Reduction and precipitation of aqueous europium (III) under an air atmosphere by near-infrared femtosecond laser pulses

Reduction and Precipitation of Aqueous Europium (III) under an Air Atmosphere by Near-Infrared Femtosecond Laser Pulses

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Abstract

To meet growing demands for the separation and recycling of rare-earth elements, photo-assisted reduction followed by precipitation is increasingly recognized as a viable non-contact approach. However, only limited light sources are currently available for these processes, because most research has focused on excitation of redox active charge-transfer bands of lanthanoid ions in the VUV and/or UV region. In this study, we carry out the reduction of Eu^{3+} to Eu^{2+} with hydrated electrons generated in water by near-infrared femtosecond laser pulses under an air atmosphere. The reduction yields are not linearly dependent on either the laser power or the concentration of 2-propanol acting as a hydroxyl radical scavenger. Addition of sulfate ions precipitates Eu^{2+} as an insoluble

$EuSO_4$ after a certain indication time. The absorption/extinction spectroscopy and transmittance measurements reveal the reduction of Eu^{3+} and growth of sulfates during the induction time. The success of precipitation by a valence change in water under an air atmosphere opens an avenue for the practical use of near-infrared light for the treatment of lanthanoid elements.

1. Introduction

Separation and recycling of rare metals are important issues for the establishment of a sustainable and green society [1]. Europium is one of the critical lanthanoids in modern technology, and its recovery from end-of-life components has been increasingly recognized as a secondary source [2]. There are several approaches to separate lanthanoids, including physical, chemical, electrochemical, and photochemical procedures [3-5]. In the case of europium, photoreduction followed by precipitation [6-10] or chromatography [11] has been proposed for the separation of europium ions from other lanthanoid ions. For the approach using precipitation, the separation of europium relies on the difference of solubility between the Eu^{2+} species and the corresponding Eu^{3+} species. For example, the solubility of $EuSO_4$ in water is three orders of magnitude lower than that of $Eu_2(SO_4)_3$ [9]. A variety of light irradiation setups have been examined. Conventionally, low-pressure and/or medium-pressure mercury lamps that show strong line emissions at 184.9 and 253.7 nm have been used to excite the charge-transfer band of Eu^{3+}. Although the reduction and precipitation using such light sources have been successful, there remain some problems to be resolved for the practical use of photochemistry for europium recovery. First, the photoreduction using VUV and/or UV light might be hindered, if contaminants in a reactant solution have strong absorption at

those wavelength regions. Second, not only long reaction time but also long induction time before the start of $EuSO_4$ precipitation —e.g., 5−30 hours depending on the irradiance—has been reported using mercury lamps [8]. Third, monochromatic light has rarely been utilized, and thus the quantum yields of reduction and precipitation, which are indispensable to compare the efficiency, have not been obtained. Nevertheless, much fundamental knowledge for the optimization of reactions has been accumulated using several hydroxyl radical scavengers [9, 12] and various solvents [6].

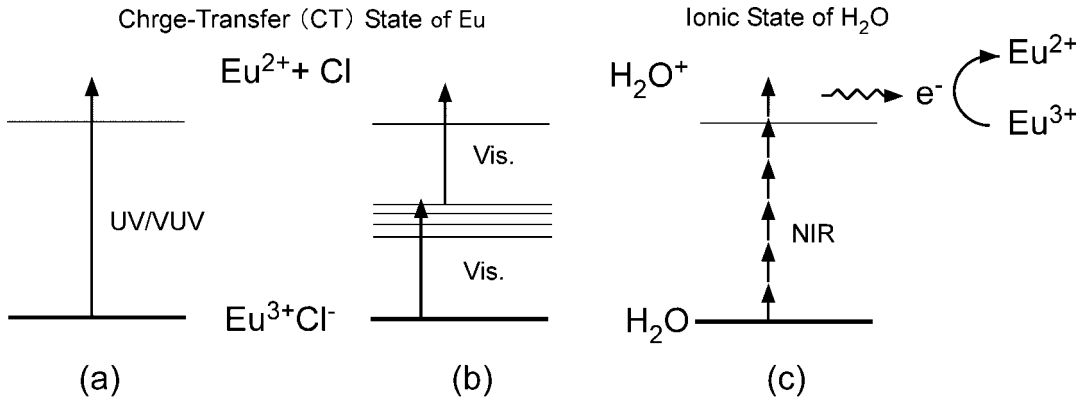

Fig. 1. Reduction of Eu^{3+} via a charge-transfer (CT) state by (a) a single photon excitation using an UV/VUV laser pulse and by (b) resonant two-photon excitation using visible laser pulses. (c) Reduction of Eu^{3+} by hydrated electrons ejected from the ionic state of water generated by nonresonant multiphoton ionization using near-infrared (NIR) laser pulses.

In contrast to conventional lamps, a pulsed laser, which is recognized as a monochromatic light with high-photon flux, is a promising light source, if the absorption wavelength of target elements and emission wavelength of the laser are overlapped. Three processes to change the valence of europium ions are shown in Fig. 1. We previously demonstrated the first approach, which is to reduce Eu^{3+} by exciting the charge-transfer (CT) band in degassed alcohol with nanosecond laser pulses of VUV or UV wavelength

(Fig. 1a) [13, 14]. The quantum yield of Eu^{3+} reduction by direct single-photon excitation to CT state using UV laser pulse (308 nm) was almost unity [13]. This procedure has been shown to be effective for not only lanthanoid ions but also noble metal ions dissolved in radioactive waste solution [15-18]. The second strategy for changing the valence of Eu^{3+} is resonant two-photon excitation to CT state via the f-f transition using visible laser pulses (Fig. 1b). We have found two photon reduction of Eu^{3+} to Eu^{2+} in nano- and picosecond pulse excitations [19, 20]. The reduction efficiencies of Eu^{3+} were largely improved from on the order of 10^{-5} to 1 by picosecond pulse excitation. The improvement would be largely reinterpreted by the simple reasons of pulse shortening. The laser intensity should have increased 1×10^4 times by the shortening pulses from 20 ns to 2 ps under the same focusing conditions. The third procedure is the reduction of lanthanoid ions with electrons ejected from solvent by nonresonant multiphoton ionization using focused near-infrared (NIR) femtosecond laser pulses (Fig. 1c) [21-23]. Lanthanoid ions were successfully reduced in degassed alcohol using this approach. Our experiences show that the one-electron reduction of Sm^{3+} in degassed alcohol is the case of the ion with the most negative reduction potential (−1.55 V vs. SHE) [22]. However, it should be mentioned that this procedure has not been applied under either an aerated condition or in water. We have reported that noble metal ions (Au^{3+}, Ag^{+}, Pd^{2+}) are easily reduced in aerated water followed by nanoparticle production [23-25]. In the cases of iron ions, the reduction of Fe^{3+} to Fe^{2+} (the reduction potential was 0.771 V vs. SHE) in water was dependent on the laser wavelength: via a two-photon absorption process (0.8 μm) or by solvated electrons (1.2 μm) [24]. For the practical use of the third procedure for the recovery of lanthanoid, it is necessary to carry out the reduction and precipitation of lanthanoid ion in water under an aerated condition.

In this study, we succeed in reducing Eu^{3+} to Eu^{2+} by hydrated electrons generated by nonresonant multiphoton ionization of water under an air atmosphere using NIR femtosecond laser pulses. The addition of 2-propanol (2-PrOH), a hydroxyl radical scavenger, is the key to performing the reduction of Eu^{3+} in water. Absorption/extinction spectroscopy and transmittance measurements reveal the time evolution of the reduction of Eu^{3+} and precipitation of Eu^{2+} as sulfate.

2. Materials and methods

$EuCl_3$•$6H_2O$ (Aldrich, 99.99%), $EuCl_2$ (Aldrich, 99.99%), and $(NH_4)_2SO_4$ (Nacalai, ≥99.5%) were used without further purification. 2-Propanol (2-PrOH, Nacalai, spectral grade, ≧99.7%) and distilled water (Nacalai) were used as received.

Femtosecond laser pulses (0.8 μm, 40 fs, <0.4 mJ, 1 kHz) were delivered from a Ti:Sapphire laser (Alpha 100/1000/XS hybrid; Thales Laser). Details of the laser experiments have been described elsewhere [25]. The laser beam was focused on the central part of a quartz cuvette (10×10×40 mm^3) by using a planoconvex quartz lens with a focal length of 50 mm. The solution (1 or 3 cm^3) was stirred by a Teflon-coated stir bar during the laser irradiation with a stirring speed of 3.0×10^2 rpm measured by a hand tachometer (HT-4200; Ono Sokki). Absorption spectroscopy was carried out 30 s after the laser irradiation experiment to avoid the interference by bubbles formed in solution with a JASCO V-750iRM or V-750ST spectrophotometer. We placed slits (height 1 mm, width 9 mm) both the reference and sample optical paths of the spectrophotometer to observe only the central part of the cuvette filled with 1 cm^3 solution. Molar absorption coefficient of Eu^{2+} in water was determined in degassed aqueous $EuCl_2$ solution, which was prepared by dissolving $EuCl_2$ in degassed water in a vacuum line.

The time evolution of the transmittance was measured by using a diode laser (635 nm) and a calibrated Si pin-photodiode. A pinhole (600 μm in diameter) was placed in both the front and back of the cuvette. The output signal from a Si pin-photo diode was collected by using a data logger (Graphtec, GL820). To avoid any disturbance caused by bubbles, the transmittance measurements of the solution (3 cm^3) were carried out 30 s after the stirring was stopped. For the preparation of specimens for emission spectroscopy, the solution was centrifuged repeatedly (1.00×10^4 rpm, 10 min). After removing the water, the residuals were sonicated in distilled water followed by centrifugation. This procedure was repeated three times. The precipitates were then separated from water by centrifugation followed by drying in a vacuum. The corrected emission spectrum of the precipitates excited at 290 nm was measured by a Hitachi F-7000 spectrofluorometer.

3. Results

3.1. Reduction of europium ions by femtosecond laser pulses

Figure 2a shows the absorption spectral changes of $EuCl_3$ aqueous solution upon laser irradiation. Before laser irradiation, the trailing edge of the charge-transfer (CT) band (Eu^{3+} and water) peaking in the VUV region was observed [26]. Two peaks centered at 248 and 320 nm appeared after the laser irradiation. These characteristic peaks were assigned to be the transition of $4f^7\rightarrow4f^65d^1$ of Eu^{2+} [27]. The time evolution of the absorbance of Eu^{2+} at 320 nm is shown in Fig. 2b. It is noted that the absorbance was not changed on the time scale of absorption spectrum measurements (3 min). The production of Eu^{2+} seems to be linearly proportional to the laser irradiation time up to 4 min and then saturated by both the 200 and 400 mW laser pulses. The linear increase of Eu^{2+} is understood that the production of reductant, i.e., hydrated electrons is linearly

dependent of the laser irradiation time since the amount of water, solvent, is sufficient. However, equilibrium between Eu^{3+} and Eu^{2+} causes the saturation of Eu^{2+} production because the reaction volume is small (1 cm^3). In order to estimate the reduction yield, we determined the molar absorption coefficient of $EuCl_2$ in water. To investigate the molar absorption coefficient of Eu^{2+} in water, the absorption spectrum of the $EuCl_2$ in degassed methanol was measured successively after the measurement of that in degassed water. The amount of $EuCl_2$ and the volume of solution are same between the two runs. We assume that the molar absorption coefficient of $EuCl_2$ in methanol is the same as the reported molar absorption coefficient of $EuBr_2$ in methanol (556 $dm^3\ mol^{-1}\ cm^{-1}$ at 330 nm) [28]. The evaluated molar absorption coefficient of $EuCl_2$ in degassed water (5.7×10^2 $dm^3\ mol^{-1}\ cm^{-1}$ at 320 nm) was comparable to that measured for $EuCl_2$ in acidic water (5.0×10^2 $dm^3\ mol^{-1}\ cm^{-1}$ at 320 nm, pH = 1) [29]. For the 10-min laser irradiation with maximum laser power (400 mW) used in this study, the conversion yields of Eu^{2+} was calculated to be 38% as shown in Fig. 2b.

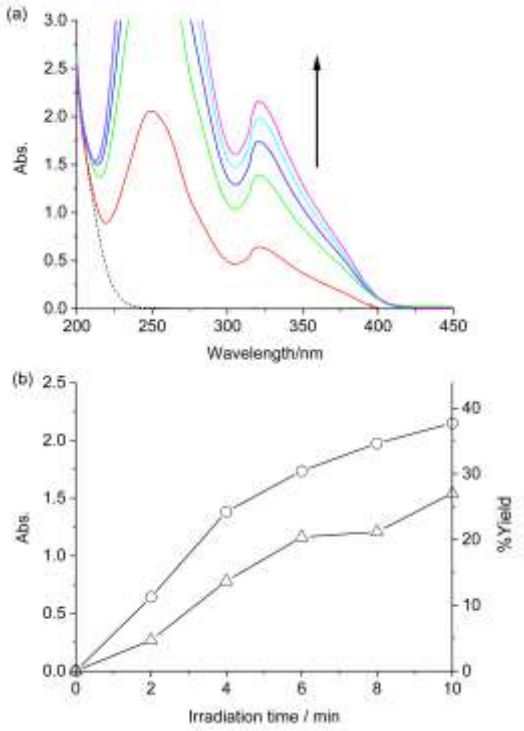

Fig. 2. (a) Absorption spectra of $EuCl_3$ (10 mM, 1 cm^3) aqueous solution before (dotted line) and after (solid lines) the laser irradiation in the presence of 1.0 M 2-PrOH. The laser power was 400 mW. Laser irradiation times from top to bottom were 10, 8, 6, 4, and 2 min, respectively. (b) Time evolution of the absorbance of Eu^{2+} at 320 nm upon laser irradiation in the presence of 1.0 M 2-PrOH. The laser power was 200 (triangles) or 400 mW (circles).

Figure 3 shows the correlation between the absorbance of Eu^{2+} and the initial concentration of 2-PrOH under the fixed laser irradiation condition (400 mW, 4 min). In order to compare the production yields, the data obtained for the 4-min laser irradiation were used to avoid the saturation effect observed in Fig. 2b. The reduction of Eu^{3+} did not occur in the absence of 2-PrOH. The production of Eu^{2+} steeply increased as the concentration of 2-PrOH increased. The absorbance became maximal at around 0.2 M of 2-PrOH, and then slightly decreased as the initial concentration of 2-PrOH increased.

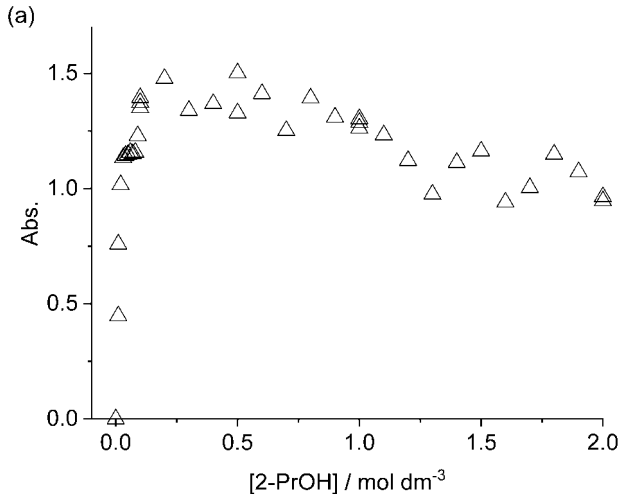

Fig. 3. The correlation between the absorbance of Eu^{2+} (320 nm) after the exposure of $EuCl_3$ aqueous solution (10 mM, 1 cm^3) to laser pulses for 4 min and the initial concentration of 2-PrOH. The laser power was 400 mW. Batch-type experiments were performed.

We then examined the effect of laser power on the yields of the production of Eu^{2+} in the presence of 0.2 M 2-PrOH (Fig. 4a). There was a threshold of Eu^{2+} formation, and then the yield of Eu^{2+} was steeply increased and saturated as the laser power increased. As seen in the log-log form of Fig. 4a, the production of Eu^{2+} was considered to be proportional to the cubic of the laser power (Fig. 4b). For the determination of the effect of laser power on the production rate of Eu^{2+}, $EuCl_3$ aqueous solutions (3 cm^3) were used to avoid the saturation effect as observed in Fig. 2b. Figure 5a shows the least-squares fit of the time evolution of the absorbance of Eu^{2+} at various laser powers. There was a threshold of the production rate of Eu^{2+}, and the production rates were linearly proportional to the laser power (Fig. 5b).

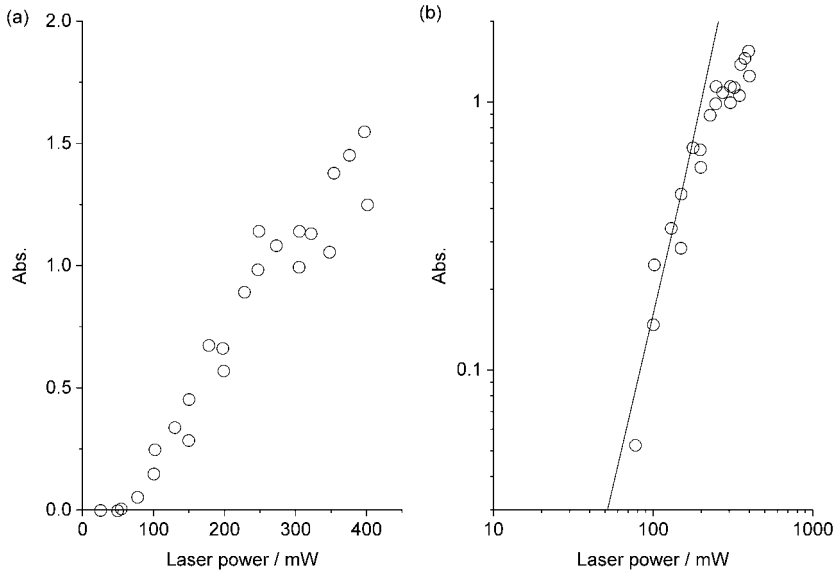

Fig. 4. Laser-intensity dependencies presented in (a) linear-linear and (b) log-log scale for the absorbance of Eu^{2+} at 320 nm. An aqueous $EuCl_3$ solution (10 mM, 1 cm^3) in the presence of 2-PrOH (0.2 M) was exposed to femtosecond laser pulses for 4 min. Batch-type experiments were performed. The line in (b) having slope 3.0 is shown to guide the eyes.

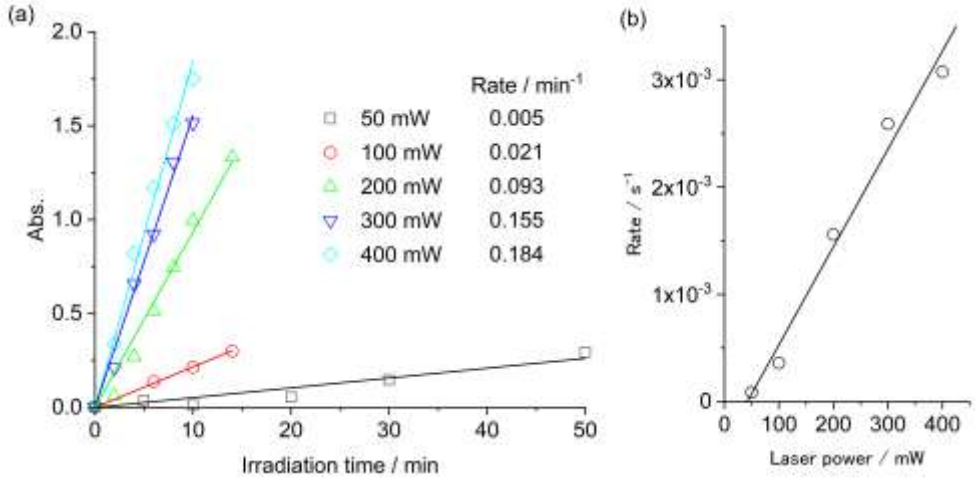

Fig. 5. (a) Time evolution of the absorbance of an aqueous $EuCl_3$ (10 mM, 3 cm^3) solution at 320 nm upon laser irradiation in the presence of 2-PrOH (0.2 M). The straight lines are least-squares fits to obtain the rates of Eu^{2+} formation. (b) The rate of Eu^{2+} formation as a function of laser power. The line in (b) is shown to guide the eyes.

3.2. Precipitation of europium ions in the presence of SO_4^{2-}

Since divalent europium was sufficiently formed in the presence of 2-PrOH, we examined the precipitation of Eu^{2+} as sulfate. Figure 6a shows the appearance of the cuvette of $EuCl_3$ aqueous solution in the presence of 2-PrOH (0.2 M) and $(NH_4)_2SO_4$ (0.2 M). Before the laser irradiation, the peak of CT band between Eu^{3+} and SO_4^{2-} was clearly observed at 235 nm (Fig. 6b). Upon laser irradiation, violet-colored light emitted like a filament was clearly visible (Fig. 6a, 2 min). Such filaments result from the balance between self-focusing by a nonlinear refractive index of water and defocusing by plasma [30]. At the same time, a strong white-light emission was observed coaxially behind the filament. As the irradiation time increased, many bubbles illuminated by white light could be clearly observed (Fig. 6a, 4 min). In addition, the solution seemed to be white due to strong light scattering with 400 mW laser power irradiation. It can also be observed that the white-light spread at a high angle after the filament. At 6- and 8-min laser irradiation, the solution became homogeneous and the angle of the spread of white-light seemed to be larger under a high laser power condition. After the laser irradiation, the absorption spectrum showed the scattering component in the whole visible region due to the formation of precipitates (Fig. 6b). We thus collected the precipitates for the emission measurements. The peak wavelength of the emission of dried precipitates was 380 nm, which was within the range of the emission peak of the other divalent europium compounds (EuS, 350 nm [31]; EuO, 357 nm [32]; EuSe, 403 nm [33]; $EuCl_2$, 404 nm [34]).

Figure 6b shows the absorption spectral changes during the laser irradiation with the power of 200 mW. After 4 min laser irradiation, the characteristic absorption of Eu^{2+} was observed, while the scattering component was negligible. Based on the

absorbance, the production of Eu^{2+} was not significantly affected by the presence of sulfate ions. As clearly shown in Fig. 6c, we cannot identify the presence of $EuSO_4$ by absorption spectroscopy because the absorption spectrum taken after 4-min laser irradiation in the presence of sulfate ions (green) was identical to that reconstructed with those of Eu^{3+} taken before laser irradiation (red) and of Eu^{2+} aqueous solution without sulfate ions (blue, Fig. 2a). We concluded that the reduction of Eu^{3+} definitely occurred, but the concentration of Eu^{2+} was not sufficient to form precipitates. However, it is emphasized that the characteristic absorption and/or extinction spectrum was observed after 6-min laser irradiation. The peak of Eu^{2+} was slightly increased, while a very broad peak centered at around 450 nm clearly appeared. The appearance of a characteristic broad peak in visible region and its red-shift in the extinction spectrum were reported for submicrometer spheres of TiO_2 [35]. If we refer to the linear relationship that the peak wavelength was 1.5 times larger than the size of the sphere, the size of spheres appeared after 6-min laser irradiation is estimated to be 300 nm. Additional 2-min laser irradiation resulted in the appearance of baseline components attributed to light scattering in the whole visible region. However, we could still recognize a hump centered at around 650 nm, which corresponds to the sphere size of 430 nm. It is mentioned that the contribution of Eu^{2+} at 8-min laser irradiation became smaller than those observed after 6-min laser irradiation. Therefore, the decrease in the Eu^{2+} peak is attributed to the formation of precipitates. Unfortunately, we could not determine the actual concentrations of Eu^{2+} and Eu^{3+} by absorption spectroscopy when precipita~~ta~~tion starts, because complicated peak analyses including scattering components are required for this determination. Further laser irradiation did not increase the absorption

(extinction) of the solution, indicating that the reaction reached equilibrium or became inefficient due to light scattering.

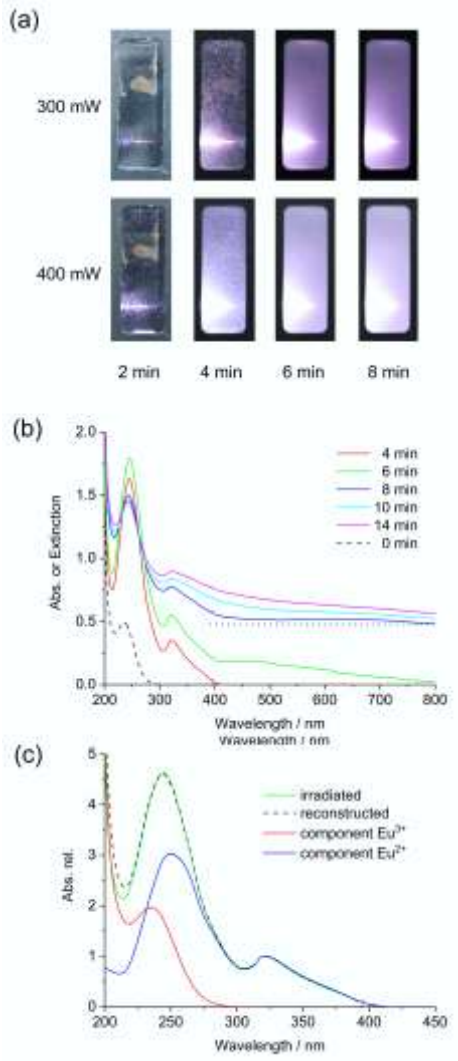

Fig. 6. (a) The appearance of the cuvette after the 2, 4, 6, and 8-min laser irradiation to $EuCl_3$ aqueous solution (10 mM, 3 cm^3) in the presence of 2-PrOH (0.2 M) and $(NH_4)_2SO_4$ (0.2 M). The laser power was 300 (upper panels) or 400 mW (lower panels). The solution was stirred during the laser irradiation. The brightness of the pictures taken after the 2-min laser irradiation was increased for better visibility. (b) Absorption spectra before (dashed line) and after the 4, 6, 8, 10, and 14-min laser irradiation (solid lines). The laser power was 200 mW. The dotted horizontal line is shown to indicate a baseline for the spectrum taken after 8-min laser irradiation. (c) Absorption spectra of $EuCl_3$ aqueous solution in the presence of 2-PrOH (0.2 M) and $(NH_4)_2SO_4$ (0.2 M). The absorption spectrum of $EuCl_3$ aqueous solution after 4-min laser irradiation (200 mW,

green) reproduced by that of Eu^{3+} taken before laser irradiation (red) and that of Eu^{2+} taken in the absence of $(NH_4)_2SO_4$ (blue). The reconstructed spectrum is shown as a dashed line.

Since the time to formation of white precipitates was dependent on the laser power, as observed in Fig. 6a, the time evolutions of the transmittance of the solution irradiated at various laser powers were measured. Figure 7 clearly shows that the transmittance was suddenly dropped after a certain induction time. Moreover, the induction time was shortened by increasing the laser power. After the sudden drop, the transmittance appeared to remain constant at 50 mW laser power, whereas the transmittance gradually decreased with a long decay rate under a high laser power condition (>100 mW). The gradually decreased component of transmittance might have been mainly related to the decrease of the reduction efficiency due to the light-scattering. Herein, we compared the laser power and induction time. The induction time is defined as the time during which no reaction occur and the transmittance is kept to 100% in this experiment. In addition, residual transmittance, which is defined as the transmittance at twice the induction time, was also compared. Induction times and residual transmittances are listed in Table 1. In order to investigate the correlation between the induction time and the laser power, we used the reciprocal of induction time as a pseudo-rate. The reciprocal of induction time was linearly proportional to laser power as shown in Fig. 7b. As for the residual transmittance, interpretation was difficult because the transmittance is determined by various factors such as the size of precipitate. Nonetheless, the residual transmittance was decreased as the laser power increased.

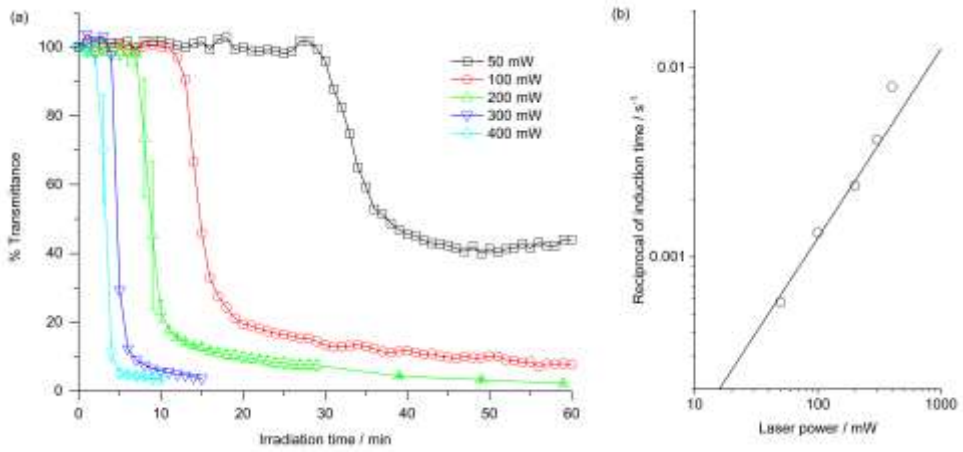

Fig. 7. (a) Time evolution of the transmittance of aqueous $EuCl_3$ (10 mM, 3 cm^3) solution at 635 nm upon laser irradiation in the presence of 2-PrOH (0.20 M) and $(NH_4)_2SO_4$ (0.20 M). The laser power was 50 (squares), 100 (circles), 200 (triangles), 300 (inverted triangles), and 400 mW (diamonds), respectively. The vertical bars give the standard deviation obtained for three different samples. (b) The correlation between the reciprocal of induction time and laser power. The line in (b) having slope 1.0 is shown to guide the eyes.

Table 1 Induction time and residual transmittance

Laser power / mW[a]	Induction time / min	%Residual transmittance
50	28.9	42.2
100	12.4	16.6
200	7.0	13.6
300	4.0	8.3
400	2.1	8.4

[a] Standard deviation of the laser power was about ±1.5%.

4. Discussion

We have achieved near-infrared femtosecond laser-induced reduction of lanthanoid ions (Eu^{3+}, Sm^{3+}, Yb^{3+}) in degassed alcohol [21-23]. In degassed alcohol, solvated electrons

would be a dominant reductant formed by nonresonant multiphoton ionization using femtosecond laser pulses. In contrast to the experiments in alcohol, many active species are formed in water. The primary reactions (1) to (5) in water are expected to be similar regardless of the excitation/ionization methods, which include radiolysis, discharges, or photolysis [36]. The reactive intermediates formed in the primary reactions are hydrated electron (e^-_{aq}), hydrogen radical (H•), and hydroxyl radical (HO•). The former two would act as reductants and HO• should be an oxidant. Therefore, the competition between reduction and oxidation determines the total reaction efficiency. For example, carbon nanoparticles are formed by the oxidation of benzene with hydroxyl radicals [37, 38], whereas reduction by solvated electrons is a dominant primary reaction to form carbon nanoparticles in the case of halogenated molecules [39, 40]. For the reduction of Eu^{3+}, hydrated electrons rather than hydrogen radicals play a dominant role, since the excitation (2) that is the origin of hydrogen radical (5) is dominated by the ionization (1). In contrast to the case of degassed alcohol, in which recombination would be a major deactivation path of solvated electron, hydrated electrons are dominantly quenched by oxygen in aerated water (6). However, the lifetime of hydrated electrons was reported to be 0.3 μs under an aerated condition [36]. The reduction of Eu^{3+} by a hydrated electron is an exergonic reaction (7) based on the reduction potentials of Eu^{3+} (−0.35 V vs. SHE) [41] and hydrated electron (−2.87 V vs. SHE) [42]. We can expect that the reduction of Eu^{3+} (10 mM) by a hydrated electron (7) rather than by hydrogen radicals (8) occurs at a diffusion-controlled rate (6.1×10^{10} mol^{-1} dm^3 s^{-1}) [43, 44]. However, the re-oxidation of Eu^{2+} by oxygen (10) occurs, since the reduction potential of oxygen is −0.18 V vs. SHE (in water) [45]. This re-oxidation might be a serious issue, because the solution is saturated by oxygen evolved in water exposed to femtosecond laser pulses [46]. A more

serious problem is the generation of hydroxyl radical, which is a strong oxidant formed in water and which reacts with Eu^{2+} (11). In addition, the multiphoton excitation of Eu^{2+} will reproduce Eu^{3+} (12), as observed in alcohol [21]. The re-oxidation processes (10) and (12) cannot be avoided. In contrast, the addition of a hydroxyl radical scavenger (13), 2-PrOH, was very effective to produce Eu^{2+}, as clearly shown in Fig. 3. The production of Eu^{2+} was maximized when the concentration of 2-PrOH was about 20 times larger than that of $EuCl_3$, but the efficiency was gradually decreased as the concentration of 2-PrOH was increased. Therefore, it was suggested that 2-PrOH radical might not act as an important reductant of Eu^{3+} (9) under our experimental condition.

$H_2O \rightarrow H_2O^{+\bullet} + e^-$ (1)

$H_2O \rightarrow H_2O^*$ (2)

$e^- + H_2O \rightarrow e^-_{aq}$ (3)

$H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + HO^\bullet$ (4)

$H_2O^* \rightarrow HO^\bullet + H^\bullet$ (5)

$e^-_{aq} + O_2 \rightarrow O_2^{-\bullet}$ (6)

$Eu^{3+} + e^-_{aq} \rightarrow Eu^{2+}$ (7)

$Eu^{3+} + H^\bullet \rightarrow Eu^{2+} + H$ (8)

$Eu^{3+} + (CH_3)_2C^\bullet OH + \rightarrow (CH_3)_2CO + Eu^{2+} + H^+$ (9)

$Eu^{2+} + O_2 \rightarrow Eu^{3+} + O_2^{-\bullet}$ (10)

$Eu^{2+} + HO^\bullet \rightarrow Eu^{3+} + HO^-$ (11)

$Eu^{2+}(H_2O) + n\,h\nu \rightarrow Eu^{3+} + OH^- + 1/2\ H_2$ (12)

$(CH_3)_2CHOH + HO^\bullet \rightarrow (CH_3)_2C^\bullet OH + H_2O$ (13)

$Eu^{2+} + SO_4^{2-} \rightarrow EuSO_4$ (14)

$n\ EuSO_4 \rightarrow (EuSO_4)_n$ (15)

The presence of induction time before precipitation starts was reported in the cases of UV lamp excitation experiments; however, the information about the valence of Eu during induction time was not obtained [8]. In this study, we showed that Eu^{2+} was clearly observed during the induction time even in the presence of sulfate ions (Fig. 6b). Moreover, the absorption spectrum of Eu^{2+} in the presence of sulfate ions was identical to that without sulfate ions (Fig. 6c). Since the concentrations of Eu^{2+} and SO_4^{2-} are sufficient to form $EuSO_4$, we expect that reaction (14) occurs at the beginning of the laser irradiation and speculate that the absorption spectrum of Eu^{2+} coordinated by sulfate ions is not strongly affected by the coordination of sulfate ions or identical to that of $[Eu(H_2O)_7]^{2+}$ [47]. Consequently, the linear relationship between the reciprocal of induction time and laser power suggests that agglomeration process (15) is rate-determining step of precipitation. Agglomerates of several hundreds of nanometers were identified by their resonant scattering wavelength just before the precipitation starts (at 6 min in Fig. 6b). Thus, Eu^{2+} would coexist as an ion and as agglomerated $EuSO_4$ of few to tens of nanometers in size at the early stage of induction time. The former is detected by its characteristic absorption peak at 320 nm, but the latter is invisible in the ultraviolet and visible wavelength region. In order to investigate what actually occurs during the induction time, in situ dynamic light scattering and X-ray absorption near edge structure measurements would be helpful [48].

5. Conclusion

This work reveals that the reactive species generated in water by femtosecond laser pulses can reduce europium ions even under an aerated condition. The absence of oxygen is not the critical factor, but hydroxyl radical scavengers are indispensable to achieve the reduction of europium ions. We performed the precipitation of europium sulfate in this study, but some lingering issues will need to be resolved to achieve the collection of lanthanoid ions from water. First, in our experiments the efficiency of reduction was saturated, probably due to the back reaction induced by multiphoton excitation of Eu^{2+}. A possible solution to this problem would be to use the laser pulse of the wavelength longer than 0.8 μm. Second, the efficiency of precipitation was decreased as observed by the transmittance measurements. This is a fundamental problem of batch-type experiments, and thus a flow-system or removal of precipitates by filtering and/or centrifugation is required to improve the precipitation procedure. Third, the induction time of the precipitation was shortened by femtosecond laser pulses, but is still a few minutes. We revealed that the reciprocal of the induction time is linearly proportional to the laser power. Therefore, one way to shorten the induction time would be to increase the laser power, but a more effective approach would be to use high-repetition laser pulses. We could use a high-repetition (>1 MHz) picosecond laser, which is a compact, reasonable, and industrially robust device. The use of such a laser would diminish the induction time of precipitation. The combination of a high-repetition laser and a flow system would be a key approach for the recycling metal ions.

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