Photochemical Reaction of Poly(ethylene glycol) on Gold Nanorods Induced by Near Infrared Pulsed-laser Irradiation

Shuji Yamashita,[1] Yasuro Niidome,*[1] Yoshiki Katayama,[1,2] and Takuro Niidome*[1,2,3]
[1]*Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395*
[2]*Center for Future Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395*
[3]*Precursory Research for Embryonic Science and Technology, Japan Science and Technology Corporation, Kawaguchi 332-0012*

(Received November 25, 2008; CL-081110; E-mail: niidome-tcm@mbox.nc.kyushu-u.ac.jp)

Pulsed-laser irradiation induced release of modified PEG chains on gold nanorods. A maximum release efficiency of 65% is obtained. The efficient release was occurred by combination of cleavage of Au–S bonds, the fragmentation of PEG chains, and the decrease of the surface area. CW-laser irradiation did not release any PEG chains; however, it was effective to increase temperature of the nanorod solution.

Photoreactions of gold nanoparticles could be induced by excitation of surface plasmon (SP) bands. Because SP bands have a large extinction coefficient, laser irradiation at the wavelength corresponding to the SP bands results in absorption of a lot of photons in a gold nanoparticle. The photons are converted into heat in the gold nanoparticle, and the heat then changes the size and shape of the gold nanoparticles.[1] Fragmentation into smaller particles[2,3] and fusion into larger particles[4] are typical examples of the reactions that can be triggered by heat.

Gold nanorods, which are rod-shaped gold nanoparticles, have transverse and longitudinal SP bands in visible and near-infrared (IR) regions, respectively. These SP bands depend on the shapes and sizes of the gold nanorods.[5] Gold nanorods are anticipated to be a new class of nanomaterial responsive to near-IR laser irradiation. It has been shown that pulsed-laser irradiation effectively transforms gold nanorods into spherical particles.[3,6] Furthermore, because near-IR light penetrates most organic molecules, gold nanorods can be triggered without damaging organic molecules in the path of laser light.[7] Therefore, gold nanorods are reported as functional materials for photothermal therapy[8–14] and controlled release of genes[12–14] and drugs.[15] Thus, near-IR irradiation to gold nanorods is a potential method to trigger their functionality.

Photothermal reactions of organic adsorbates are sensitive to surface modifications of gold nanorods. Here, we evaluated the photoreactions of PEG-modified gold nanorods.[16] PEG is a biocompatible and hydrophilic polymer that is frequently used for biorelated applications. In this study, we evaluated the photoinduced reactions (thermochemical reactions) of PEG chains depending on the type, intensity, and duration of laser light. This work provides basic information related to the thermochemical reactions of surface molecules on gold nanorods triggered by light irradiation.

Figure 1 shows extinction spectra of the PEG–nanorods before (a) and after (b–e) laser irradiation. Experimental details are shown in the Supporting Information.[17] Pulsed-laser (1064 nm, 25 mJ/pulse, 20 Hz (500 mW), $\phi \approx 4$ mm) irradiation decreased the extinction of the longitudinal SP bands in near-IR regions ($\approx$900 nm) and gave new SP bands at around 680 nm. After 10 min of laser irradiation, the longitudinal SP at about 900 nm disappeared.

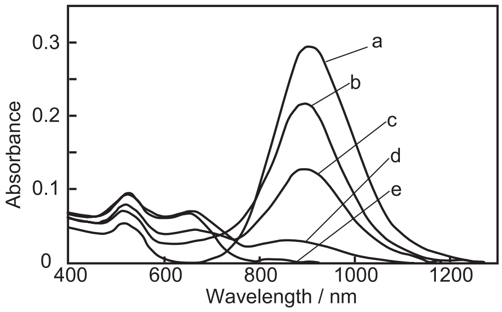

Figure 1. Absorption spectra of PEG-modified gold nanorods in water before (a) and after (b–e) pulsed-laser irradiation: (a) 0 mW–0 min, (b) 500 mW–0.5 min, (c) 500 mW–1 min, (d) 500 mW–5 min, (e) 500 mW–10 min.

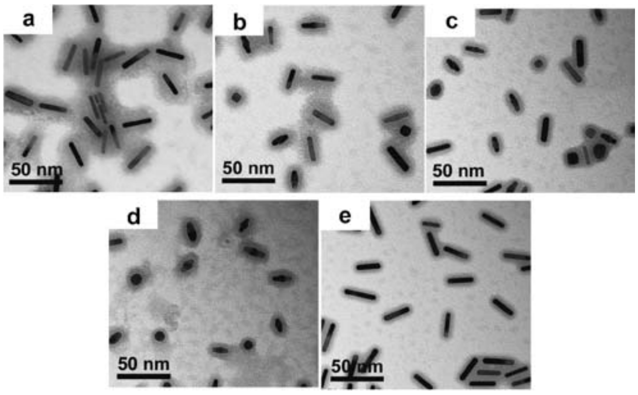

Figure 2. TEM images of PEG-modified gold nanorods before (a) and after (b–e) near-IR laser irradiation: (a) 0 mW–0 min, (b) pulsed-laser 100 mW–10 min, (c) pulsed-laser 200 mW–10 min, (d) pulsed-laser 500 mW–10 min, (e) CW-laser 500 mW–10 min.

Morphologies of the gold nanorods before and after the laser irradiations were observed by TEM (Figure 2). The PEG layer was stained with phosphotungstic acid. The change of shape to spherical and ϕ-shaped nanoparticles was dependent on intensity of the pulsed laser, (Figures 2b–2d). On the other hand, CW-laser irradiation (500 mW) did not change the shape of the gold nanorods (Figure 2e), indicating that the CW-laser irradiation was not sufficient to induce such changes in the gold nanorods, while 500 mW pulsed-laser light dramatically changed the shape of the gold nanorods (Figure 2d).

Amounts of released PEG chains after the laser irradiations

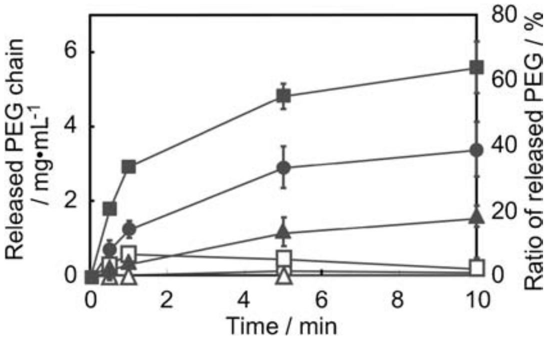

Figure 3. Amounts of released PEG chain and ratios of the released PEG after laser irradiations. ■: pulsed-laser 500 mW–10 min, ●: pulsed-laser 200 mW–10 min, ▲: pulsed-laser 100 mW–10 min, □: CW-laser 500 mW–10 min, ○: CW-laser 200 mW–10 min, △: CW-laser 100 mW–10 min.

were measured[18] and then plotted against the laser irradiation time (Figure 3). When the pulsed-laser irradiated the PEG-modified gold nanorods, release of the PEG chain was dependent on the laser power. When 500 mW (25 mJ/pulse) pulsed-laser light was irradiated to the gold nanorods for 10 min (*closed squares*), about 65% of PEG chains were released from the surfaces of the gold nanorods, indicating that transient and intense heating of gold nanorods induced by the pulsed-laser irradiation was effective to release the PEG chains. In contrast, the irradiation of the CW-laser showed little PEG release from the gold nanorods even at 500 mW laser irradiation. Continuous and moderate heating induced by the CW-laser irradiation was not enough to release the PEG chain; however, temperature of the gold nanorod solutions increased by the CW-laser irradiation, while the pulsed laser did not increase temperature of the solutions (see Figure S1 in the Supporting Information).[17] In the case of the CW-laser irradiation, maintaining the shape of the gold nanorods during the laser irradiation continuously increased the temperature of the solution.

A possible driving-force for the PEG release is the decrease of the surface area accompanying the photothermal reshaping of gold nanorods into spherical particles. If a gold nanorod (65 × 11 nm) is transformed into a spherical particle, its surface area decreases by about 33%. This cannot explain such high release efficiency (65%). The inconsistency between the surface decrease and the experimental release efficiency would originate from the thermochemical reactions contributing the release of the PEG. Ah et al. reported the photoinduced dissociation of thiol molecules from surfaces of gold nanoparticles by the cleavage of Au–S bonds.[19,20] It would also be possible that the pulsed-laser irradiation induced dissociation of the PEG chains from gold nanorod surfaces and that some dissociated PEG chains would not return to the nanorod surfaces. That is, in the presence of oxygen, PEG chains cleaved as $\mathrm{mPEG_{5000}{-}S\bullet}$ would be oxidized to $\mathrm{mPEG_{5000}{-}SO_3}$ and the release of the PEG chains thus result. Molecular weights of the dissociated PEG chains were evaluated by mass spectrometry (Figure S2).[17] As a result, lower molecular weight of PEG chains than the original PEG chains was detected, indicating that fragmentation of the PEG chain occurred during the pulsed-laser irradiation.

In this study, we showed basic data on photoreactions of the gold nanorods irradiated by pulsed- and CW-laser light. The pulsed-laser light induced efficient release of the PEG chains (65%) that was caused by three factors; the photoinduced reshaping of gold nanorods into spherical particles, the cleavage of Au–S bonds, and fragmentation of the PEG chain. If a functional molecule such as a drug is linked to terminal of the PEG chain on the gold nanorods, the pulsed-laser light will trigger release of the drug to where the drug is required in the body. In contrast, CW-laser light contributed the efficient photothermal conversions without changing the shape and surface structure of the gold nanorods. Thus, CW laser will be appropriate for photothermal therapy. These results provide information for developments of functional nanomaterials for controlled drug release systems and photothermal therapy.

This research was supported by a Grant-in-Aid for Scientific Research (B) (Nos. 19300172 and 18310069) from the Japan Society for the Promotion of Science (JSPS) and PRESTO from the Japan Science and Technology Agency.

References and Notes

1 A. O. Govorov, H. H. Richardson, *Nanotoday* **2007**, *2*, 30.
2 A. Takami, H. Kurita, S. Koda, *J. Phys. Chem. B* **1999**, *103*, 1226.
3 S.-S. Chang, C.-W. Shih, C.-D. Chen, W.-C. Lai, C. R. C. Wang, *Langmuir* **1999**, *15*, 701.
4 Y. Niidome, A. Hori, T. Sato, S. Yamada, *Chem. Lett.* **2000**, 310.
5 J. Pérez-Juste, I. Pastoriza-Santos, L. M. Liz-Marzán, P. Mulvaney, *Coord. Chem. Rev.* **2005**, *249*, 1870.
6 S. Link, C. Burda, M. B. Mohamed, B. Nikoobakht, M. A. El-Sayed, *J. Phys. Chem. A* **1999**, *103*, 1165.
7 R. Weissleder, *Nat. Biotechnol.* **2001**, *19*, 316.
8 X. Huang, I. H. El-Sayed, W. Qian, M. A. El-Sayed, *J. Am. Chem. Soc.* **2006**, *128*, 2115.
9 H. Takahashi, T. Niidome, A. Nariai, Y. Niidome, S. Yamada, *Nanotechnology* **2006**, *17*, 4431.
10 H. Takahashi, T. Niidome, A. Nariai, Y. Niidome, S. Yamada, *Chem. Lett.* **2006**, *35*, 500.
11 T. Niidome, Y. Akiyama, M. Yamagata, T. Kawano, T. Mori, Y. Niidome, Y. Katayama, *J. Biomater. Sci.-Polym. Ed.*, in press.
12 H. Takahashi, Y. Niidome, S. Yamada, *Chem. Commun.* **2005**, 2247.
13 Y. Horiguchi, T. Niidome, S. Yamada, N. Nakashima, Y. Niidome, *Chem. Lett.* **2007**, *36*, 952.
14 Y. Horiguchi, S. Yamashita, T. Niidome, N. Nakashima, Y. Niidome, *Chem. Lett.* **2008**, *37*, 718.
15 A. Shiotani, T. Mori, T. Niidome, Y. Niidome, Y. Katayama, *Langmuir* **2007**, *23*, 4012.
16 T. Niidome, M. Yamagata, Y. Okamoto, Y. Akiyama, H. Takahashi, T. Kawano, Y. Katayama, Y. Niidome, *J. Control. Release* **2006**, *114*, 343.
17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
18 B. Skoong, *Vox Sang.* **1979**, *37*, 345.
19 C. S. Ah, H. S. Han, K. Kim, D.-J. Jang, *J. Phys. Chem. B* **2000**, *104*, 8153.
20 C. S. Ah, H. S. Han, K. Kim, D.-J. Jang, *Pure Appl. Chem.* **2000**, *72*, 91.

Published on the web (Advance View) January 31, 2009; doi:10.1246/cl.2009.226