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To cite this article: Yoshiteru Mizukoshi et al 2018 Jpn. J. Appl. Phys. 57 0102A5

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Comparison of reductive nanoparticle preparation using plasma and ultrasound irradiation in aqueous solution

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Received May 22, 2017; accepted August 29, 2017; published online November 20, 2017

In this review, reductive nanoparticle preparation using plasma generated in aqueous solutions is described. The reduction mechanism of Au(III) ions and the plasma reaction sites are characterized in comparison with the sonochemical reaction sites generated by ultrasound irradiation to aqueous solutions. The contribution of organic additives such as surfactants, water-soluble polymers, and alcohols to the reduction is also addressed. © 2018 The Japan Society of Applied Physics

1. Introduction

Exotic methods, namely, gamma ray, electron beam, and ultrasound irradiations and plasma treatment, have been used to generate excited states in aqueous solutions, which are utilized to synthesize and modify nanomaterials. In this review, the reductive preparation of metal nanoparticles using plasma in water is described.

When a short-pulsed high voltage with a high repetition frequency is applied to a couple of metal electrodes in water, glow discharge is generated near the gap between the metal electrodes. This is called solution plasma (hereafter referred to as SP).1) In this method, the voltage required for the discharge is several kV, which is as low as the voltage needed for plasma generation in the gas phase. This is because the water vapor phase (gas phase) generated near the electrode gap by Joule heating lowers the breakdown voltage to the same order as that in conventional gas phase plasma; SP is generated in the water vapor phase, and it shows an interface between water (liquid phase)/water vapor (gas phase). The conductivity of the aqueous solution is an important factor for generating SP. In order to generate SP, Joule heating is needed so that the solution should include some electrolytes. However, when the conductivity is very high (e.g., seawater), electric current passes through the conductive solution, rather than discharges, between the metal electrodes. Thus, it is difficult to generate SP in highly conductive solutions. Figure 1 shows a schematic model of the plasma generated in water proposed by Takai et al.1) The size of the generated SP corresponds to the gap between the electrodes, typically 1–3 mm or smaller. As SP is generated in the water vapor phase, the influence of the dissolved gas in the bulk solution is insignificant.

The schematic model of SP is similar to the reaction site generated by ultrasound irradiation to water. When high-power ultrasound is irradiated to water, tiny bubbles are generated in the rarefaction phase of the ultrasound because dissolved gas emerges as bubbles under a decreased pressure phase (i.e., Henry’s law). The size of the generated bubbles depends on the frequency of the irradiated ultrasound. When the frequency is high, the bubbles become smaller.2) The generated bubbles implosively collapse after their growth and shrink in the acoustic field. In the process of collapse, the energy of the bubbles is condensed to create high-energy hot spots where the temperature and pressure are extremely high.3) The sequential phenomenon induced by the sonication is called acoustic cavitation, which is influenced by various conditions of the sonicated system. To generate extreme conditions, the kind of dissolved gas in the sonicated solution is crucial. A gas having a high specific heat ratio is suitable to obtain a high temperature via the adiabatic collapse of the bubbles. A gas having a low thermal conductivity is preferable to restrict the dissipation of the localized high energy generated by the bubble collapse.4) Therefore, rare gases such as argon, which has a high specific heat ratio and a relatively low thermal conductivity, have been generally used to enhance the effect of acoustic cavitation.

Some attempts have been made to estimate the extreme conditions inside the collapsing bubbles by experimental5–7) and calculative approaches.8–11) The estimated temperatures are different depending on the approaches used, but generally high, i.e., above several thousands of degrees. Chemistry related to acoustic cavitation is referred to as sonochemistry. Sonochemistry has been applied to the study of various reactions, not only in materials processing, but also in environmental remediation, sterilization, and others.12–15)

The temperature of the hot spots generated by ultrasound is not clearly defined.16) This is because the lifetime of the hot spot is short, depending on the frequency of the irradiated ultrasound, typically on the microsecond order, making it difficult to estimate and interpret the obtained temperature. In addition, it was reported that the core of a collapsing bubble

Fig. 1. (Color online) Schematic diagram of the plasma generated in water.
The reactive species in situ-formed using SP and ultrasound, such as hydrogen and hydroxyl radicals, can be used for nanomaterial processing. Metal ions or complexes in the aqueous solution can be reduced to form metal nanoparticles when SP is generated in the solution or when ultrasound is irradiated to the solution. The preparation methods for nanoparticles were experimentally veriﬁed. Saito et al.22) reported the reduction of HAuCl4 in the presence of an anionic surfactant, sodium dodecylsulfate (SDS). Large dendritic Au particles were formed in the beginning of plasma treatment. In a prolonged treatment, the large particles were dissolved into smaller ones due to nitric acid generated by the plasma reaction from atmospheric nitrogen molecules. They measured hydrogen and hydroxyl radicals by the spin trap-ESR technique using N-tert-butyl-

2. Reduction of metal ions by SP

The reactive species in situ-formed using SP and ultrasound, such as hydrogen and hydroxyl radicals, can be used for nanomaterial processing. Metal ions or complexes in the aqueous solution can be reduced to form metal nanoparticles when SP is generated in the solution or when ultrasound is irradiated to the solution. The preparation methods for nanoparticles by the reduction of metal ions can be classified as bottom-up methods. Conventional chemical reductions of metal ions by reducing agents such as hydrazine, sodium tetrahydroborate, and so on can also be categorized as bottom-up methods. In bottom-up methods using SP and ultrasound, in situ-generated reducing agents can be used, which is an advantage of such methods over conventional chemical reductions because the reducing agents are often hazardous or toxic.

The reduction of Au(III) ions and the preparation of Au nanoparticles have been extensively investigated using aqueous phase plasma including SP because the formation of Au nanoparticles can be easily confirmed from the change in the color of the solution due to the surface plasmon resonance.23) Dominant reductants in situ-formed by the plasma in water were considered to be plasma electrons,24–27) hydrogen radicals,22,28–31) hydrated electrons (\(e_{\text{aq}}^-\)),28) and hydrogen peroxide.32) Among them, the contributions of hydrogen radicals and hydrogen peroxide to the reduction were experimentally verified.

Patel et al.32) synthesized Au nanoparticles from Au ions using plasma generated by DC power supply. In their experimental setup, one of the electrodes was not immersed in HAuCl4 aqueous solution. They excluded the direct supply of electrons from the electrodes to Au ions because Au nanoparticles were not formed when both electrodes were immersed in the solution. They proposed the contribution of hydrogen peroxide to the reduction of Au ions. They tried to reduce Au ions in the presence of titanium(IV) oxysulfate—sulfuric acid, which works as a scavenger of hydrogen peroxide. Considering the fact that Au ions were not reduced to form Au nanoparticles in the presence of the scavenger, they concluded that hydrogen peroxide served as a reducing agent to synthesize Au nanoparticles. On the other hand, since it is difficult to experimentally clarify the reduction of metal ions by plasma electrons and hydrated electrons, their contribution to the reduction is unclear at present.

3. Effect of organic additives on reduction

Nanoparticle preparation by plasma reduction was reported in the absence and presence of surfactants or protective agents. Hao et al. reported the reduction of HAuCl4 in KOH aqueous solution.33) They focused on the effects of discharge duration on the size and size distribution of Au nanoparticles formed in the absence of protective agents. With the increase in discharge duration, the Au nanoparticles became smaller and the size distribution became narrower, which were attributable to the electric charging of the formed Au nanoparticles.

Kim et al. investigated HAuCl4 reduction in a solution containing ethylene glycol, poly(vinyl pyrrolidone) (PVP), and KCl to generate a large number of small Au nanoparticles. The main factor for the formation of the nanoparticles was considered to be electrons generated in the plasma.25)

Bratescu et al. reported the shape control of Au nanoparticles.34) In this case, cationic hexadecyltrimethylammonium chloride (CTAC) was used as the protective agent. They investigated the pH dependence of the size of the formed Au nanoparticles and concluded that the surface composition of Au nanoparticles depends on the preparation.
conditions and thus determined the electrostatic interaction among the nanoparticles, which altered their final size. Cho et al. reported the reduction of HAuCl₄ in reverse micelles by SP⁵⁻ using a solution of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in dodecane. SP synthesis, where the dominant reductants were hydrogen radicals, preferentially provided multiple twinned Au nanoparticles in comparison with the conventional reduction by sodium tetrahydroborate.

As mentioned above, PVP, SDS, CTAC, AOT, and so on worked as protective agents for the formed particles or water-in-oil micelles in the bottom up preparation of nanoparticles. However, the effects of plasma on the organic protective agents or their contributions to the reduction were not adequately addressed. On the other hand, plasma in water has been applicable to the decomposition of harmful organic substances.⁶⁻ If plasma generated in water is effective for the decomposition of organic pollutants, the decomposition of surfactants, water-soluble polymers, or alcohols, and their contribution to the reduction are worth considering.

The contribution of organic solutes to the reduction has been a generally accepted concept in the sonochemical preparation of metal nanoparticles by the reduction of the corresponding metal ions. Nagata et al. reported the preparation of Au nanoparticles by the reduction of NaAuCl₄ under ultrasound irradiation.⁷⁻ They measured the sonochemical reduction rates of Au ions in the presence of various kinds and a range of concentrations of organic solutes. The rates increased when the concentration of the solute was high. The acceleration effect on the reduction of the added alcohol was enhanced when the alkyl chain was long. This was explained by the hydrophobicity of the solute, i.e., more hydrophobic alcohols or surface-active molecules were accumulated in the gas/liquid interface, and preferentially exposed to the direct or indirect effects of the hot spot. In contrast, the reduction rate was very low without organic additives, indicating that the main source of the reductants was the organic additives and that the contribution of the hydrogen radicals generated from the decomposition of water molecules was limited. The authors proposed that three kinds of reducing species were generated in the sonolysis of aqueous solutions containing organic solutes such as surfactants or alcohols.⁸⁻⁻¹⁰

(1) Hydrogen radicals: generated from the sonolysis of water molecules in hot spots,
(2) Rpy: radicals formed from the direct pyrolysis of non-volatile surfactants in the vicinity of the collapsing hot spot or volatile alcohols in the collapsing hot spot, and
(3) Rab: secondary radicals formed via reactions, typically hydrogen abstraction from the alkyl chain of the surfactants, water-soluble polymers or alcohols by primary radicals such as hydroxyl radicals and hydrogen radicals originating from the sonolysis of water molecules.

The contribution of hydrogen radicals to the reduction can be easily estimated by measuring the reduction rate without any additives. The Rab contribution can be estimated by comparison with the radiochemical reaction by gamma rays.⁹⁻¹⁰ When gamma rays are irradiated to an aqueous solution, water molecules are decomposed.

\[
\text{H}_2\text{O} \rightarrow e_{\text{aq}}^-, \cdot \text{H}, \cdot \text{OH}, \text{etc.}
\]

The generated hydrated electrons (e_{aq}⁻) and hydrogen radicals are strong reductants, while the hydroxyl radicals are strong oxidants.¹⁰⁻ A gas/liquid interface is not formed by gamma irradiation, differently from the cases of ultrasound or SP, but the reactive species are localized along the ray track (so-called “spur”). The reductants generated by gamma irradiation can be utilized for the reduction of metal ions to form metal nanoparticles,¹¹⁻¹².¹³⁻¹⁴ Hydrated electrons are scavenged by N₂O and converted into hydroxyl radicals under N₂O atmosphere:

\[
e_{\text{aq}}^- + \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{N}_2 + \cdot \text{OH} + \cdot \text{OH}^-.
\]

Using these reactions, the generation rates of hydroxyl radicals (and hydrogen radicals) can be controlled by adjusting the irradiated dose rate of gamma rays. Generated hydroxyl radicals recombine to form hydrogen peroxide, which can be easily determined by a colorimetric method through the oxidation of Fe(II) ions.¹³⁻¹⁴

Under the condition that the generation rate of hydrogen peroxide in the bulk solution by gamma rays was the same as that by ultrasound irradiation, the reduction rate of Au(III) ions by gamma rays was much lower than that by sonication. Because the rate under gamma irradiation corresponded to the contribution of R_{ab} to the reduction, the gap between the rates by the sonication and gamma irradiation was considered to be due to R_{py}. The degrees of the R_{ab} and R_{py} contributions to the reduction depended on the kind of noble metal ion to be reduced. R_{py}, rather than R_{ab}, significantly contributed to the NaAuCl₄ reduction.³⁵⁻¹⁶ On the other hand, in the case of the reduction rates of the K₂PtCl₄/SDS system, the rates generated using ultrasound and gamma rays were almost the same, suggesting that R_{py} did not take part in the reduction of Pt(II) ions.³⁸⁻¹⁹

Mizukoshi et al. reported the sonochemical reduction rates of H₂PtCl₆ in the presence of surfactants such as anionic SDS, anionic sodium dodecylbenzenesulfonate (DBS), and non-ionic polyethylene glycol monostearate (PEG-MS).³⁹⁻¹⁰ The reduction of Pt(IV) ions proceeded via the formation of Pt(II) ions. The reduction rates from Pt(IV) ions to Pt(II) ions depended on the concentration of the surfactant: the rates reached their maximum at the critical micelle concentration (CMC) of anionic surfactants (SDS: 8 mmol/L, DBS: 3 mmol/L). In the case of non-ionic PEG-MS, the maximum rate was obtained at 0.4 mmol/L, which was 10 times higher than the CMC. However, the rate from Pt(II) ions to Pt(0) was almost constant regardless of the kind and concentration of the surfactants. The difference in the reduction rate between the two processes was considered to stem from different reducing species participating in the reductions of Pt(IV) and Pt(II) ions. R_{py} reduced Pt(IV) ions to Pt(II) ions in the first step, and R_{ab} was the main factor in the second reduction step, i.e., from Pt(II) ions to Pt(0). When Pt(IV) ions were reduced in the presence of DBS, the reduction proceeded accompanying the CO and CH₄ evolutions. This fact together with the very low reduction rate without DBS clearly indicates that the contribution of the DBS to the Pt ion reduction is significant.

Grieser’s group paid attention to the adsorption of the organic solutes at the liquid/gas interface induced by ultrasound irradiation. They investigated the sonochemical reduction of HAuCl₄ and the sonoluminescence in the presence of alcohols.⁴³⁻ They reported that the amount of AuCl₄⁻ reduced in the presence of ethanol, 1-propanol, and 1-butanol depended on the surface excess of alcohol at the gas/solution interface.
interface. The dependence on the surface excess of alcohol was observed regardless of the kind of alcohol, the concentrations, and the frequency of the irradiated ultrasound. A significant decrease in the sonoluminescence intensity was observed in the presence of alcohols, and the effect of alcohol addition on sonoluminescence intensity was also correlated with the surface excess of alcohol.

A similar effect of adding organic additives on noble metal ion reduction was observed in the reaction of SP. Mizukoshi et al. prepared noble metal nanoparticles using SP in aqueous solutions containing Au, Pd, or Pt chlorocomplexes. They measured the reduction rate of Au(III) ions by a colorimetric method and found that the rate was accelerated by the addition of anionic SDS and decelerated in the absence of SDS. This result indicates that surface-active molecules seem to be preferentially accumulated at the gas/liquid interface. The dependence on the surface excess of alcohol was also correlated with the reduction rate of Au(III) ions. A larger amount of CO2, which was formed in the PEG-MS solution, was evolved; this is similar to the sonochemical reduction of noble metal ions. ESR-spin trapping experiments showed the formation of carbon radicals together with hydroxyl radicals, suggesting that radicals originating from SDS decomposition by SP contributed to the reduction. However, when the non-ionic surfactant PEG-MS was employed instead of anionic SDS, the reduction of Au(III) ions hardly proceeded. A larger amount of CO2, which was formed in the PEG-MS solution, was evolved; this was considered to be due to the structure of the PEG-MS molecule consisting of “CH2–CH2─O” units. On the other hand, the SDS solution provided a larger amount of CO and a smaller amount of CO2 than the PEG-MS solution, which seemed to be preferable for the reduction of Au(III) ions. As a result, it is important to select suitable organic solutes, which are precursors of the reducing species for the reduction of noble metal ions using SP.

Sudare et al. investigated the effect of alcohol addition on the reduction of Au(III) ions by the SP. They found that the reduction rate was significantly accelerated by the addition of a small amount of ethanol. The highest rate, 35.2 times higher than the rate without ethanol, was observed when the ethanol molar fraction was 0.089. This interestingly corresponded to the fraction where the molar volume of ethanol was minimum and that of water was maximum. They carefully confirmed that the effects of UV illumination, reaction products, and pH change on the reduction reaction were not responsible for the acceleration. In addition, they compared the acceleration effects of methanol, ethanol, and 2-propanol, and reported that the high reduction rate was observed in the presence of a more hydrophobic alcohol, 2-propanol. This was explained by the accumulation of more hydrophobic alcohols at the gas/liquid interface of SP. Sudare et al. considered that secondary radicals, i.e., the above-mentioned radicals, contributed to the reduction. This mechanism is similar to that in the sonochemical hot spot.

Sudare et al. also reported the detailed mechanism of the acceleration of Au(III) ion reduction. They detected hydroxyl radicals by the ESR-spin trapping technique. The maximum yield was observed when the ethanol molar fraction was 0.089, providing the highest reduction rate of Au(III) ions. A linear correlation between the surface excess of ethanol molecules and the yield of hydroxyl radicals was also observed. Thus, they concluded that the main pathway of the radical formation was the ethanol reaction at the gas/liquid interface of SP. They supposed that the hydrogen abstraction reaction from the ethanol molecule at the gas/liquid interface \[ \text{C}_2\text{H}_5\text{OH} + \text{H} \rightarrow \text{CH}_2\text{CHOH} + \text{H}_2 \] is the main reaction for hydroxyl radical formation, and that the contribution of UV light and the reaction in the gas phase could be negligible. The features of the representative preparation methods shown in this review are summarized in Table 1.

### 4. Conclusions

In this review, we showed that the reduction of metal ions by SP was similar to the sonochemical reduction. The history of sonochemistry is long, dating back to the early 20th century. Since the 1980s, sonochemistry has significantly developed largely owing to the accumulated knowledge stored in radiochemistry. On the other hand, SP has been in the dawn period so that there is much room to be explored. A deeper insight into SP reactions is expected to be obtained by comparing SP with other excited reaction sites formed in aqueous systems, such as sonochemical hot spots.
Table I. Features of the representative preparation methods shown in this review.

<table>
<thead>
<tr>
<th>Reduction method</th>
<th>Solvent</th>
<th>Metal ion</th>
<th>Protective agent</th>
<th>Other additives</th>
<th>Reductant and its source</th>
<th>Nanoparticle size (nm)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 22</td>
<td>SP</td>
<td>Water</td>
<td>HAuCl₄ 0.3-0.65 mmol/L</td>
<td>SDS</td>
<td>H radical Water</td>
<td>20–150</td>
<td>Large dendritic particles were formed.</td>
</tr>
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<td></td>
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<td>Particle size decreased with long-term processing.</td>
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<td>Anisotropic particles were formed.</td>
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<td>PVP decreased average size of nanoparticles.</td>
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<td>Spherical particles were obtained by KCl addition.</td>
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<td>Anisotropic particles were formed.</td>
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<td></td>
<td>Particle size depended on the initial Au ion concentration.</td>
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<td>H₂O₂ prevented the aggregation of the particles.</td>
</tr>
<tr>
<td>Ref. 25</td>
<td>SP</td>
<td>Ethylene glycol in water</td>
<td>HAuCl₄ 0.1 mmol/L</td>
<td>PVP KCl</td>
<td>Electron Water</td>
<td>16.38 ± 0.48</td>
<td>Increase in the discharge duration led to formation of smaller Au nanoparticles with</td>
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<td>narrower size distribution.</td>
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<td>Electrostatic repulsion stabilized the formed particles.</td>
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<td>Most particles were spherical.</td>
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<td></td>
<td></td>
<td>Small Au nanoparticles were formed in high-pH solution.</td>
</tr>
<tr>
<td>Ref. 32</td>
<td>Microplasma in He flow</td>
<td>Water</td>
<td>HAuCl₄ 2.5 µmol/L–1 mmol/L</td>
<td>None</td>
<td>H₂O₂ Water</td>
<td>&gt;10–ca. 180</td>
<td>Nanoparticles had different crystal structures (single crystal, multiple twinned, etc.).</td>
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<tr>
<td></td>
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<td>SDS accelerated the reduction, but PEG-MS did not.</td>
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<td>With the progress of reduction, CO and CO₂ were evolved.</td>
</tr>
<tr>
<td>Ref. 33</td>
<td>SP</td>
<td>Water</td>
<td>HAuCl₄ 0.5 mmol/L</td>
<td>None KOH</td>
<td>Electron Water</td>
<td>23.2–64.0</td>
<td>Addition of ethanol accelerated the reduction of Au ions.</td>
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<td></td>
<td>Organic radicals were identified by ESR (Ref. 47).</td>
</tr>
<tr>
<td>Ref. 34</td>
<td>SP</td>
<td>Water</td>
<td>HAuCl₄ 1 mmol/L</td>
<td>CTAC NaOH (for pH adjustment)</td>
<td>H radical Water</td>
<td>1–10</td>
<td>Addition of surface-active organics accelerated the reduction of Au ions.</td>
</tr>
<tr>
<td>Ref. 35</td>
<td>SP</td>
<td>Water in dodecane (reversed micelle)</td>
<td>HAuCl₄ 2 mmol/L</td>
<td>AOT</td>
<td>H radical Water</td>
<td>6.3 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>Ref. 45</td>
<td>SP</td>
<td>Water</td>
<td>HAuCl₄ Na₃PdCl₄, H₂PtCl₆ 0.2, 1.0 mmol/L</td>
<td>SDS PEG-MS</td>
<td>Organic radical H radical PEG-MS Water</td>
<td>20–30</td>
<td></td>
</tr>
<tr>
<td>Ref. 46</td>
<td>SP under N₂</td>
<td>Ethanol–water mixture</td>
<td>HAuCl₄ 0.3 mmol/L</td>
<td>None</td>
<td>Organic radical Ethanol</td>
<td>ca. 10–35</td>
<td></td>
</tr>
<tr>
<td>Ref. 37</td>
<td>Ultrasound under air or Ar</td>
<td>Water</td>
<td>NaAuCl₄ 0.1–1.0 mmol/L</td>
<td>SDS PEG-MS</td>
<td>Alcohols Water soluble polymers Ketones</td>
<td>Organic radical H radical Organic additives Water</td>
<td></td>
</tr>
</tbody>
</table>

a) SDS: Sodium dodecylsulfate, PVP: Poly(vinyl pyrrolidone), CTAC: Hexadecyltrimethylammonium chloride, AOT: sodium bis(2-ethylhexyl)sulfosuccinate, PEG-MS: polyethylene glycol monostearate.
Yoshiteru Mizukoshi received his Doctor of Engineering (2000) from Osaka Prefecture University. He worked at Osaka Prefectural College of Technology (2001–2005), and Nagasaki University (2005–2006). Now, he is working at Institute for Materials Research, Tohoku University as an Associate Professor. His research interests are focused on the excited reaction site generated in aqueous system, and their applications for synthesis and modification of nanomaterials, degradation of hazardous organic chemicals, sterilization of water, etc.

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Kenji Okitsu received his Ph.D. degree (1997) from Osaka Prefecture University. Now, he is working at Osaka Prefecture University as a Professor. His research interests are focused on the sonochemical synthesis of metal nanoparticles and sonochemical degradation of hazardous organic chemicals.