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Fabrication of oxidation-resistant Ge colloidal nanoparticles by pulsed-laser ablation in aqueous HCl

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Abstract:	Spherical Ge nanoparticles with diameters of 20-80 nm were fabricated by laser ablation of a Ge single crystal in water and in aqueous HCl using subpicosecond laser pulses (1040 nm, 700 fs, 100 kHz, and a pulse energy of 10 μJ). We found that the as-synthesized nanoparticles suffered rapid oxidization followed by dissolution when laser ablation was conducted in pure water. In contrast, oxidation of Ge nanoparticles produced in dilute HCl and stored intact was minimal, and colloidal dispersions of the Ge nanoparticles remained stable up to 7 days. It was elucidated that dangling bonds on the surfaces of the Ge nanoparticles were terminated by Cl, which inhibited oxidation, and that such hydrophilic surfaces might improve the dispersibility of nanoparticles in aqueous solvent.
Response to Reviewers:	see attachment

Response to Reviewer's Comments

Manuscript ID: APYA-D-16-02399 by Hamanaka et al.

Reviewer #1:

This work describes the preparation of stable Ge nanoparticles by using laser ablation method in the presence of HCl. The results are interesting, and the method is unique. I think it can be published after minor revision.

1) I noticed that the stability of the colloidal systems is tightly dependent on the concentration of HCl. I suggest the authors to discuss the phenomenon deeply using some theories, such as DLVO and electrical double layer theories.

Author reply: Firstly, please allow me to express our sincere gratitude for your careful review and rigorous comments on behalf of our group. We noticed that the stability of Ge colloidal nanoparticles is depending on the HCl concentration. Higher concentrations of HCl destabilized the colloidal suspensions and induced agglomeration of Ge nanoparticles which produced precipitates. The reason why Ge NPs agglomerated at high HCl concentrations is discussed in the revised manuscript within the framework of the DLVO theory. We consider that agglomeration of Ge nanoparticles at high HCl concentrations can be explained by high acidity of the solution. According to the DLVO theory, the rate of aggregation of nanoparticles is determined by a balance between the van der Waals attraction and the electrostatic repulsion (double-layer repulsion). Higher repulsion potential prevents the agglomeration and stabilizes the colloidal systems. The repulsion potential can be enhanced by higher surface potential, and the surface potential depends on hydrogen ion concentrations in the aqueous solution, which is evaluated using a pH value (potential of hydrogen). The surface potential of NPs increases with change in the pH value of the solution from that on the isoelectric point. In this study, the pH values are varied by changing the HCl concentrations. We presume that excess hydrogen ions reduced the surface potential of Ge nanoparticles and repulsion potential was weakened, which resulted in agglomeration of Ge nanoparticles at high HCl concentrations. These discussions are added to the section of "Results and discussions" of the revised manuscript.

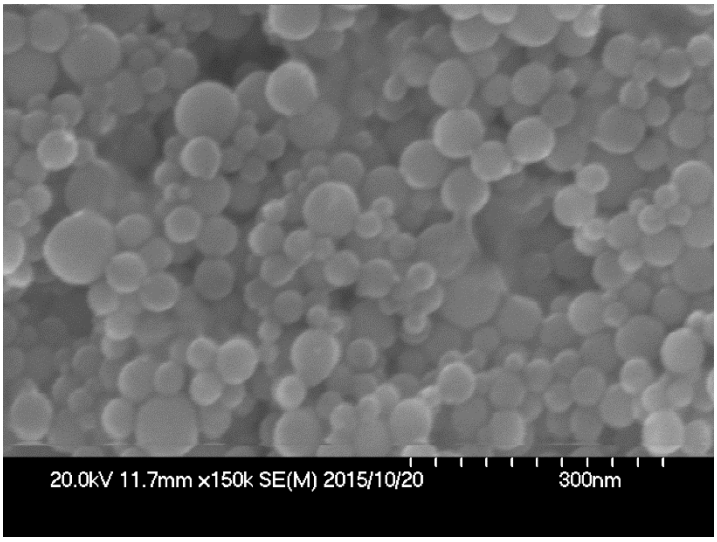
2) Can HCl be replaced by the salts, for example, NaCl?

Author reply: We appreciate a useful suggestion by the referee and would like to investigate the effect of NaCl for future research, because mechanisms of Cl-termination by laser ablation in aqueous HCl should be elucidated to answer this question. Now we cannot answer whether fabrication of Cl-terminated Ge nanoparticles by laser ablation in NaCl aqueous solutions is possible. But, even if Cl-terminated Ge nanoparticles can be obtained in NaCl solution, we expect that there is great differences in stabilities of colloids between NaCl and HCl solutions. One of the reasons is differences in pH values of these solutions. As mentioned above, based on the DLVO theory, to maintain stable colloidal dispersions, increasing the repulsion potential between particles and preventing agglomeration are needed. To do that, (1) high surface potential and (2) low counter ion concentrations are effective. Changing the pH value of the solution from that on the isoelectric point can shift the surface potential. Hence, pH adjustment is very important for obtaining stable colloidal dispersions. The pH value of NaCl

solutions is constant, 7, and independent of NaCl concentration. However, pH value of aqueous HCl is less than 7 and strongly depends on HCl concentrations (in this study, pH = 2.5~3.9 for 0.01~0.0005 % HCl). On the other hand, high concentrations of the salts usually reduce the repulsion potential, and thus, agglomeration of particles easily occurs in high concentrations of NaCl.

3) I noticed that the size of Ge nanoparticles reaches to 80 nm. The particles with such a large size should be a polyhedron other than a sphere. It is better to supply high-magnification TEM or SEM images.

Author reply: Nanoparticles have diameters of 20~80 nm and the largest one reaches ~100 nm. We have examined high-magnification SEM images of these Ge nanoparticles to confirm whether large nanoparticles have polyhedral shapes as the referee pointed out. However, we could not find a clear evidence of a polyhedral nanoparticles even in the high-magnification images (the example of the images is shown below), while the deviation from a perfect sphere was observed. As far as we know, reports of polyhedral shaped nanoparticles fabricated by laser ablation in liquids are rare, especially with 100 nm or larger particles. According to the previous research, such comparatively large nanoparticles with a spherical shape are formed by transformation from smaller nanoparticles (10 nm or less) through melting and coalescence induced by repeated laser pulses (H. Wang et al., Angew. Chem. Int. Ed. 49, 6361 (2010).)). Thus, non-polyhedral shapes of our Ge nanoparticles with diameters of ~80 nm can be understandable in the same way.



Response to Reviewer's Comments

Manuscript ID: APYA-D-16-02399 by Hamanaka et al.

Reviewer: #2

This manuscript provided a new method for preparation of stable Ge NPs in aqueous solution by laser ablation. It was found that Ge NPs synthesized in HCl solution are more stable than those in pure water, and an optimal HCl concentration was obtained. The manuscript was also well organized and written. I recommend the publication of this manuscript on Applied Physics A after revised based on the following comments.

1. The author claimed that the formation of Ge-Cl bonds on the surface can stabilize Ge NPs. Why do Ge NPs agglomerate at high HCl concentrations?

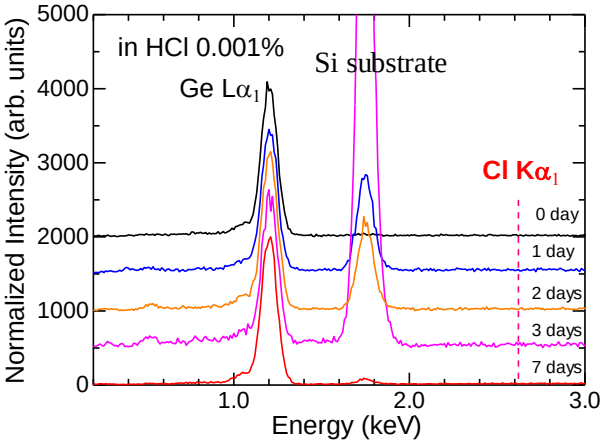
Author reply: First of all, please allow me to express our sincere gratitude for your careful review and rigorous comments on behalf of our group. We consider that agglomeration of Ge NPs at high HCl concentrations is due to high acidity of the solution. Stability of colloidal dispersions has been successfully explained by the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory. Based on this theory, the rate of aggregation of NPs is determined by a balance between the van der Waals attraction and the electrostatic repulsion. The repulsion potential is enhanced when surface potential increases, which can effectively prevent agglomeration of NPs. The surface potential of NPs is dependent on concentrations of hydrogen ions in aqueous solutions, which is evaluated using a pH (potential of hydrogen) value. Changing the pH value of the solution from that on the isoelectric point shifts the surface potential of NPs. In this study, HCl concentrations were changed between 0.01~0.0005 %, which results in variation of pH values. Therefore, we hypothetically conclude that excess hydrogen ions reduce both the surface potential of NPs and repulsion potential, which results in agglomeration, while the pH value on the isoelectric point cannot be known for our Ge NPs. Such considerations are added to the section of "Results and discussions" in the revised manuscript.

2. Why were there no Ge-Cl bonds signals observed at the first couple days after Ge NPs were synthesized in HCl solution?

Author reply: We examined minutely the Raman spectra of Ge nanoparticles measured at 0 and 1 day after the synthesis. We can observe that weak spectral features maybe due to Ge-Cl bonds appear around 150 and 450 cm^{-1} in the Raman spectra displayed with an enlarged scale (revised version of Fig. 6). Ge-Cl signals are very weak compared to Ge signals at 0 and 1 day, but their relative intensities increase significantly after 7 days. This result suggests that most of the as-synthesized Ge nanoparticles were not Cl-terminated and termination of the surface Ge bonds by Cl proceeds for 7 days. The other possible mechanism is as follows. Both the Cl-terminated and non-terminated Ge nanoparticles are formed in the as-synthesized dispersion and content ratios of Cl-terminated Ge nanoparticles increases with time because non-terminated nanoparticles are rapidly agglomerated or decomposed. These considerations are added to the section of "Results and discussions" in the revised manuscript.

3. Why was no Cl peak found in EDX spectra for Ge NPs prepared in HCl solution?

Author reply: As the referee pointed out, no EDX signal of Cl was detected for Ge nanoparticles in which Ge-Cl bonds were detected by Raman spectroscopy (please refer the following figure). We suppose that no detectable EDX signal of Cl was due to too small Cl contents in the sample. One Ge nanoparticle with a diameter of 40 nm (average value) contains about 1500000 Ge atoms. However, the total number of surface atoms in the same nanoparticle is roughly estimated to be 1/100 of that. This estimation suggests that the ratio of the number of Cl atoms to the total Ge atoms included in the sample is ~1/100 even if all of the Ge atoms on the surface are terminated by one Cl atom. Therefore, the EDX signal of Cl may be very weak compared to that of Ge (below the noise level), and thus, could not be detected.



List of Corrections for Manuscript ID: APYA-D-16-02399 by Y. Hamanaka et al. (resubmitted to *Applied Physics A*)

1. page 7, second paragraph, Results and discussions: A new paragraph was inserted into page 7 to interpret the relation between the stability of Ge colloids and HCl concentrations.
2. last line of page 10 – line 7 of page 11, Results and discussions: The sentences about the temporal growth of the Raman bands of Ge-Cl bonds are added.
3. page 14, References: A new reference [24] was added. The reference [24]–[30] in the original version were changed to [25]–[31].
4. Figure: Resolution of the insets in Figure 3 were improved.
5. Figure: Figure 6 was updated and a sentence was added to its caption (page 15).

Fabrication of oxidation-resistant Ge colloidal nanoparticles by pulsed laser ablation in aqueous HCl

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Abstract

Spherical Ge nanoparticles with diameters of 20–80 nm were fabricated by laser ablation of a Ge single crystal in water and in aqueous HCl using subpicosecond laser pulses (1040 nm, 700 fs, 100 kHz, and a pulse energy of 10 μJ). We found that the as-synthesized nanoparticles suffered rapid oxidization followed by dissolution when laser ablation was conducted in pure water. In contrast, oxidation of Ge nanoparticles produced in dilute HCl and stored intact was minimal, and colloidal dispersions of the Ge nanoparticles remained stable up to 7 days. It was elucidated that dangling bonds on the surfaces of the Ge nanoparticles were terminated by Cl, which inhibited oxidation, and that such hydrophilic surfaces might improve the dispersibility of nanoparticles in aqueous solvent.

Keywords: laser ablation in liquid, nanoparticle, surface passivation, colloidal dispersion, group IV semiconductor

1 Introduction

In recent years, pulsed laser ablation in liquids has attracted attention as a method to produce nanoparticles from a wide variety of bulk materials and their colloidal solutions [1, 2]. As compared to other methods such as chemical synthesis and vapor-phase synthesis, nanoparticle processing can be executed easily by laser ablation in liquids, which saves time because no special environment such as vacuum, heat, or chemical reagents is needed. In addition to these characteristics, laser ablation in liquids has an advantage in that the resulting nanoparticles are rarely contaminated because only the target materials and solvents are used in the apparatus [3]. Nanoparticles obtained by laser ablation in pure liquids initially have a bare surface. However, bare nanoparticles usually form instable colloidal solutions because they easily aggregate and immediately precipitate [4, 5]. To improve the dispersibility of nanoparticles in solvents and provide stable nanoparticle colloids, various surfactant molecules are used to coat the nanoparticles, e. g. sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB); these are often added to the solvents before ablation is started [3, 4]. Surfactants can be used to control nanoparticle size by terminating nanoparticle growth [4]. Surface functionalization is also important in terms of bio-application of nanoparticles because it confers chemical and *in vivo* biocompatibilities [2].

Semiconductor nanoparticles have attracted increasing attention over the past 30 years because of their excellent properties for photonics applications such as LEDs, photovoltaic devices, fluorescent biomarkers, and photocatalysts [6]. In addition to liquid-phase chemical synthesis and vapor-phase synthesis, nanoparticles of compound semiconductors, as well as those of elemental semiconductors, have been synthesized by laser ablation in liquids [5, 7–12]. Among the various kinds of semiconductors used, Ge has a comparatively large exciton Bohr radius that increases the

quantum confinement effect, even for large nanoparticles [13]. These characteristics suggest that the bandgap energy of Ge nanoparticles strongly depends on particle size, which results in size-tunable absorption onset over a wide range of wavelengths, from near-infrared to visible [14–17]. Additionally, Ge nanoparticles exhibit strong emission likewise Si nanostructures, despite having the indirect bandgap structures of a group IV semiconductor. Near-infrared and visible emissions have been reported for Ge nanoparticles, which were assigned to bandgap recombination and recombination in surface oxidized layers, respectively [15, 16, 18–22]. Especially, bare Ge nanoparticles are easily oxidized in water and subsequently dissolve [14]. However, a proper surfactant that can prevent oxidation has not yet been found for Ge nanoparticles prepared by pulsed laser ablation in aqueous solutions.

We noticed in a previous study that a passivation layer could be formed on the surface of a Ge wafer treated with HCl due to removal of oxides and Cl termination [23]. Inspired by these findings, in the current study, we successfully synthesized colloidally stable Ge nanoparticles by the pulsed laser ablation of a Ge target in dilute HCl without any additional surfactants, whereas Ge nanoparticles synthesized in pure water were easily dissolved due to oxidization. The mechanisms for protecting the Ge nanoparticles from rapid oxidation and stabilization of the colloidal suspensions were investigated.

2 Experimental

Ge nanoparticles were synthesized by laser ablation of a Ge target in distilled water or aqueous HCl with concentrations of 0.0005–0.01% using a femtosecond pulsed laser (FCPA μJewel™ D-1000, IMRA America). The wavelength, pulse duration, repetition rate, and pulse energy of the

laser were 1040 nm, 700 fs, 100 kHz, and 10 μJ, respectively. The laser beam was focused onto the (100) surface of a Ge single crystal through an f-θ lens with a focal length of 170 mm. The Ge target was placed in a glass beaker filled with the respective solvents, keeping the target surface ~2 mm below the surface. During the ablation process, the laser beam repeatedly scanned the target surface by computer-controlled Galvano mirrors for 2 h.

The absorption spectra of the Ge nanoparticle suspensions synthesized by laser ablation were measured by a standard double-beam spectrophotometer (JASCO V570). For further analysis, the nanoparticle suspensions were deposited onto silicon substrates and dried in air. Then, the sizes and shapes of the nanoparticles were observed using a scanning electron microscope with a field emission cathode (FE-SEM, Hitachi S-4700). The elemental composition of the nanoparticles was measured using an energy-dispersive X-ray spectroscope (EDX, HORIBA EMAX-7000) on the SEM. Characterization by Raman spectroscopy was also conducted on the nanoparticles deposited on silicon substrates using a micro-Raman spectrometer (JASCO NRS-3300). A 532-nm laser was used for the excitation source.

3 Results and discussion

Reddish-brown solutions were obtained by laser ablation of the Ge single crystal in both distilled water and various concentrations of aqueous HCl, thus indicating the formation of aqueous suspensions of Ge nanoparticles. Each of the suspensions was stored in a glass bottle and kept in the dark for more than 7 days to avoid photo-oxidation [14]. Over time, the color of each suspension became gradually lighter. The discoloring behavior can be seen in photographs of the samples in the insets of Fig. 1. Discoloration of the suspension prepared and maintained in distilled water

proceeded relatively rapidly, and a transparent solution was obtained after 7 days without precipitate formation. This result indicates that the as-prepared Ge nanoparticles were quickly dissolved in water. In contrast, the suspensions prepared and kept in aqueous HCl maintained their reddish-brown color, even after 7 days, although the discoloration speed depended on the HCl concentration. In the case of relatively high HCl concentrations, black precipitates formed as the discoloration progressed, suggesting that the nanoparticles aggregated into large assemblies. This means that dissolution of the nanoparticles was suppressed in aqueous HCl. Differences in discoloration behavior were clearly observed by absorption spectroscopy. Figures 1a and b show the temporal changes of the absorption spectra of the nanoparticle suspensions prepared and kept in distilled water and 0.001% aqueous HCl, respectively. In both cases, the as-prepared suspensions exhibit strong absorption across a wide range of near-infrared to near-ultraviolet wavelengths. The absorption edge is positioned below 1 eV. Such spectral features for Ge reflect an electronic band structure with an indirect bandgap of 0.67 eV. Although absorption of the suspension in distilled water rapidly decreased and diminished over the 7 days, the decreased absorption of the suspension in aqueous HCl over the 7 days occurred more slowly. Strong absorption was maintained for 2 days after preparation and did not diminish, even after 7 days. These results suggest that HCl plays an important role in preventing the dissolution of Ge nanoparticles and that a proper concentration of HCl works as a stabilizer for Ge colloidal suspensions.

The temporal evolution of the absorbance at 3.0 eV for both suspensions is shown in Fig. 2. In the same figure, data for the suspensions prepared in aqueous HCl with concentrations of 0.0005%, 0.001%, 0.005%, and 0.01% are also provided. Figure 2 clearly shows that the rate of decrease in absorbance strongly depended on the HCl concentration because absorbance decreased faster for

suspensions in higher concentrations of HCl. These results reveal that the stability of colloidal suspensions in 0.0005% and 0.001% aqueous HCl was higher than that in higher HCl concentrations. In 0.005% and 0.01% HCl, the absorbance decreased as rapidly as in pure water. However, unlike in distilled water where the nanoparticles dissolved, the absorbance decrease in HCl was caused by faster aggregation and precipitation of nanoparticles. This result means that higher concentrations of HCl prevent dissolution of the Ge nanoparticles but they also destabilize the colloidal suspensions and produce precipitates.

Destabilization of colloidal suspensions in excessive concentrations of HCl, that is agglomeration of nanoparticles, can be qualitatively interpreted by the DLVO theory for the stabilization of colloidal dispersions [24]. According to this theory, the possibility of aggregation of nanoparticles is determined by a balance between the van der Waals attraction and the electric double-layer repulsion (electrostatic repulsion). Unlike the van der Waals attraction, the double-layer repulsion is sensitive to variations of electrolyte concentration and pH (potential of hydrogen) values. The repulsion potential is enlarged as the surface potential of a colloidal particle increases. The surface potential depends on hydrogen ion concentration of the aqueous solution which is commonly evaluated using the pH value, where the surface potential increases as a pH value changes away from that on the isoelectric point. Consequently, the repulsion potential is depending on the hydrogen ion concentrations and sensitive to the pH values. In this study, the pH value was changed between 3.9 and 2.5 when the HCl concentration was increased from 0.0005 to 0.01 %. We suppose that within these concentration ranges higher concentrations of HCl decreased the surface potential of Ge nanoparticles and the repulsion potential was suppressed, which resulted in agglomeration of Ge nanoparticles.

Figures 3a–c show SEM images of nanoparticle suspensions obtained by laser ablation in distilled water. Spherical nanoparticles with diameters of 20–80 nm are observed just after synthesis [Fig. 3a] and on the following day [Fig. 3b]. These nanoparticle diameters are quite small as compared to those of Ge nanoparticles prepared by laser ablation in water with more intense nanosecond laser pulses (60 mJ, 532 nm, 10 Hz), which provided nanoparticle diameters of 200–1000 nm [11]. However, a nanoparticle diameter greater than 20 nm is larger than those of Ge nanoparticles that exhibit bandgap widening due to the quantum confinement of carriers, which is less than 10 nm [14–17, 20, 21]. As shown in Fig. 3c, after being kept in water for 7 days, the nanoparticles completely vanished and only uniform substances were produced, which indicates that the Ge nanoparticles rapidly decomposed in distilled water. Therefore, decomposition of the Ge nanoparticles resulted in discoloration of the colloidal suspensions, as observed by the absorption measurements. When ablation was conducted in 0.001% HCl and the colloidal suspension was stored intact (Figs. 3d–f), the spherical nanoparticles did not decompose, even after 7 days, as was expected from the absorption measurements. The diameters of the nanoparticles were same as those of the nanoparticles obtained in distilled water. However, non-spherical particles are observed in Fig. 3c (7 days after synthesis), which were probably due to coupling, fusion, or partial dissolution of the spherical particles.

To identify the elemental components of the spherical nanoparticles and the transformed products formed in distilled water, Raman and EDX spectra were measured. Figures 4a and b show the Raman and EDX spectra, respectively, of Ge nanoparticles prepared in distilled water (the same as those shown in Figs. 3a–c). The Raman spectra of the as-synthesized Ge nanoparticles and those 1 day after synthesis exhibit a sharp peak at approximately 300 cm^{-1}, with a broad tail on the

low-frequency side. The sharp peak can be assigned to the zone-center optical phonon of crystalline Ge with a diamond structure [25]. The broad component on the low-frequency side of the zone-center mode is often observed in nanocrystalline semiconductors such as porous Si and Ge, and it is due to the relaxation of the momentum conservation rule between phonons and photons [26]. After 7 days, the Raman peak of the Ge optical phonon substantially weakens and a new Raman peak appears at approximately 440 cm^{-1}. The frequency of this peak agrees well with that of the A_1 mode of trigonal GeO_2, which is the most intense Raman peak of GeO_2, suggesting that Ge nanoparticles are oxidized in water [27]. The formation of GeO_2 is supported by the results of the EDX measurements, which showed that the oxygen content increased with time. The EDX spectra in Fig. 4b show that the $K\alpha_1$ peak of O is very weak just after the synthesis, but its intensity gradually increases with time. Ehman et al. reported the fast chemical transformation of Ge films to GeO_2 in water and their subsequent dissolution to metagermanic acid (H_2GeO_3) [28]. Such a transformation was also observed for Ge colloidal nanoparticles with average diameters of 3–19 nm dispersed in aqueous solution [14]. Consequently, we conclude that our Ge nanoparticles synthesized and stored in water underwent a gradual transformation to GeO_2 and probably to H_2GeO_3 within 7 days, although we could not confirm the formation of H_2GeO_3.

The abovementioned insights obtained for Ge nanoparticles fabricated in distilled water suggest that proper concentrations of HCl inhibit oxidation of Ge nanoparticles, and hence the nanoparticles are stable (not dissolved). To elucidate the mechanism of preventing oxidation, the elemental compositions of the Ge nanoparticles synthesized in aqueous HCl were also investigated. Figure 5 shows the EDX spectra of Ge nanoparticles synthesized in 0.001% HCl, which provided the most stable colloidal suspension. The $K\alpha_1$ peak of O was not detected throughout the whole period up to 7

days, and only the $L\alpha_1$ peaks of Ge were observed, which clearly indicates that HCl has an excellent oxidation suppression effect.

The Raman spectra of the same nanoparticles are depicted in Fig. 6. Only the zone-center mode of crystalline Ge at approximately 300 cm^{-1} and a weak tail on the low-frequency side were observed for the as-synthesized nanoparticles and those 1 day after synthesis, just like the Ge nanoparticles prepared in distilled water. However, after 7 days, three additional peaks appear at approximately 130, 175, and 450 cm^{-1}; the Ge zone-center mode also remained. The most remarkable feature is a broad peak at approximately 450 cm^{-1}, which is coincident with the frequency of the stretching vibrational mode of Ge–Cl_x bonds assigned for Cl-terminated Ge nanoparticles [21]. Observation of the Ge–Cl_x stretching mode indicates that Cl was bonded on the surfaces of the Ge nanoparticles. The low-frequency peaks at approximately 130 and 175 cm^{-1} were not assigned because Raman spectra in the frequency region below 400 cm^{-1} have not been reported for Cl-terminated Ge nanoparticles. Thus, the Raman spectrum was compared to the spectra for several species of germanium chlorides. Frequencies reported for Raman active vibrations of $GeCl_4$, Ge_2Cl_6, and Ge_5Cl_{12} are indicated in the bottom part of Fig. 6 [29–31]. Among them, the vibrational modes below 200 cm^{-1} and above 400 cm^{-1} were assigned to the vending and stretching modes of the Ge–Cl_x bonds, respectively, and those at approximately 200–300 cm^{-1} were assigned to the Ge–Ge stretching mode [31]. Two lower-frequency peaks observed for the Ge nanoparticles, 130 and 175 cm^{-1}, can be assigned to the vending modes of the Ge–Cl_x bonds because the frequencies are within the range for the vending vibrations. Therefore, we conclude that Ge–Cl_x bonds formed on the surfaces of the Ge nanoparticles and that the surface dangling bonds were terminated with chlorine. We can see similar spectral features due to the Ge–Cl_x bonds also in the Raman spectra with an

enlarged scale for the as-synthesized nanoparticles and those 1 day after synthesis (Fig. 6). These Raman results show that the relative intensities of the Ge–Cl_x peaks to the Ge-Ge peak increased after 7 days. We consider that such a temporal change in relative intensities of Ge–Cl_x peaks can be interpreted by following two mechanisms. (1) Most of the as-synthesized Ge nanoparticles were not Cl-terminated and termination of the surface Ge bonds by Cl proceeds for 7 days. (2) Ge nanoparticles without Cl-terminated surfaces were rapidly agglomerated or decomposed. As a result, the Cl-terminated nanoparticles remained as colloidal dispersions after 7 days.

It was reported that Cl-terminated surfaces were created on a Ge wafer by immersing it in an aqueous HCl solution and that a hydrophilic surface was created by this treatment [23]. Hence, Ge nanoparticles with surfaces terminated by chlorine are possibly hydrophilic and thus disperse well in aqueous solutions. Consequently, these results indicate that the surface termination of Ge nanoparticles by chlorine is very effective for stabilizing Ge colloidal nanoparticles in aqueous solutions, as well as protecting the nanoparticles from oxidation.

4 Conclusions

Colloidal dispersions of spherical Ge nanoparticles with diameters of 20–80 nm were synthesized by laser ablation of a Ge single crystal in distilled water or aqueous HCl. We demonstrate that the most stable colloids were obtained with an HCl concentration of 0.001%, whereas Ge nanoparticles synthesized in water rapidly decomposed due to oxidation. The excellent stability of the Ge colloidal nanoparticles synthesized in aqueous HCl can be explained by the formation of hydrophilic surfaces that originate in the termination of surface dangling bonds by chlorine, which also suppresses oxidation.

Funding: This study received no funding.

Conflict of Interest: The authors declare that they have no conflict of interest.

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Figure Captions

Fig. 1 Absorption spectra of colloidal suspensions of the Ge nanoparticles synthesized and kept in **a** pure water and in **b** 0.001% aqueous HCl measured 0–7 days after synthesis. Photographs of the nanoparticle dispersions are shown in the insets

Fig. 2 Time variation of absorbance at 3.0 eV for Ge colloidal suspensions synthesized and stored in water and various concentrations of aqueous HCl

Fig. 3 SEM images of the Ge nanoparticles obtained by laser ablation and stored in **a–c** pure water and **d–f** 0.001% aqueous HCl. Size distribution histograms of the corresponding Ge nanoparticles are shown in the insets

Fig 4 a Raman spectra and **b** EDX spectra of Ge nanoparticles synthesized and stored in water for 0, 1, and 7 days

Fig. 5 EDX spectra of Ge nanoparticles synthesized and stored in 0.001% aqueous HCl for 0, 1, 2, 3, and 7 days

Fig. 6 Raman spectra of Ge nanoparticles synthesized and stored in 0.001% aqueous HCl for 0, 1, and 7 days. The frequency positions of the Raman-active molecular vibrations of $GeCl_4$, Ge_2Cl_6, and Ge_5Cl_{12} are indicated on the lower part of the graph. Dotted lines are the same spectra in an enlarged scale

Figure1

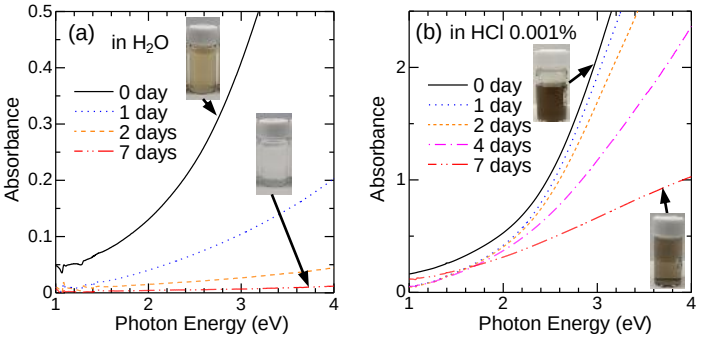

(a)
in H_2O
0 day
1 day
2 days
7 days
Absorbance
Photon Energy (eV)
(b) in HCl 0.001%
0 day
1 day
2 days
4 days
7 days
Absorbance
Photon Energy (eV)

Figure2

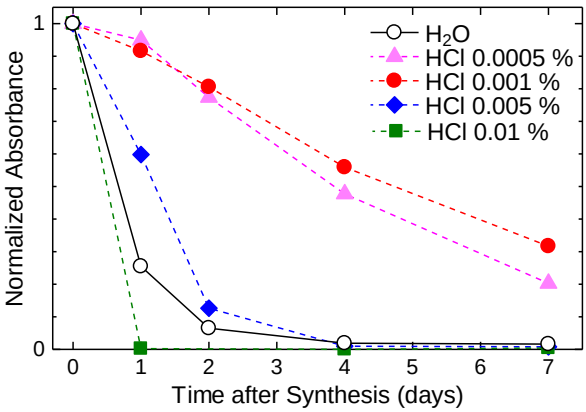

1
0
Normalized Absorbance
0
1
2
3
4
5
6
7
Time after Synthesis (days)
H2O
HCl 0.0005 %
HCl 0.001 %
HCl 0.005 %
HCl 0.01 %

Figure3

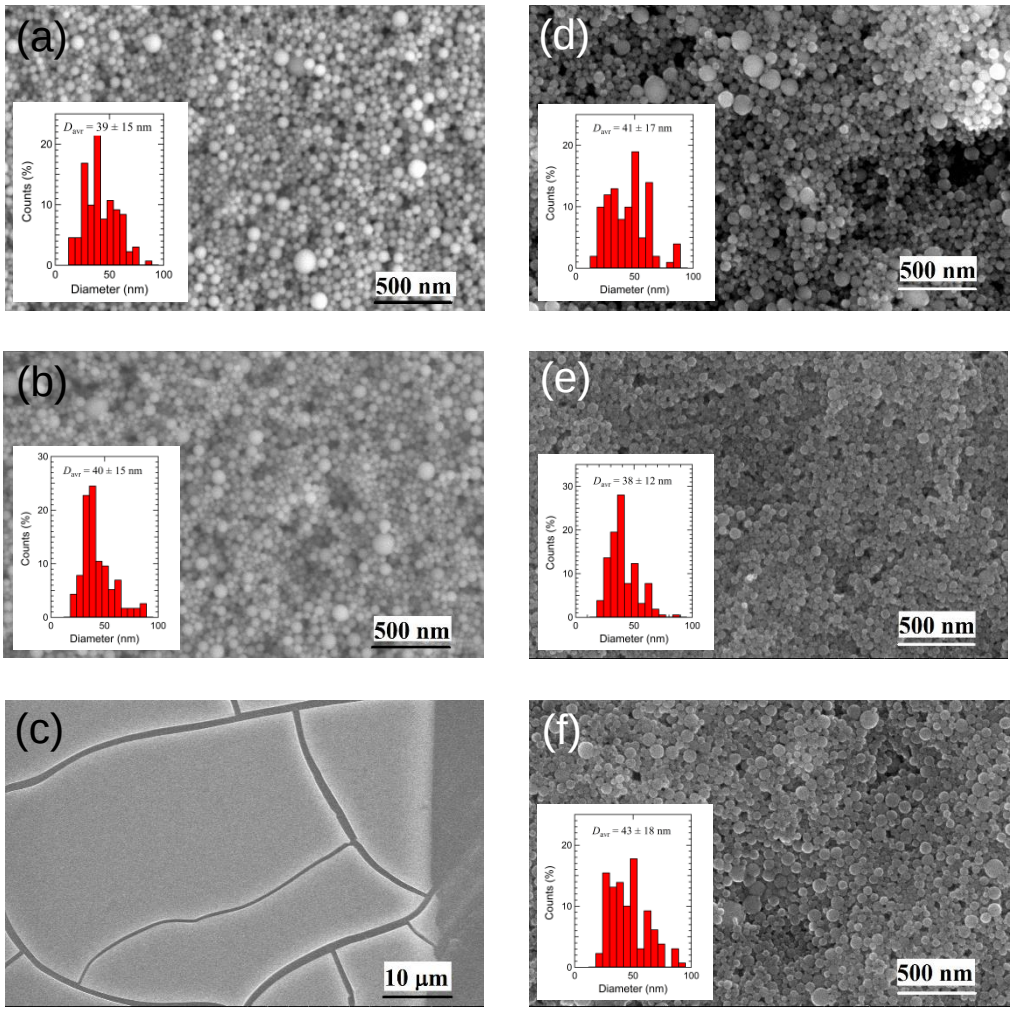

(a)
D_{avr} = 39 ± 15 nm
Counts (%)
Diameter (nm)
500 nm
(b)
D_{avr} = 40 ± 15 nm
Counts (%)
Diameter (nm)
500 nm
(c)
10 μm
(d)
D_{avr} = 41 ± 17 nm
Counts (%)
Diameter (nm)
500 nm
(e)
D_{avr} = 38 ± 12 nm
Counts (%)
Diameter (nm)
500 nm
(f)
D_{avr} = 43 ± 18 nm
Counts (%)
Diameter (nm)
500 nm

Figure4

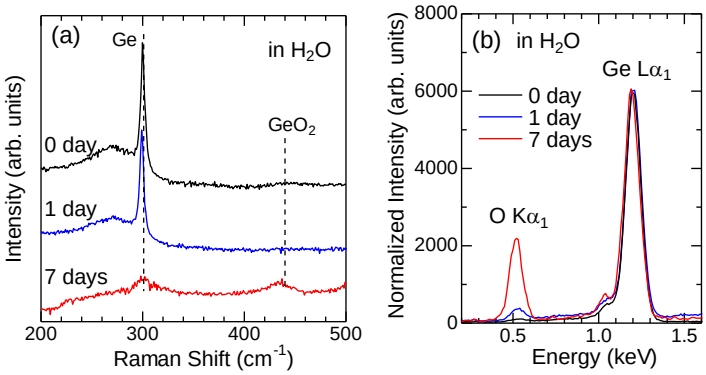

(a)
Ge
in H_2O
GeO_2
0 day
1 day
7 days
Intensity (arb. units)
200
300
400
500
Raman Shift (cm^{-1})
(b)
in H_2O
Ge $L\alpha_1$
0 day
1 day
7 days
O $K\alpha_1$
Normalized Intensity (arb. units)
8000
6000
4000
2000
0
0.5
1.0
1.5
Energy (keV)

Figure5

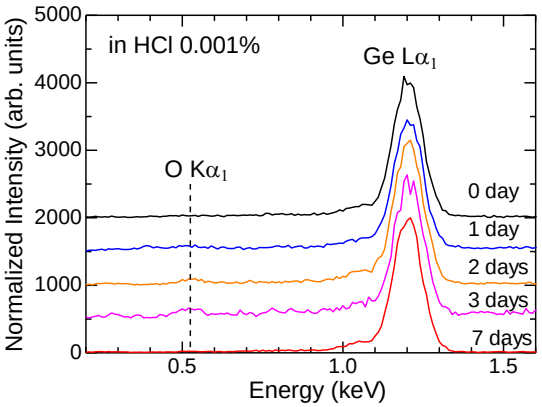
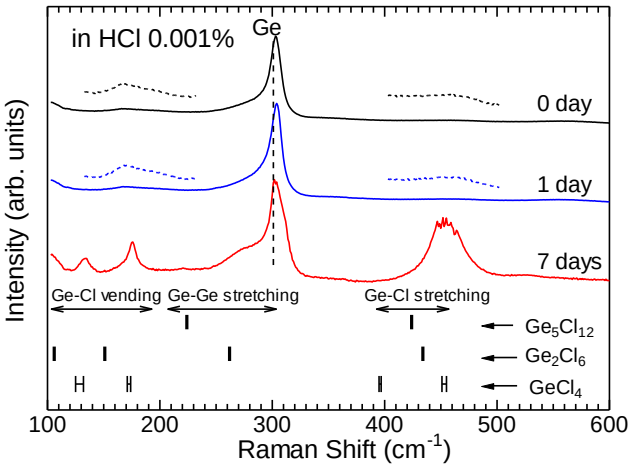

in HCl 0.001%
Ge Lα1
O Kα1
0 day
1 day
2 days
3 days
7 days
Normalized Intensity (arb. units)
Energy (keV)
5000
4000
3000
2000
1000
0
0.5
1.0
1.5

Figure6


in HCl 0.001%
Ge
0 day
1 day
7 days
Ge-Cl vending
Ge-Ge stretching
Ge-Cl stretching
Ge_5Cl_{12}
Ge_2Cl_6
$GeCl_4$
Intensity (arb. units)
100
200
300
400
500
600
Raman Shift (cm^{-1})