

Formation of Unique Nanoparticle Agglomerates During Laser Ablation of CaO Powders in Ethanol

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We conducted laser ablation of calcined shell powder and CaO powder dispersed in ethanol. Results showed that laser ablation induced the formation of nanoparticles and the formation of gel-like structures. Observations of the temporal change of the colloidal solution during laser ablation revealed that the gel-like structures formed rapidly after laser ablation for ca. 30 min, suggesting that the gel-like structures form via the agglomeration of CaO nanoparticles formed by laser ablation. Results showed that the gel-like structures (CaO nanoparticle agglomerates) were positively charged, suggesting that the balance between the positive charge of CaO nanoparticles which comes from the source CaO powders and the negative charge provided by ethanol during laser ablation plays a key role in NP agglomeration. It was also demonstrated that the gold-CaO and platinum-CaO nanocomposites are obtainable simply by mixing colloids of positively charged CaO gel-like structures and colloids of negatively charged gold or platinum nanoparticles.

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1. Introduction

Since the first report by Fojetik et al. [1], laser ablation in liquids (LAL) has attracted much attention as a technique for synthesizing colloidal nanoparticles (NP) [2-5]. One notable feature of LAL is that a colloidal NP solution containing no supplemental substance is obtainable by LAL because NPs are fundamentally obtainable by laser ablation of a target material in pure solvent. The consequent absence of supplemental substances enables observation of some unique properties of colloidal NPs that are difficult to observe for colloidal NPs synthesized using other methods, such as chemical reduction methods, for which various substances such as by-products and stabilizing reagents are included in the colloidal solutions. One example is inorganic ions such as Cl⁻. This typical substance causes salting-out of colloidal NPs. It acts as a stabilizing reagent of gold NPs when added to a solution in which LAL is conducted because inorganic ions are adsorbed onto the clean surface of gold NPs, thereby providing a supplemental electric charge [6,7]. Another example is that LAL for organic crystals dispersed in water can produce stable colloidal NPs without the addition of stabilizing reagents [8].

As described herein, we conducted LAL for CaO powder obtained by calcination of *Corbicula japonica* shell powder dispersed in ethanol to produce CaO NPs. Shells of *Corbicula japonica*, a popular edible shellfish in Japan, are discarded in huge amounts after the shell meat is removed for use as food. Utilization of their shells as a functional material such as CaO NPs is important for efforts at increasing the recycling of industrial wastes. Results showed an interesting phenomenon as well as NP formation.

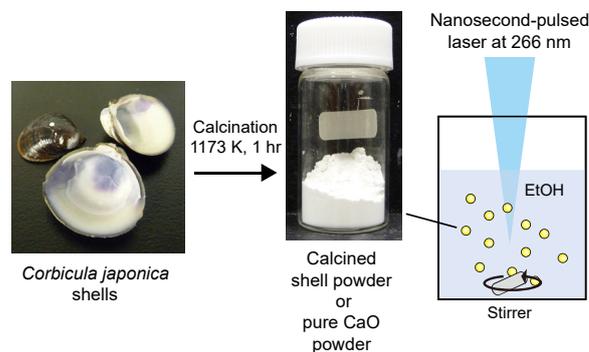


Fig. 1 Experiment setup of LAL to obtain CaO NPs from calcined shell powder or “pure” CaO powder.

2. Experiments

A typical LAL setup to obtain CaO NPs is presented in Fig. 1. CaO powder derived from shell (hereafter we refer to it as calcined shell powder) was prepared by calcination of *Corbicula japonica* shells at 1173 K for 1 hr and milling them [9]. We also conducted LAL for “pure” CaO powder (hereafter we refer to it as CaO powder) because calcined shell contains inorganic elements such as Mn [10]. The CaO powder was prepared by calcination of CaCO₃ powder (Fujifilm Wako Pure Chemical Corp., 99.5%) at 1273 K for 2 hr. Then 8.0 mg of the powder was dispersed in 10 mL of ethanol in a glass vial. Water was not used as a solvent because a considerable degree of hydroxylation of CaO took place. A focused beam of 266 nm output of a nanosecond-pulsed Nd:YAG laser (GCR-150; Spectra-Physics K.K.) was irradiated into the colloidal solution. The spot size on the liquid–air interface was ca. 2 mm. The laser fluence on

the liquid–air interface was adjusted at ca. 0.66, 0.83, and 1.0 J/cm². The colloidal solution was stirred during LAL. To observe temporal changes of the colloidal solutions during LAL, *in situ* measurements were taken of the transmission spectra of the colloidal solutions during LAL. This spectrum measurement used 3 mL of colloidal solution settled in a cubic glass cell. The probe light from a Xe lamp transmitted through the cell was monitored using a multi-channel spectrometer (PMA-10; Hamamatsu Photonics KK). The colloidal solutions were stirred during LAL. The morphology and the crystalline structure of the products were observed respectively using scanning electron microscopy (SEM, JCM-6000 Plus; JEOL and SU8000; Hitachi High-Technologies Corp.), and an X-ray diffraction spectrometer (XRD, MiniFlex; Rigaku Corp.). To conduct electrophoresis of colloidal particles, two stainless steel (SUS304) plate electrodes (10 mm × 10 mm × 1 mm) were immersed in 10 mL of the colloidal solutions. The distance between the electrodes was adjusted to 10 mm. Then DC voltage at 200 V was applied between the two electrodes for 5 min. Gold and platinum NP colloidal solutions to be mixed with CaO NP colloids were prepared with LAL using a method reported elsewhere [11]. Briefly, a piece of gold or platinum plate immersed in 10 mL of ethanol was irradiated by a focused beam of 1064 nm output of a nano-second-pulsed Nd:YAG laser (GCR-200; Spectra-Physics K.K.) at 72 J/cm² for 10 min. The absorption spectrum of the gold NP solution and the atomic absorption spectroscopy measurements suggested that the concentration of gold contained in a gold NP solution obtained in this condition was ca. 1.1×10^{-2} mg/mL.

3. Results and Discussion

Photographs presented in Fig. 2 show temporal appearance changes of a calcined shell powder colloidal solution during LAL. At 30 min, no marked change was observed, but the precipitated large powder amounts were smaller, indicating that the laser irradiation induced particle fragmentation. At 60 min, the colloidal solution appearance changed drastically. The colloidal solution opacity decreases, but gel-like structures floating in the solution are visible. The gel-like structures were also observed at 90 min, but they disappeared at 120 min.

Figs. 3 and 4 respectively shows SEM images and XRD spectra of the colloidal particles sampled at various laser irradiation times. The SEM images show that the particle size decreased with increasing laser irradiation time. In the XRD spectra, the diffraction peaks are weakened and broadened by continuing laser irradiation, indicating that the particle size decreased, but the peak position is almost equal to that of the powder before LAL. No formation of Ca(OH)₂ and CaCO₃, which can be generated by the following reaction with water and CO₂ dissolved in the solvent, was observed.



For those reasons, we concluded that the powder fragmentation progressed. However, no marked composition change or crystalline structure change occurred during LAL.

It is remarkable that LAL generated the gel-like structures. Fig. 5 shows a higher magnification SEM image of

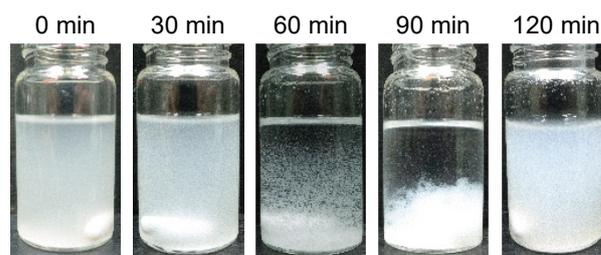


Fig. 2 Temporal appearance change of calcined shell powder colloids in ethanol during LAL. The laser fluence was 1.0 J/cm². These images were taken after stopping stirring. While stirring, the gel-like structures observed in the 60 and 90 min samples floated throughout the solution.

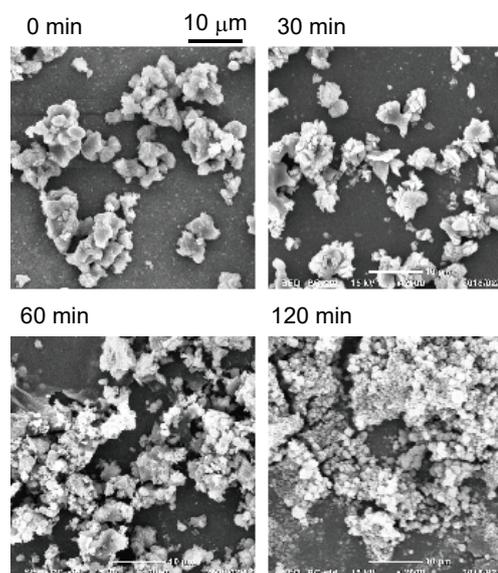


Fig. 3 SEM images of calcined shell powder sampled during LAL in ethanol. The laser fluence was 1.0 J/cm².

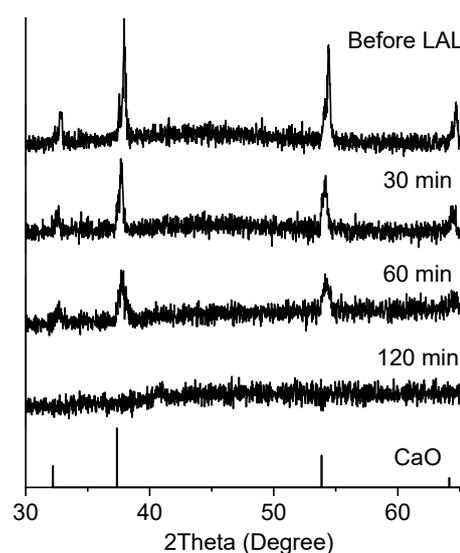


Fig. 4 XRD spectra of calcined shell powder during LAL in ethanol. The laser fluence was 1.0 J/cm². A small shift of the peak position compared with that of the standard data is attributable to eccentricity error.

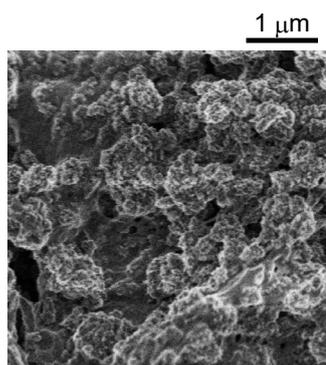


Fig. 5 Higher magnification SEM image of calcined shell powder sampled after LAL in ethanol for 60 min: colloids containing the gel-like substance. The laser fluence was 1.0 J/cm^2 .

the gel-like structures. A substance with complex surface structure and pores is observed. In addition, when the colloidal solutions containing the gel-like structures were dried, the dried powder volume was greater than that of the source powder, implying that the gel-like structure density was lower than that of the source powder. Materials with such complex surface structures and low density are expected to be useful as a support of catalytic NPs because of their large surface area. Therefore, we conducted additional investigations of the component and the formation mechanisms of the gel-like structures.

To clarify the component and formation mechanisms of the gel-like structures, we first conducted LAL of CaO powder using the same LAL conditions (Fig. 6) to clarify whether gel-like structure formation is a characteristic feature of calcined shell powder. Results demonstrated that LAL for CaO powders showed similar effects to that shown by LAL for the calcined shell powder. Gel-like structures were observed at 60 min, revealing that the gel-like structure formation is connected with a property of CaO, the main component of calcined shells. For the following experiments, we used CaO because it is purer than calcined shells, which contain various impurities [10].

Next, we observed temporal changes of the colloidal solutions more precisely to assess the gel-like structure formation dynamics. To do so, we introduced an *in situ* observation method. Fig. 7 portrays a transmission spectrum of CaO colloids before LAL and that of a colloidal solution containing the gel-like structures. These spectra show that the transmittance at 800 nm is an appropriate indicator to observe the gel-like structure formation dynamics. Fig. 8 portrays temporal changes in the transmittance at 800 nm during LAL in several different conditions. The increase in the transmittance attributable to the gel-like structure formation is clearly visible. It is remarkable that the gel-like structure formation did not occur gradually from the beginning of LAL, but instead occurred abruptly after some laser irradiation duration.

Such behavior of the gel-like structure formation dynamics observed in Fig. 8 provides important insight into their formation mechanism. From Fig. 5, two possible formation mechanisms can be inferred. The first mechanism is that the gel-like structures would form via the agglomeration of NPs because particle-like structures smaller than

100 nm are visible. The second mechanism is that the gel-like structures would form because of laser-induced etching (formation of porous structures) of the bulk particles because many pores are observed in Fig. 5. However, the results presented in Fig. 8 seem to reduce the likelihood of the second mechanism because etching of bulk particles



Fig. 6 Temporal change of CaO colloid appearance in ethanol during LAL. The laser fluence was 1.0 J/cm^2 . These pictures were taken while stopping stirring. While stirring, the gel-like structures observed in the 60 and 90 min samples were floating throughout the solution.

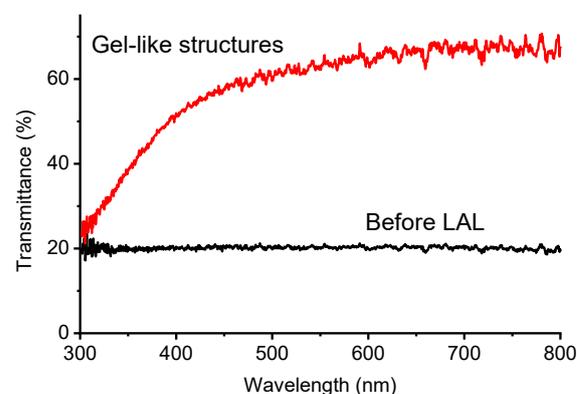


Fig. 7 Typical transmission spectra of a CaO colloids in ethanol before LAL and after formation of the gel-like structures obtained by *in-situ* measurement. For this experiment, LAL was conducted using a 3 mL solution. The laser fluence was 0.83 J/cm^2 .

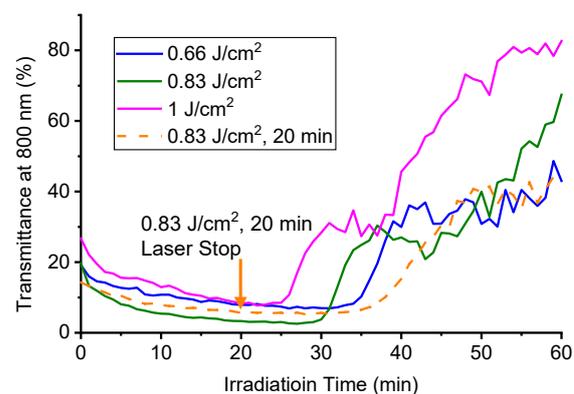
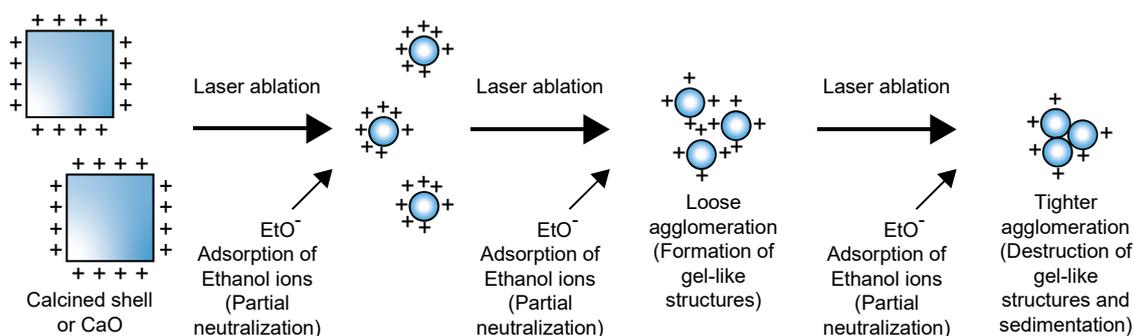


Fig. 8 Temporal transmittance change of CaO colloids during LAL at some laser fluences. LAL was conducted using 3 mL colloidal solution in these experiments. Therefore, gel-like structure formation occurred faster than that observed in Figs. 2 and 6. The dotted line (0.83 mJ/cm^2 , 20 min) shows a result of an observation in which LAL was stopped before the formation of gel-like structures (at 20 min).

occurs gradually from the beginning of LAL and causes no abrupt change. That finding strongly suggests that the gel-like structures are formed via NP agglomeration. Fig. 8 also shows that i) the gel-like structure formation occurred faster as the laser intensity became higher, and ii) the gel-like structure formation occurred even after LAL was stopped (dotted line). These findings indicate that gel-like structure formation occurred when the NP concentration reached threshold, suggesting that gel-like structures form via NP agglomeration.

In addition to the NP concentration, the electric charge of NPs that provides repulsive force between NPs is an important factor for colloidal NP agglomeration. Therefore, we have used an electrophoresis technique to investigate the electric charge of the CaO colloidal particles. As shown in Fig. 9, CaO particles in colloids before and after LAL were deposited on the negative electrode after electrophoresis, indicating that CaO particles are positively charged before and after LAL. We also confirmed that the original CaO powders are positively charged. In fact, they were attracted by a negatively charged polyethylene film, indicating that the positive charge of the colloidal CaO particles derive from the source CaO particles. The positive charge must be generated during the calcination process, although that point was not confirmed.

Although quantitative determination of the change in the electric charge during LAL was difficult from this experimentally obtained result, the fact that CaO particles are positively charged provides an important insight into the NP agglomeration mechanism. In an earlier study [11], we investigated the electric charge of gold NPs prepared using LAL in ethanol. The zeta potential of gold NPs generated in ethanol was -20 mV. Negative charge of the gold NPs is attributed to ethanol molecules adsorbed onto the gold NPs, perhaps because ethanol molecules have a negative charge attributable to their electrolytic dissociation. When assuming that such adsorption of ethanol molecules and donation of negative charge will occur also for CaO NPs generated by LAL in ethanol, the adsorption of ethanol is expected to result in the partial neutralization of positively charged CaO NPs. When LAL is continued, the neutralization will progress, leading to a decrease in the electric repulsive force between NPs. When the balance of the positive charge of CaO NPs and the negative charge provided by ethanol reaches some point, NP agglomeration will begin. Furthermore, in conditions of loose agglomeration, the agglomerates form gel-like structures. The mechanism proposed above is presented in Scheme 1.



Scheme 1 Possible formation mechanism of the gel-like structures during LAL for calcined shell powder and CaO powder in ethanol.

This laser-induced neutralization of CaO NPs by ethanol is also supported by the fact that the colloids obtained after LAL for 180 min were less stable than those obtained after LAL for 60 min. As presented in Fig. 10, the gel-like structures contained in the colloids obtained after LAL for 60 min remained for more than one week, but the colloids obtained after LAL for 180 min were deposited, suggesting that the colloids obtained after LAL for 180 min are more neutralized than those obtained after LAL for 60 min. Additionally, results suggest that the disappearance of gel-like structures by LAL for longer duration (120 min in Fig. 2 and 180 min in Fig. 6) would result from neutralization. The progression of the neutralization will change loose agglomeration to tighter agglomeration, thereby leading to the destruction of the gel-like structures. Additionally, we have conducted LAL for CaO powder in 1-propanol because it was shown earlier that 1-propanol provides more

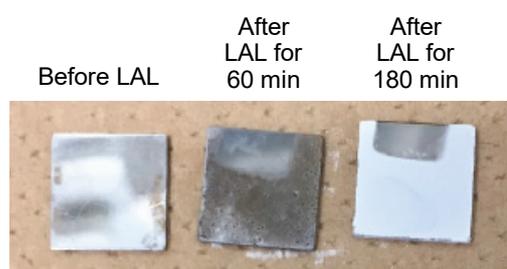


Fig. 9 Images of the negative electrodes (stainless steel plate) after electrophoresis at 200 V for 5 min for CaO colloids before LAL, after LAL for 60 min (containing the gel-like structures), and after LAL for 180 min (after disappearance of the gel-like structures).

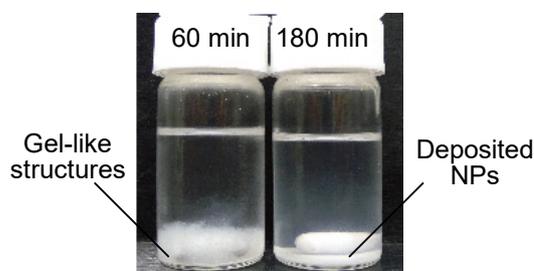


Fig. 10 CaO colloids observed 1 week after LAL. Colloids after LAL for 60 min (containing the gel-like structures) and colloids after LAL for 180 min (after disappearance of the gel-like structures) are shown.

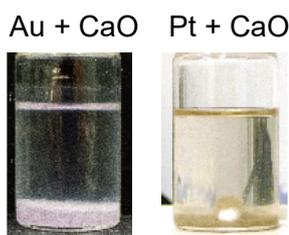


Fig. 11 Colloids obtained by mixing a colloidal solution containing CaO gel-like structures with a colloidal solution of gold or platinum NPs prepared by LAL in ethanol.

negative charge for gold NPs than ethanol in LAL [11]. Results showed no gel-like structure formation, suggesting that the balance between the positive charge of the CaO NPs and the negative charge provided by solvent is a key factor in gel-like structure formation.

Finally, using the positive charge of the gel-like structures, we demonstrated preparation of gold-CaO nanocomposites by mixing a colloidal solution of the positively charged gel-like structures with a colloidal solution of negatively charged gold NPs prepared using LAL in ethanol. Such a complex (CaO supported metal NPs) can be a model material of catalysis, as shown by earlier reports [12,13]. Figure 11 shows a colloidal solution obtained by mixing. The Au/CaO weight ratio was ca. 1:80. A violet gel-like structure was obtained and the solution became almost colorless, indicating that gold NPs were adsorbed onto the gel-like structures. Furthermore, when a similar experiment was conducted using platinum NP colloids in ethanol, brown gel-like structures were obtained (Fig. 11), indicating that platinum-CaO NP nanocomposites were formed successfully.

4. Conclusion

This study demonstrated that LAL of calcined shell powder and CaO powder dispersed in ethanol caused the formation of gel-like structures. Results of *in-situ* observation of the formation dynamics suggest that gel-like structures formed via CaO NPs agglomeration. Results also suggest that the NP agglomeration was induced by the partial electric neutralization of positively charged CaO NPs by adsorption of negatively charged ethanol during LAL. In other words, the balance of the positive charge and the negative charge is expected to be a key factor in gel-like structure formation. Moreover, using the positive charge of the gel-like structures, we demonstrated that gold-CaO and platinum-CaO nanocomposites are obtainable by mixing negatively charged gold and platinum NP prepared by LAL in ethanol with the positively charged gel-like structures. Such composites can be a model material of catalysis. Future work will be undertaken to investigate the composites'

catalytic properties. We also plan to observe the electric charge change during LAL quantitatively, for example using zeta potential measurements, to confirm the proposed gel-like structure formation mechanisms.

Acknowledgments

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References

- [1] A. Fojtik, and A. Henglein: *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, 97, (1993) 252.
- [2] T. Tsuji, K. Iryo, H. Ohta, and Y. Nishimura: *Jpn. J. Appl. Phys. Part 2 - Lett.*, 39, (2000) L981.
- [3] T. Tsuji, T. Hamagami, T. Kawamura, J. Yamaki, and M. Tsuji: *Appl. Surf. Sci.*, 243, (2005) 214.
- [4] T. Tsuji, D. H. Thang, Y. Okazaki, M. Nakanishi, Y. Tsuboi, and M. Tsuji: *Appl. Surf. Sci.*, 254, (2008) 5224.
- [5] T. Tsuji, M. Nakanishi, T. Mizuki, M. Tsuji, T. Doi, T. Yahiro, and J. Yamaki: *Appl. Surf. Sci.*, 255, (2009) 9626.
- [6] J. P. Sylvestre, S. Poulin, A. V. Kabashin, E. Sacher, M. Meunier, and J. H. T. Luong: *J. Phys. Chem. B*, 108, (2004) 16864.
- [7] V. Merk, C. Rehbock, F. Becker, U. Hagemann, H. Nienhaus, and S. Barcikowski: *Langmuir*, 30, (2014) 4213.
- [8] K. Yuyama, T. Sugiyama, T. Asahi, S. Ryo, I. Oh, and H. Masuhara: *Appl. Phys. A*, 101, (2010) 591.
- [9] T. Ishigaki, H. Miyazaki, M. Egawa, S. Sugahara, Y. Seike, H. Suzuki, and T. Ota: *J. Ceram. Soc. Jpn.*, 124, (2016) S1.
- [10] J. Iguchi, M. Isshiki, Y. Takashima, Y. Yamashita, and M. Yamashita: *Fish. Sci.*, 80, (2014) 1089.
- [11] T. Tsuji, T. Mizuki, M. Yasutomo, M. Tsuji, H. Kawasaki, T. Yonezawa, and F. Mafune: *Appl. Surf. Sci.*, 257, (2011) 2046.
- [12] M. Censabella, V. Torrisi, S. Boninelli, C. Bongiorno, M. G. Grimaldi, and F. Ruffino: *Appl. Surf. Sci.*, 475, (2019) 494.
- [13] E. Ogel, M. Casapu, D. E. Doronkin, R. Popescu, H. Stormer, C. Mechler, G. Marzun, S. Barcikowski, M. Turk, and J. D. Grunwaldt: *J. Phys. Chem. C*, 123, (2019) 5433.

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