Synthesis and Modification of Metal Nanoparticles by Plasma over an Aqueous Solution under Pressurized Argon

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Abstract. Metal–based nanoparticles have been used in diverse industrial applications owing to their physicochemical properties. Here, the electric field produced by pulsed high–voltage discharge plasma over an aqueous solution surface that was generated under high–pressure argon environment would be employed to synthesis and to modify metal materials. The plasma reactor was made of stainless steel and contained two sapphire windows to monitor the plasma performance. The experiments were conducted at room temperature (25 − 28 °C) with argon environment at a pressure of 3.0 MPa and the DC power supply at 18.6 kV was introduced into the reactor through the electrode to generate pulse electrical discharge plasma. The metal rod electrode which was used as a material source for nanoparticles generation was placed over an aqueous solution containing glycine, as carbon source, to introduce electrical discharge plasma. The scanning transmission electron microscopy which was equipped with energy dispersion spectroscopy (STEM coupled with EDS) indicated that titanium dioxide and iron oxide with and without carbon covered were successfully produced in nano–scale (<100 nm).

Introduction

It was well known that the particles with diameters between about 1 nm to 1 μm which is in the three–digit nanometer range can be called as nanoparticles. However, in general, the particles from 1 to 100 nm are defined as nanoparticles. Nanoparticles involving metal–based nanoparticles have been widely applied in industrial applications such as medicine, the food industry, cosmetics, electronics, and the chemical industry owing to their physicochemical properties (Azzazy et al., 2012; Maekawa et al., 2012; Jeevanandam et al., 2018; Sharma et al., 2019). In addition, due to their size, the nanoparticles also have a high surface energy, very large specific surface area, and quantum confinement.

Several ways, such as biological, chemical, and physical techniques, have been introduced for nanoparticles generation (Yamada et al., 2018; Bilal et al., 2019). The physical method leads to drive the nanoparticles generation by decreasing the size of the material, on the contrary, the biological and the chemical methods tend to form the nanoparticles through molecular or atomic constructions. The chemical methods are the most popular methods to generate nanoparticles owing to its simplicity and convenience equipment. This process can be operated in mild and simple conditions; however, this process cannot avoid the toxic chemical agents in the synthesis procedure, and accordingly, it may result in hazardous and contaminants residues. Conversely, the chemical agents were not employed in physical synthesis method, hence the hazardous and the contaminants on the products were not found. However, the operating costs are high and should be considered. Compared to physical and chemical
synthesis methods, the biological synthesis method is recognized as an environmentally friendly and inexpensive. Although the chemical agents were eliminated and substituted by molecules generated by living organisms, in this method, the undesired biological contaminants are still generated, and the reproducibility is also restricted.

In order to eliminate the matters, here, the pulsed discharge plasma over an aqueous solution under argon environment would be utilized to produce nanoparticles from titanium or iron rod. Titanium dioxide nanoparticles generally were applied in the printing ink, paints, synthetic fibers, paper, plastics, electronic components, ceramics, rubber, cosmetic, and food industries (Haider et al., 2019). While iron oxide nanoparticles can be applied in magnetic storage, energy storage, gas sensor, electrochemical, cancer therapy, and biomedical treatments (Sangaiya and Jayaprakash, 2018). Plasma was generally expressed as the fourth state of matter which is constructed when gases are a highly ionized gas. At this state, the charged particles such as electrons, positive and negative ions as well as neutral atoms were found abundantly and may deliver energy. In other words, when the electrical discharge plasma was introduced over the aqueous solution, a diverse of physical and chemical processes may occur to generate active species (Locke et al., 2006; Wahyudiono et al., 2012; Puliyalil et al., 2018; Wahyudiono et al., 2019). Hence, plasma can be applied widely for different applications and make it interesting for various applications.

Materials and Methods

Materials
All chemicals were used as accepted without further purification. Glycine (CAS. No. 56−40−6; Product No.077−00735) and distilled water (CAS. No. 7732−18−5; Product No. 049−16787) that were used as the aqueous solution media were bought from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Argon (purity greater than 99.99%) was bought from Sogo Kariya Sanso, Inc. Japan. The aqueous solution media consisted of 100 g of glycine which was dissolved in 1 L of distilled water. Titanium (T1−451485, Nilaco, Japan) and iron (FE−221487, Nilaco, Japan) rods with 1.0 mm in diameter were employed as an electrode.

Experimental Method
Fig. 1 describes an apparatus scheme for the pulsed discharge plasma generation which was used in this work. The main apparatus consisted of a high pressure chamber and a DC pulsed plasma power supply. The chamber was made of stainless steel with a volume of 25 mL (SUS316, AKICO, Japan) and allowed to work at 150 °C and 30 MPa. This chamber was assembled with two sapphire windows, and hence, it allows to monitor the plasma generation performance. The electrical discharge plasma application over the surface of an aqueous solution was introduced via a metal electrode as an anode, which was managed at 3.0 mm distance from an aqueous solution surface. The distance between the aqueous solution surface and the inside wall chamber as the cathode was about 3 cm. The experiments were performed as follows. The aqueous solution containing glycine was fed into the chamber manually, and it was closed tightly after the argon gas was purged into the chamber to replace the air. Next, the chamber was pressurized by argon via a needle valve to 3.0 MPa. The experiments were carried out at room temperature; however, a K−type thermocouple was inserted frequently in the chamber to monitor experiment temperature. After the desired operating condition was reached, the DC pulsed power supply at 18.6 kV (MPC; Suematsu Electronics MPC2000S) was applied into the chamber via electrode to introduce the pulse electrical discharge plasma. The pulse discharge plasma repetition rate was 4 pulses per second (pps). There are no variations of applied voltage, plasma repetition rate, and operating pressure during experiments. The number of pulsed discharges was 20000 pulses. To measure and to monitor the breakdown voltage and current, the digital oscilloscope (TDS2024C, Tektronix Inc.) was attached in the plasma apparatus. After experiments, the collected aqueous solution products were accommodated in the sealed bottles and immediately analyzed with the ultraviolet−visible (UV−vis) spectrophotometer (V−550, Jasco Corporation, Japan). The morphology and elemental maps of the generated particle were characterized by using transmission electron microscopy (TEM) (JEM−2100Plus, Japan Electronic Co., Ltd.) with energy−dispersive X−ray spectroscopy (EDX) (JEOL, JED−2300T & Gatan, GIF Quantum ER).
Results and Discussion

Fig. 2 shows the photograph of the collected aqueous solution products upon pulsed discharge plasma application. Clearly, the color of the collected aqueous solution products was dark (black color). It was well known that the pulsed discharge plasma may take place when the electrical discharge plasma was applied to the aqueous environment. This may promote to result in individual effects such as the generation of various radicals, intense ultraviolet radiation, over−pressure shock wave, and strong electrical field (Locke et al., 2006; Wahyudiono et al., 2012; Vukusic et al., 2016; Puliyalil et al., 2018). Next, the reactive chemical species such as radicals and molecular species will interact and cleavage the chemical compounds including glycine containing carboxyl and amine groups. As a result, the deterioration reaction of glycine occurs and may result in carbon particles (Wahyudiono et al., 2012, Hayashi et al., 2017a, 2017b). Wahyudiono et al. (2012) informed that the deterioration reaction was found when they introduced the pulsed discharge plasma over an aqueous solution surface containing pyrrole compound. The color of the aqueous solution products became light brown due to the pyrrole deterioration reaction occurs during the pulsed discharge plasma application. They also informed that at the high−pressure conditions, the high voltage was needed for breakdown voltage to construct an electric field and raising applied voltage may improve the electric field intensity of an
aqueous solution. Consequently, the electrons within the area own more energy and bombard the aqueous solution containing pyrrole with a higher speed to result in the higher pyrrole conversion. Similar results were also obtained when Hayashi et al. (2017a, 2017b) conducted experiments to generate carbon particles from an aqueous solution containing amino acids by introducing an electrical discharge plasma under pressurized argon gas. They also found that the color of the aqueous solution products became dark due to the glycine deterioration reaction. They explained that the reactive species in a larger amount was transferred into the aqueous solution during pulsed discharge plasma application at higher pressure conditions promotes to the generation of carbon particles from amino acids.

Fig. 3. UV−vis spectra of an aqueous solution products after the pulsed discharge plasma application: (a) Titanium; (b) Iron.

Fig. 3 exhibits the UV−vis spectra of the collected aqueous solution products after the pulsed discharge plasma treatment under pressurized argon gas. This analysis is mostly the first method employed to identify the generation and the existence of metal nanoparticles, including iron and titanium, due to the phenomenon of surface plasmon resonance. Prior to analysis, the collected aqueous solution products were dialyzed with a dialysis membrane (Spectra/Por3, Spectrum Laboratories Inc., CA, USA) to release the remaining glycine. From this figure, it can be seen that the absorptions at around 200 to 300 nm and 260 nm were found in spectra of the collected aqueous solution products containing titanium and iron particles, respectively. Perhaps, these absorption peaks were sourced from titanium and iron oxide nanoparticles (Centi et al., 2000; Brik et al., 2001; Ma et al., 2004; Tanabe and Ozaki, 2016; Turakhia et al., 2019) that were produced from electrode consumption during pulsed discharge experiments (Saito et al., 2015; Kohut et al., 2018; Kim et al., 2019).

Next, the collected particle products were characterized into scanning transmission electron microscopy which was associated with energy dispersion spectroscopy (STEM coupled with EDS) apparatus device. This tool is simple and may identify the elements exist in the collected particle products. Figs. 4 and 5 display the TEM images and the elemental composition of the collected particle products after the pulsed discharge plasma treatment with titanium and iron as an electrode, respectively. The color coding of elements is as follow: titanium or iron (b), oxygen (c), and carbon (d). These figures exhibit that the titanium or iron, oxygen, and carbon elements can be found obviously in the collected particle products. The elements of oxygen and carbon may come from the glycine deterioration during applying the pulsed discharge plasma over the surface of an aqueous solution containing glycine compound (Hayashi et al., 2017a, 2017b, 2018). Hayashi et al. (2018) conducted experiments for oligomerization of glycine by applying pulsed discharge plasma over the glycine solution surface under argon environment. They reported that the repetition of the pulsed discharge plasma application seems to have the power to decompose a glycine compound into its derived compounds, such as acetic acid and ammonia, in the aqueous solution. In this work, note that the glycine intermediate compounds generated from the glycine decomposition during experiments were not identified. Furthermore, as informed before, Hayashi et al. (2017a, 2017b) have been successfully produced carbon materials from an aqueous solution containing glycine by introducing an
electrical discharge plasma under pressurized argon gas. In the case of titanium and iron elements, the presence of them in the collected particle products may come from the ejection of the titanium or iron electrode surface which was employed as an anode during the pulsed discharge plasma experiments (Centi et al., 2000; Brik et al., 2001; Ma et al., 2004; Saito et al., 2015; Tanabe and Ozaki, 2016; Kohut et al., 2018; Turakhia et al., 2019, Kim et al., 2019). It was well known that the electrode erosion during applying electrical discharge plasma is mostly to be an unwanted phenomenon and therefore this phenomenon should be prevented. Here, as informed above, the electrode erosion phenomenon was utilized to generate nanoparticles via electrical discharge plasma. Consequently, the electrode erosion status changes from an unwanted product (contaminant) to the desired process products. Eventually, it could be said that although the detailed information regarding the structure type of titanium or iron was not presented, this method may simplify the metal nanoparticles fabrication including titanium and iron.

Fig. 4. The STEM–EDS of the collected particle products with titanium as an electrode.

It has been known that when the electrical discharge plasma was introduced in the aqueous solution or over the aqueous solution surface, the high reactivity of the active species and molecular generation might be produced, such as hydroxyl radicals, molecular hydrogen, molecular oxygen, hydrogen peroxide, hydroperoxyl radical, superoxide anion, etc. They seemed to have responsible for the decomposition of the organic compounds, however, the hydroxyl radical and hydrogen peroxide have been known as the main reactive species contributing to the decomposition of the organic compounds. Simultaneously, the application of electrical discharge plasma may also lead to a diversity of physical processes such as shock wave generation, electrical fields, and ultraviolet radiation (Locke et al., 2006; Wahyudiono et al., 2012; Puliyalil et al., 2018; Wahyudiono et al., 2019). Moreover, the metal electrode erosion may also occur during the pulsed discharge plasma application to result in metal particles in nanoscale (Potocky et al., 2009). The robust introducing electrical discharge plasma in the aqueous solution media may drive to an increase in the collision of high energy electrons with molecules, as a result, the water molecules dissociation is more efficiently occur to result in the active species.
Next, the active species especially hydroxyl radicals will interact to defeat the glycine molecules to generate its derived compounds. The active species may decay the membrane glycine through the hydrogen abstraction from $\alpha$–carbon of peptide bonds $\text{–CO–NH–}$. The reaction involved in this deterioration process is complicated, since essentially every chemical compound can be produced via different reaction manners, and in this work, due to the intermediate compounds from the glycine deterioration reaction were not analyzed, the glycine deterioration reaction can be represented by the following overall reaction: glycine + hydroxyl radical $\rightarrow$ amides and carbonyls (Garrison 1987; Berger et al., 1999; Parvulescu et al., 2012). The presence of iron or titanium ions that were originated from the erosion of electrode may give an influence on the aqueous solution properties thereafter they are believed to drive and to participate to the plasma formation over an aqueous solution, and these metal ions also may improve the glycine deterioration reaction. At this condition, the generation of iron or titanium oxide particles in the aqueous solution media through the direct oxidation may occur due to the existence of hydrogen peroxide as oxygen–rich (Ashkarran et al., 2010; Kim et al., 2011; Kang et al., 2019; Haghighi and Poursalehi, 2019). Even, the iron or titanium particles also may interact with carbons generated from the glycine deterioration reaction to form iron or titanium carbide (Abdullaeva et al., 2013; Haghighi and Poursalehi, 2019). Due to the limitation of the analytical equipment, the high–resolution transmission electron microscopy analysis was not conducted to characterize the interaction between iron or titanium particles and carbon. Finally, it was expected that this brief explanation of the simple plausible reaction route may explain the synthesis of metal nanoparticles including iron and titanium by using pulsed discharge plasma in or over an aqueous solution media.

**Conclusions**

The iron and the titanium nanoparticles were successfully generated by applying a pulsed discharge plasma over an aqueous solution surface under high–pressure argon gas. The iron or the titanium rod electrode was employed as nanoparticles source. The experiments were carried out at room
temperature under pressurized argon at 3 MPa with 18.6 kV applied voltage. The UV–vis spectrophotometer indicated that the absorption between 200 – 300 and 260 nm which were originated from the titanium and iron nanoparticles were found obviously in the collected samples. The STEM–EDS revealed that the collected particle products consisted of iron or titanium, oxygen, and carbon elements. Based on the results, it could be judged that the process described herein is an innovative way and can update the information for synthesis metal–based nanoparticles by pulsed discharge plasma under argon environment.

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