spectrum of Au_{25} clusters on TiO_2 particles (negative ion mode).

and/or N719 (3.0 mg) with a mixture of *tert*-butanol and acetonitrile (volume ratio of 1 : 1, 100 μL). Acetic acid (50 μL) was added to adjust the pH to 3, and then the mixture was left for 12 h.

For the experiment determining the effect of glutathione as a coadsorbent for N719-sensitized TiO_2 photoelectrodes, the preparation procedure was the same as above, except that a 1.7 μm thick TiO_2 photoelectrode was soaked in a mixture of *tert*-butanol and acetonitrile (5 mL, volume ratio of 1 : 1) containing N719 (3.0 mg, Dyesol) and glutathione (10 mM or 100 mM) for 12 h. Acetic acid (50 μL) was added to adjust the pH to 3 before the addition of glutathione.

3. Results and Discussion

To check stability of the glutathione-capped Au_{25} clusters on a TiO_2 photoelectrode, optical absorption spectra were measured. An optical absorption spectrum of water solution

containing the glutathione-capped Au_{25} clusters is characteristic of thiol-capped Au_{25} clusters and indicates a quantum confinement effect of the electrons in the Au_{25} clusters, as shown in Figure 1(a). A peak is observed at 667 nm (indicated by a filled circle), which is assigned to the HOMO-LUMO transition in the Au_{13} core of Au_{25} [25, 26, 31, 33]. Strong absorption in the VIS range characteristic of surface plasmon resonance originating from gold nanoparticles was not observed. After a TiO_2 electrode was soaked in an aqueous Au_{25} cluster solution, a peak at 667 nm was also observed in an optical absorption spectrum of the TiO_2 electrode containing the Au_{25} cluster, which indicates that electronic properties of Au_{25} clusters were maintained on the TiO_2 electrode. Structural stability of the Au_{25} clusters was evidenced by the transmission electron microscopy (TEM) image, as shown in Figure 1(b). The Au_{25} clusters were almost uniform and dispersed over the TiO_2 particles. The average diameter of the Au_{25} clusters was 1.7 nm, which is slightly larger than those previously reported (1–1.2 nm) [34, 35].

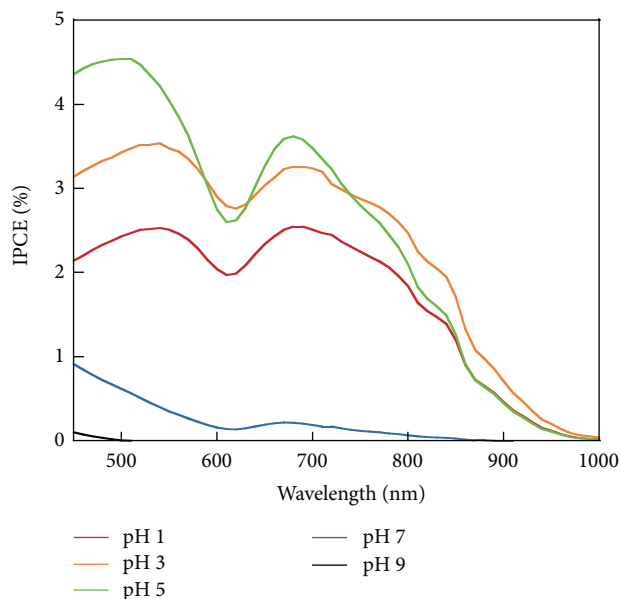


FIGURE 2: IPCE spectra of Au_{25} cluster solutions at different pHs.

This is probably caused by aggregation of Au_{25} clusters induced by the electron beam during TEM measurement. Note that the morphology of the Au_{25} clusters was stable after the IPCE measurements as shown in Figure S3. To further confirm the formation of Au_{25} clusters, the TiO_2 electrode decorated with Au_{25} clusters was studied by laser desorption/ionization mass spectrometry (LDI-MS) in the negative ion mode. The most abundant peak was centered at 5308 m/z and formed a pattern resulting from a series of fragments and recombined ion peaks that were consistent with $\text{Au}_{25}(\text{glutathione})_{18}$ (Figure 1(c)) [34]. Other Au clusters and aggregates of Au_{25} clusters on the TiO_2 particles were not detected. These results suggest that the structure of the Au_{25} cluster does not change dramatically during adsorption onto the TiO_2 particles.

The adsorption properties of the Au_{25} cluster onto the TiO_2 electrode depend on the solution pH. To examine the adsorption properties, the IPCE of the Au_{25} cluster-sensitized TiO_2 photoelectrode prepared using different pH solutions is plotted as a function of excitation wavelength, as shown in Figure 2. To avoid fluctuation of IPCE originating from variation of the thickness of TiO_2 and to allow comparison between electrodes, we prepared thin TiO_2 layers with a thickness of $3.4\ \mu\text{m}$ on FTO substrates, which are thinner than a typical DSSC ($\sim 20\ \mu\text{m}$). The IPCE of the TiO_2 photoelectrode containing Au_{25} in the pH range 1–7 exhibited a peak around 670–690 nm, which is related to the absorption spectrum of Au_{25} on TiO_2 photoelectrodes prepared in various pH (Figure S4) and indicates that photoinduced electron injection into the conduction band of TiO_2 occurs via the excited state of Au_{25} . Note that no peaks in absorption spectra in the range $>450\ \text{nm}$ for a TiO_2 electrode support the indication of photoinduced electron injection of Au_{25} (Figure S5). The optical absorption peak around 670–690 nm is ascribed to the HOMO-LUMO transition. Thus,

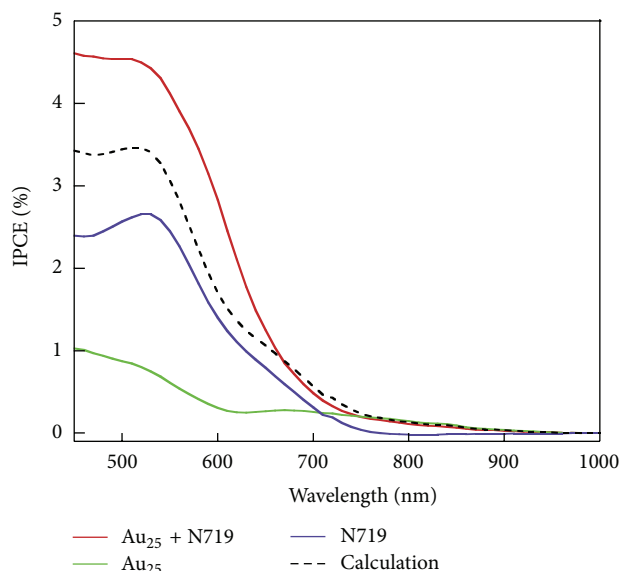


FIGURE 3: IPCE spectra of TiO_2 photoelectrodes sensitized by glutathione-protected Au_{25} clusters, N719 and coadsorbed glutathione-protected Au_{25} clusters and N719, and the calculated Au_{25} clusters and N719 spectrum.

the corresponding IPCE is attributed to electron transfer from LUMO of Au_{25} to the TiO_2 conduction band. The IPCE at $\lambda < 600\ \text{nm}$ was also observed, which should be attributed to electron transition from a deeper level, such as HOMO-2 and HOMO-5, to LUMO and that from HOMO to LUMO+1 and LUMO+2.³⁷ In the pH range of 1–5, the IPCE increased with increasing pH. In contrast, the IPCE decreased when the pH > 7 . The pKa values of the carboxyl groups of glutathione are 2.05 and 3.40 [36] and the isoelectric point of the TiO_2 (anatase) surface is 6.89 [37]. Thus, the Au_{25} clusters adsorb onto the TiO_2 electrode when the pH of the Au_{25} solution is in the range of 2–6 because the negatively charged $-\text{COO}^-$ groups of glutathione and the positively charged TiO_2 surface interact electrostatically. In contrast, at pH = 1, almost all carboxyl groups are protonated, so they are not electrostatically attracted to the positively charged TiO_2 surface; therefore, the IPCE is reduced. Furthermore, when the pH > 7 , the TiO_2 surface is negatively charged, which strongly suppresses the interaction between negatively charged TiO_2 and negatively charged $-\text{COO}^-$ groups.

To examine the effects of the addition of glutathione-protected Au_{25} clusters on N719-sensitized TiO_2 electrode, the IPCE of glutathione-protected Au_{25} clusters and N719 coadsorbed onto a TiO_2 electrode were measured (Figure 3). As reference, the IPCE of glutathione-protected Au_{25} clusters or N719 adsorbed onto TiO_2 electrodes were also measured, respectively. The IPCE of the TiO_2 photoelectrode containing Au_{25} clusters or N719 exhibited peaks around 675 nm and 510 nm, respectively. The IPCE of the TiO_2 photoelectrode sensitized with both glutathione-protected Au_{25} clusters and N719 was significantly greater than the ICPE of the TiO_2 photoelectrode sensitized with only N719 and exhibited the characteristic peak originating from N719 at 510 nm. A peak

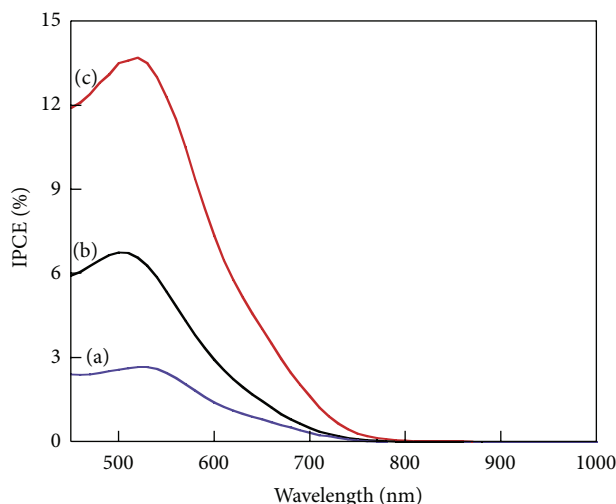


FIGURE 4: IPCE of (a) N719-sensitized TiO_2 photoelectrode and after addition of (b) 1 mM and (c) 0.1 mM of glutathione.

at 675 nm originated from the glutathione-protected Au_{25} clusters may be hidden in large values of IPCE. It should be noted that the values of the IPCE are higher than the values calculated for addition of Au_{25} clusters and N719, which indicates that the glutathione-protected Au_{25} clusters may suppress competitive adsorption and aggregation of N719 and behave as a coadsorbent. The photocurrent-voltage characteristic for the TiO_2 photoelectrode sensitized with both glutathione-protected Au_{25} clusters and N719 under AM 1.5 solar light illumination revealed that the photoenergy conversion efficiency was 0.034%, which is greater than those of 0.005 and 0.007% for the TiO_2 electrodes sensitized with Au_{25} or N719, respectively (Figure S6). To examine the effects of glutathione ligand on Au_{25} clusters, the IPCE of N719-sensitized TiO_2 photoelectrodes prepared from N719 solutions at pH = 3 with or without glutathione were measured, as shown in Figure 4. The IPCE of the N719-sensitized TiO_2 photoelectrode increased with the addition of glutathione (10 mM). However, further addition of glutathione (100 mM) reduced the IPCE of the N719-sensitized TiO_2 photoelectrode because glutathione began to occupy the TiO_2 surface instead of N719. The amount of N719 molecules on TiO_2 photoelectrodes is 4.1×10^{-8} , 1.2×10^{-8} and 9.4×10^{-9} mol/cm² for N719, N719 with 10 mM and 100 mM of glutathione, respectively. Thus, the increase in IPCE is not due to increase in the amount of N719 molecules, which suggests that glutathione acts as a coadsorbent. Generally, coadsorbent molecules possess carboxylic end-groups because such groups can anchor to the semiconductor surface [21–23]. In this case, glutathione molecules anchored on the TiO_2 surface may suppress back electron transfer from the semiconductor conduction band to the electrolyte and/or avoid competitive adsorption and aggregation of N719. Note that the increase in IPCE in the TiO_2 photoelectrode sensitized with both glutathione-protected Au_{25} clusters and N719 is not due to the increased amount of N719. Typically, the amount of N719 molecules on a TiO_2 photoelectrode is calculated from absorption spectra

of a solution containing N719 after N719 molecules are desorbed onto the TiO_2 photoelectrode in NaOH aqueous solution [38]. In this case, it was difficult to calculate the amount of N719 molecules adsorbed on the TiO_2 photoelectrodes, because Au_{25} clusters also desorbed and were detected along with N719 in the absorption spectrum, preventing the exact amount of N719 from being calculated. However, the amount of N719 adsorbed on the TiO_2 photoelectrode exposed to N719 alone may be higher than that on the Au_{25} cluster and N719 coadsorbed TiO_2 photoelectrode. This is because adsorption of N719 onto the TiO_2 surface will be suppressed by adsorption of glutathione-protected Au_{25} clusters in the TiO_2 photoelectrode containing coadsorbed dyes.

Furthermore, the value of IPCE in the NIR region increased in the TiO_2 photoelectrode sensitized with both glutathione-protected Au_{25} clusters and N719, and an IPCE signal was detected up to 900 nm, which is an improvement compared with that sensitized with N719 alone (~760 nm). It is suggested that the glutathione-protected Au_{25} clusters act as a co-adsorbent to increase the IPCE as well as an NIR-active sensitizer.

4. Conclusions

In conclusion, cosensitization by glutathione-protected Au_{25} clusters on N719-sensitized TiO_2 photoelectrodes was achieved. Glutathione-protected Au_{25} clusters were stable after adsorption onto TiO_2 photoelectrodes, as confirmed by absorption spectra, TEM, and LDI-MS measurements. The IPCE of the TiO_2 photoelectrode with adsorbed glutathione-protected Au_{25} clusters depended on the pH of the preparation solution. Addition of glutathione-protected Au_{25} clusters increases the IPCE of the N719 adsorbed TiO_2 electrode, and the wavelength of photoelectric conversion was extended to 900 nm in the NIR range. This result suggests that glutathione-protected Au_{25} clusters should behave as both a coadsorbent to increase IPCE and an NIR-active sensitizer, which opens new methodologies for the design of coadsorbents with sensitization properties.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

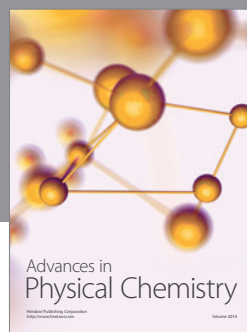
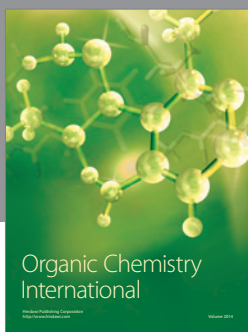
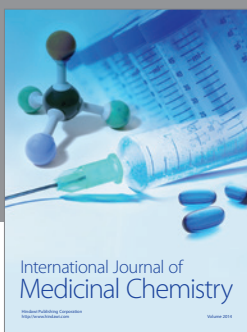
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