ABSTRACT: Nanomaterials that comprise titanium dioxide (TiO₂) nanoparticles have received much attention owing to their wide applications; presently, the green synthesis of TiO₂ nanoparticles is a developing research area. In this study, the TiO₂ nanoparticles were synthesized through a DC-pulsed discharge plasma over an aqueous solution surface under a high-pressure argon environment. The titanium-rod electrode was utilized as the material source for the TiO₂ nanoparticle generation. Experiments were performed at room temperature with pressurized argon at 1−4 MPa. To generate a pulse electrical discharge plasma, a DC power supply of 18.6 kV was applied. The Raman spectroscopy showed that the TiO₂ nanoparticle with a brookite structure was formed dominantly. The scanning transmission electron microscopy equipped with energy dispersion spectroscopy (STEM coupled with EDS) indicated that TiO₂ coated with carbon and that without carbon coating were successfully produced at the nanoscale. The process presented here is an innovative process and can update the existing information regarding the synthesis of metal-based nanoparticles using pulsed discharge plasma under an argon environment.

INTRODUCTION

Nanomaterials comprising metal-based nanoparticles have been applied in various industrial applications such as chemical industry, food industry, cosmetics, medicine, and electronics owing to their physicochemical properties (electrical, magnetic, optical, etc.). Nanoscale materials also demonstrate high surface energy, quantum confinement, and a very large specific surface area. TiO₂ nanoparticles, as metal oxide particles, are defined as particles of TiO₂ having diameters less than 100 nm. This metal-oxide nanoparticle was also named nanocrystalline TiO₂, ultrafine TiO₂, or microcrystalline TiO₂. Titanium dioxide can be found abundantly in the Earth’s crust and possesses unique physical and chemical properties. Hence, it can have various applications such as pigments in paints, sensors, medical implants, cosmetics, and ultraviolet (UV) sunscreens. This material is also conventionally applied in smart windows, catalysis, photovoltaics, optoelectronics, batteries, fuel cells, and antifogging and self-cleaning surfaces.

As metal-based nanoparticles may have a broad range of applications in various science and technology fields, diverse methods such as biological, physical, and chemical methods have been proposed and designed for their production, including TiO₂ nanoparticle production. Physical method tends to focus on metal-based nanoparticle synthesis via the reduction of the material’s size (top-down approach), while the chemical and biological methods are focused on generating metal-based nanoparticles via atomic or molecular constructions (bottom-up approach). Various chemical synthesis methods have been used to produce metal-based nanoparticles in large amounts within a short time period, with a good adjustment in the size distribution. It is a simple and easy method to perform but, in the majority of cases, employs a toxic reagent or solvent for producing various morphologies of metal-based nanoparticles. Consequently, this method may produce contaminants and hazardous residues. In contrast, the physical synthesis methods did not comprise organic solvent contamination. Hence, this method is more advantageous than the chemical synthesis method in terms of avoiding organic solvent contamination. This method also facilitates a higher production yield owing to its comparatively fast process. The physical synthesis method may avoid the production of toxic chemicals and allow uniformity in the metal-based nanoparticle...
distribution. However, the physical synthesis method has a high production cost and provides a poor quality and smaller quantity of metal-based nanoparticles as compared to the chemical synthesis method. As a bottom-up approach, the biological synthesis method is an inexpensive and environmentally friendly method for metal-based nanoparticle synthesis. However, the existence of unwanted biological contaminants and restricted reproducibility are the main drawbacks of this method.9,10

It is known that electrical discharge plasma in liquids or in gas–liquid media, and especially water, can be used for many applications such as material (nanoparticles) synthesis, chemical synthesis, chemical liquid-solution analysis, decomposition of chemicals in pollution control, biomedical or biological treatment, and polymer processing, as this technique comprises a simple, versatile, and robust process.11–13 Herein, pulsed electrical discharge plasma generated over an aqueous solution surface was employed as a media for metal-based nanoparticles’ synthesis from titanium metal. The novelty of this work lies in the method of the particle generation from titanium metal rod, which can avoid unwanted contaminants.

RESULTS AND DISCUSSION

When the electrical discharge plasma is applied over the surface of an aqueous solution or in the aqueous solution, physical and chemical processes may occur, such as the generation of active species (active molecules and radicals).14−17 The active species include oxygen, hydrogen, hydroperoxyl radicals (oxidative species) and hydrogen radicals (reductive species), aqueous electrons, and superoxide radical anions. As the electrical discharge plasma produced active species in the gas environment near the aqueous solution surface, these active species could dissolve into the aqueous solution to generate hydrogen peroxide. The reductive species then become an important factor in the reduction reaction of metal ions into metal nanoparticles, while the oxidative species was transformed into the aqueous solution. The electrons within the area have more energy and bombarded the aqueous solution containing pyrrole at a higher speed. A similar phenomenon was also observed when Hayashi et al. performed experiments to produce carbon materials from an aqueous solution containing amino acids by applying electrical discharge plasma under pressurized argon gas.18,19 They reported that a high voltage was required for realizing the breakdown voltage for the gas at the higher-pressure conditions to generate an electric field, and an overpressure shock wave.14

In this work, the discharge plasma was directly introduced and contacted over the aqueous solution surface where the propagation of the streamer channel may occur to promote various chemical and physical processes. The reactive chemical species such as radicals (OH, H, O, and HO2) and molecular species (H2O2, HO2, and O2) may react and cleave the glycine structures containing a carboxyl group (−COOH, C==O, and −OH functional group) and an amine group (−NH2). The increasing environmental pressures may promote a shorter reaction time and a larger number of diffusive cones for generating discharge while applying the electrical discharge plasma at the surface of the aqueous solution containing glycine;15,20 the decomposition reaction rate of glycine in generating carbon materials also increases as the operating pressures increase. Although the reason for this is still unclear, it explains why carbon materials were generated only under high operating pressure. As a result, the collected aqueous solution products became darker as the operating pressures increased. Wahyudiono et al. reported that the decomposition reaction of the chemical compound increased on increasing the operating pressures when they applied the pulsed discharge plasma over an aqueous solution surface containing pyrrole.14 They reported that a high voltage was required for realizing the breakdown voltage for the gas at the higher-pressure conditions to generate an electric field, and an overpressure shock wave.14

To separate the remaining unreacted glycine from the collected aqueous solution product, it was dialyzed using a dialysis membrane (Spectra/Por3, Spectrum Laboratories Inc.,

**Figure 1.** Photographs of aqueous solution products obtained after treatment by pulsed discharge plasma under an argon environment (a) room temperature (0.1 MPa) and (b) 1.0 MPa, (c) 2.0 MPa, (d) 3.0 MPa, and (e) 4.0 MPa.
California). The pore size of the membrane was approximately 5 nm. The collected aqueous solution product was then analyzed using a UV−vis spectrophotometer. This type of analysis is generally the first technique employed for detecting the generation and existence of metal nanoparticles, including titanium, owing to the phenomenon of surface plasmon resonance. Figure 2 presents the UV−vis spectra of the collected aqueous solution products after treatment with pulsed discharge plasma under argon atmospheric pressure and pressurized argon gas (0.1, 2, and 4 MPa). It shows that the absorption between 200 and 300 nm was found to be strong under all the considered conditions of pressurized argon gas and especially at 4 MPa. These absorption peaks were probably caused by titanium oxide nanoparticles23−25 that were generated from the titanium-rod electrode consumption during the pulsed discharge experiments.12,26−30

Kolikov et al. performed the experiments with pulsed electrical discharge plasma as a disinfection in the treatment of the wastewater from the sewerage from hospitals and industries.26 They reported that the metal electrode underwent erosion owing to the pulsed electrical discharge plasma in an aqueous solution, which resulted in the generation of metal nanoparticles in the aqueous media. Saito and Akiyama reviewed the formation of metal nanoparticles using electrical discharge plasma in liquid media.12 They concluded that the solid metals introduced into the liquid media not only act as electrodes but also as metal-iod source materials for generating metal nanoparticles. Recently, Kim and Kim confirmed that the application of electrical discharge plasma in liquid media is a simple, versatile, and environment-friendly method for generating metal nanoparticles.30 Based on these researches, it could be stated that TiO2 nanoparticles have been successfully produced by the application of pulsed electrical discharge plasma over an aqueous solution containing glycine via the titanium-electrode erosion under pressurized argon gas.

To understand the generation of TiO2 nanoparticles, the collected particle products were observed using scanning transmission electron microscopy coupled with energy-dispersive spectroscopy (STEM coupled with EDS) apparatus. This tool is simple and facilitates the identification of the elements present in the collected particle products. Figure 3 presents the TEM image and the elemental composition of the TiO2 nanoparticles when the pulsed electrical discharge plasma was applied at an argon pressure of 3 MPa. The color coding of the elements in Figure 3b−d is as follows: titanium (b), oxygen (c), oxygen−titanium (d), carbon (e), and carbon−titanium (f). These images show the presence and distribution of titanium, oxygen, and carbon. In general, the electrode erosion caused by the electrical discharge plasma is an unwanted phenomenon and hence this phenomenon should be prevented in the application of pulsed discharge plasma over or in liquid solution media. However, as mentioned previously, in this work, the titanium-rod electrode erosion phenomenon was used as a material source for nanoparticle generation, and this titanium-rod electrode was placed over an aqueous solution containing glycine to generate electrical discharge plasma. Thus, the electrode erosion status is shifted from an unwanted product (contaminant) to the desired process products. It is widely accepted that pulsed discharge plasma in contact with an aqueous solution medium may initiate chemical and physical processes involving the generation of active species (molecules and radicals) and UV radiation and shock-wave generation. Hence, the potential decomposition of the glycine compound may occur during the pulsed discharge plasma application on the aqueous solution media. Even Parkansky et al. reported that eroded particles from titanium-rod electrodes during the application of electrical discharge plasma could enhance the decomposition of methylene blue in aqueous solution media.31 They explained that the decomposition rate of methylene blue was encouraged by the interaction of hydrogen peroxide with the particle...
surface to form titanium peroxide. As shown in Figure 3, oxygen and carbon were found in the collected TiO₂ particle products and appeared to be attached to the TiO₂ nanoparticle surface. These elements may have originated from the glycine molecule via its decomposition reaction during the pulsed discharge plasma application.²¹,²² It should be noted that owing to the reduction of the titanium-rod electrode, the distance between the titanium-rod electrode tip and the aqueous solution media may perhaps change, which may affect the distribution of the electric field and, thus, the distribution of the charge; therefore, the overall electrical discharge plasma was not investigated.

In this work, using ImageJ software, the particle-size distribution of the collected particle products was determined according to the TEM images. At least 300 images of different particles were randomly selected for each experimental condition. As shown in Figure 4, it was discovered that the sizes of the collected particle products were less than 100 nm. The average size of the collected particle products was approximately 50.61, 21.38, 12.24, and 7.8 nm when the experiments were performed at argon pressures of 1, 2, 3, and 4 MPa, respectively. It was observed that the increase in the operating pressures resulted in a decrease in the size and the narrowing of the distribution of the collected particle products. It was already known that increasing the operating pressure in the pulsed discharge plasma system would result in an increase in the applied bias voltage to generate the plasma.¹⁴,³² Saito et al. reported that the excitation temperature increased as the applied bias voltage was increased for various electrolyte concentrations in the plasma system.³³ They concluded that the higher applied voltage in the plasma system was effective in synthesizing small metal nanoparticles owing to the high excitation temperature. However, they also explained that the metal nanoparticle generation in the plasma system was also affected by the physical properties of the electrode material, such as its chemical stability, electrical conductivity, density, thermal conductivity, ionization energy, vapor pressure, and melting temperature. Wahyudiono et al. reported that, as the operating pressure increased, the wavelength of the pulsed discharge plasma radiation decreased, and the pulsed discharge plasma was generated by a large number of diffusive cones.¹⁴ An increase in the number of bright spots on the cathode is also observed, and these spots may be distributed uniformly over the cathode ring edges. Consequently, the species, including particles, that were ejected from the metal electrode during the pulsed discharge plasma application underwent a rapid decrease in temperature to avoid the growth of the particles.

The collected TiO₂ particle products were analyzed using Raman spectroscopy. This analysis was performed to understand the distinct chemical fingerprint that can provide information regarding the chemical bonds conjugated with the diverse molecules present in the materials, including TiO₂ particles, which are generated by the pulsed discharge plasma in the aqueous solution containing the glycine compound. This is a noncontact, nondestructive, convenient, and powerful technique that also requires pretreatments of the specimen and can be applied to a variety of materials. Figure 5 shows the typical Raman spectroscopy plot for the vibrational properties of the TiO₂ particles. Several phenomena were observed when the Raman spectroscopy analysis was used for the characterization of the TiO₂ nanoparticles. These phenomena include the symmetric stretching vibration of O−Ti−O in TiO₂, which results in the E₉ peak; symmetric bending vibration of O−Ti−O, which results in the B₁₈ peak; and antisymmetric bending vibration of O−Ti−O, which results in the A₁₈ peak.³⁴–³⁷ As shown in Figure 5a, strong Raman peaks were clearly observed at 150, 212, and 502 cm⁻¹. These Raman bands can be
associated with the Raman active modes of the brookite structural phase with the symmetries of $E_g$ for the 150 cm$^{-1}$ band and $B_{1g}$ for the 212 and 502 cm$^{-1}$ bands. Anitha et al. reviewed the recent developments in the synthesis, modification, properties, and energy-related applications of TiO$_2$ as n- and p-type transparent semiconductors. They summarized that brookite TiO$_2$ possesses several Raman active modes (nine $A_{1g}$, nine $B_{2g}$ and nine $B_{3g}$), which are assigned as follows: $A_{1g}$ (127/128, 155/156, 194, 245/246, 412, and 637/638 cm$^{-1}$), $B_{1g}$ (133, 213/214, 322/323, and 501/502 cm$^{-1}$), $B_{2g}$ (365/366, 395/396, 460/461, and 583 cm$^{-1}$), and $B_{3g}$ (172, 287/288, and 545 cm$^{-1}$). It is well known that the applied pulsed discharge plasma over an aqueous solution surface via a metal-electrode may result in a gradual metal-electrode erosion. This phenomenon may occur because the metal electrode was employed to realize the constant bombardment of high-energy electrons for maintaining the current that is transferred to the aqueous solution media. The material ejection from the surface of a metal electrode occurs to generate metal particles. In the case of titanium as an electrode, it was employed as a material source for nanoparticle generation, and it seemed that the TiO$_2$ nanoparticles with brookite structure were formed owing to the high-energy electrons bombarding the aqueous solution containing the deposited TiO$_2$ particles.

Srivatsa et al. reported the generation of brookite TiO$_2$ particles under energetic ion impact. They explained that under high applied bias voltages, the dense ions may provide sufficient energy to encourage the restructuring of the deposited TiO$_2$ particles. Furthermore, they explained that, although the deposited TiO$_2$ particles required a certain amount of energy to realize a particular structure, for instance, by raising the deposition temperature, the certain energetic condition can be realized for the particular structure generation at room temperature via the application of a bias voltage during the pulsed discharge plasma process. When the Raman spectroscopy was applied at active normal modes for the vibration of the organic molecules in the range of 400–4000 cm$^{-1}$, the Raman peaks with strong intensity at 1346, 1578, and 5447 cm$^{-1}$, which were assigned to the D band, G band, and 2D band, respectively, were clearly observed (see Figure 5b). The G band provides information regarding the bond stretching of the $sp^2$ carbon atoms, while the D band provides information regarding the breathing modes of the $sp^2$ carbon atoms. These two peaks are general for amorphous, noncrystalline, and diverse disordered forms of carbons observed in the Raman spectroscopy. This Raman spectrum indicated that the carbon materials were generated from an aqueous solution containing glycine via the application of pulsed discharge plasma under pressurized argon gas. Accordingly, the titanium and carbon atoms generated owing to the titanium electrode erosion and the glycine decomposition reaction during the application of pulsed discharge plasma may interact to generate titanium carbide (TiC) nanoparticles. As shown in Figure 6b, the HRTEM image reveals that lattice-fringe spacing of approximately 0.22–0.24 nm corresponding to the distance of the titanium carbide (111) plane was observed in the collected TiO$_2$ particle products. Hence, it could be stated that, during the application of the pulsed discharge plasma over an aqueous solution containing glycine compound via a titanium-rod electrode, there is a sufficient amount of carbon atoms to interact with the titanium atom for generating titanium carbide nanoparticles. It should be noted that the concentrations of titanium and carbon atoms, which may affect the formation reaction of titanium carbide, were not determined.

As reported by previous researchers, two phenomena are observed during the application of pulsed discharge plasma over an aqueous solution containing organic material. They include the decomposition reaction of organic materials that exist in the aqueous solution and the degradation of an electrode, which may result in the generation of metal particles at the nanoscale. Accordingly, the titanium and carbon atoms generated owing to the titanium electrode erosion and the glycine decomposition reaction during the application of pulsed discharge plasma may interact to generate titanium carbide (TiC) nanoparticles. As shown in Figure 6b, the HRTEM image reveals that lattice-fringe spacing of approximately 0.22–0.24 nm corresponding to the distance of the titanium carbide (111) plane was observed in the collected TiO$_2$ particle products. Hence, it could be stated that, during the application of the pulsed discharge plasma over an aqueous solution containing glycine compound via a titanium-rod electrode, there is a sufficient amount of carbon atoms to interact with the titanium atom for generating titanium carbide nanoparticles. It should be noted that the concentrations of titanium and carbon atoms, which may affect the formation reaction of titanium carbide, were not determined.

It has been mentioned above that the application of pulsed electrical discharge plasma in the aqueous solution media can result in the generation of strong electric fields that may result in a variety of physical and chemical processes. The main chemical process can be reflected by the various reactive-species generation in an aqueous solution media, while the most important phenomenon in the physical process is the generation of shockwaves and UV (ultraviolet) radiation.
Although the physical and chemical reactions during the application of pulsed electrical discharge plasma in an aqueous solution media are complicated, these two phenomena may promote the desirable chemical reaction and possess the ability to decompose organic compounds including glycine.\textsuperscript{14,19} The existence of radical quenchers and electrolytes in the aqueous solution media may also have an influence on the decomposition reaction rate. In addition, the conductivity of the aqueous solution media may also result in a reduction in the active-species generation and affect the pulsed electrical discharge in an aqueous solution media; conversely, it can promote a higher rate of UV radiation.\textsuperscript{14,30} The release of ions and particles owing to the metal-electrode erosion into an aqueous solution media can also influence the chemical reactions. Hence, these physical and chemical processes were expected and can explain the glycine decomposition and the interaction between the titanium particles and the glycine decomposition products during pulsed discharge plasma application over a water surface under pressurized argon gas.

The general plasma—chemical decomposition mechanism of organic compounds in aqueous solution media was initiated by the generation of chemically active species through the interaction between the electrical discharge plasma with water as a medium. The molecules of water underwent a dissociation reaction to form hydroxyl and hydrogen radicals due to the collision between the water molecules and the electrons that were generated in the aqueous solution media during the application of pulsed electrical discharge plasma. In the subsequent reactions, the electron collisions may result in diverse radicals. Hence, reactive species such as hydrogen peroxide, oxygen, and hydrogen were observed during the application of pulsed discharge plasma, although the formation of the superoxide ion as a radical reduction and that of the hydroxyl ion as radical oxidation are responsible for the decomposition of the organic compounds. Moreover, the UV radiation may also drive the dissociation reaction of hydrogen peroxide and water, which can enhance the generation of hydroxyl radicals. Thus, it can be assumed that the two major reactions that occur during the application of pulsed discharge plasma in the aqueous solution media containing glycine comprise water dissociation and hydrogen peroxide generation:\textsuperscript{14,17,51}

\begin{equation}
H_2O \rightarrow H^\ast + OH^\ast
\end{equation}

\begin{equation}
2H_2O \rightarrow H_2O_2 + H_2
\end{equation}

The intense application of electrical discharge plasma in aqueous solution media may result in an increase in the collision of high-energy electrons with molecules; hence, the dissociation of water molecules more efficiently results in the formation of reactive species. At the same time, the high-energy electrons and reactive species also interact and attack the glycine molecules, which results in its derived compounds. The hydroxyl radicals attack the membrane glycine via hydrogen abstraction from $\alpha$-carbon of peptide bonds $\text{–CO–NH}$$\cdots$. The reaction involved in this process is complex as, in principle, every chemical compound may be generated via different reaction routes. In this work, the intermediate compounds generated from the decomposition reaction of glycine were not observed. Hence, the glycine decomposition reaction was represented by the following overall reaction: glycine + hydroxyl radical $\rightarrow$ amides and carbonyls.\textsuperscript{11,52,53}

In addition to the existence of titanium ions generated from the titanium-rod electrode, erosion may affect the aqueous solution properties, and thereafter, they are believed to promote and contribute to the plasma formation over an aqueous solution; these metal ions may also enhance the decomposition reaction of glycine. This can be explained as follows. During the pulsed discharge plasma application, a significant amount of UV light was generated, which may affect the TiO$_2$ particle products that were generally considered as a catalyst in the photocatalytic processes. As a result, the decomposition reaction of glycine in the aqueous solution progresses. In this work, the plasma presence around the titanium-rod electrode, as an anode, resulted in gradual erosion during the application of the pulse voltage. The ejection of the titanium particles from the titanium-rod electrode surface into the aqueous solution media containing the glycine compound does not result in the TiO$_2$ particle generation. However, the existence of hydrogen peroxide, which is oxygen rich, in the aqueous solution media may promote the generation of TiO$_2$ particles via the direct oxidation of titanium particles.\textsuperscript{49,54–56}

The titanium particles also simultaneously interacted with the carbon generated from the glycine decomposition reaction to form titanium carbide. Furthermore, Haghighi and Poursalehi also reported that titanium carbide can be generated by the reaction between carbon and titanium dioxide under arc discharge plasma in a liquid solution.\textsuperscript{39} Based on these results, there was good evidence that the application of pulsed discharge plasma via a titanium-rod electrode over the aqueous solution containing the glycine compound may result in the generation of titanium oxide through an oxidation reaction and titanium carbide nanoparticles through the interaction between titanium and its oxide particles with carbon, which was generated through the decomposition reaction of glycine. The simple plausible reaction mechanism for the generation of the titanium carbide and titanium dioxide particles is as follows:\textsuperscript{49}

\begin{equation}
C_2H_3NO_2 + e^\ast \rightarrow C^\ast + \text{intermediate compounds}
\end{equation}

\begin{equation}
Ti + H_2O \rightarrow TiO_2 + H_2
\end{equation}

\begin{equation}
Ti + C^\ast \rightarrow TiC
\end{equation}

\begin{equation}
TiO_2 + 3C^\ast \rightarrow TiC + 2CO
\end{equation}

\section{CONCLUSIONS}

TiO$_2$ nanoparticles were successfully synthesized by applying a DC-pulsed discharge plasma over an aqueous solution surface under a high-pressure argon environment. The titanium-rod electrode was employed as the material source for the TiO$_2$ nanoparticle generation. Experiments were performed at room temperature under an argon environment (1–4 MPa). The DC power supply of 18.6 kV was applied to generate a pulsed electrical discharge plasma. The UV$–\text{vis}$ spectrophotometer indicated that the absorption occurred between 200 and 300 nm, which originated from the TiO$_2$ nanoparticles in each collected sample. The Raman spectroscopy showed that the TiO$_2$ nanoparticle with brookite structure was formed dominantly owing to the high-energy electrons bombarding the aqueous solution containing the deposited TiO$_2$ particles. The STEM coupled with EDS indicated that TiO$_2$ with and without a carbon coating was produced at the nanoscale. Finally, it can be stated that an innovative process is presented herein that can be used to update the information regarding
MATERIALS AND METHODS

Materials. All the chemicals were used as received 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 purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. The glycine compound was selected based on previous works. Argon (purity greater than 99.99%) was bought from Sogo Kariya Sanso, Inc., Japan. The aqueous solution media were prepared as follows. One hundred grams of glycine was dissolved in 1 L of distilled water and stirred (Rexim, RSH-1DR, AS ONE, Japan) for approximately 30 min at room temperature. This aqueous solution was then stored in a desiccator at room temperature. It should be noted that other types of chemicals were not applied as solution media during the course of the experiment.

Experimental Method. Figure 7 illustrates the apparatus scheme used for electrical discharge plasma generation over an aqueous solution surface under an argon environment. The autoclave was fabricated from stainless steel of a volume of 25 mL (SUS316, AKICO, Tokyo, Japan) and allowed to work at a temperature of 150 °C and pressure of 30 MPa. This autoclave was equipped with two sapphire windows to monitor the plasma generation performance. The generation of electrical discharge plasma over the aqueous solution surface was started using a titanium rod as an anode with a diameter of 1.0 mm (TI-451485, Nilaco, Tokyo, Japan), which was positioned at a distance of 3.0 mm from the surface of an aqueous solution. This titanium rod was covered by poly(ether ether ketone) (PEEK) as an insulator, and the annular space was sealed using an O-ring (Teflon) placed around the outer surface of the rod to prevent gas leakage. The distance between the aqueous solution surface and the inside wall chamber as the cathode is 3 cm. The experiment was performed as follows. Initially, the aqueous solution containing glycine (7 mL) was loaded into the autoclave manually. After the lid of the chamber was set, the autoclave was introduced during the experiments, and the pulse discharge plasma repetition rate was 4 pulses per second (pps) with a duration of 20,000 pulses. During the experiments, the digital oscilloscope (TDS2024C, Tektronix Inc., Beaverton, OR) that was equipped with a high-voltage probe and current transformer was employed to measure the breakdown voltage and current.

The collected aqueous solution products were accommodated in a vial, transferred to a spectrometric quartz cell, and analyzed using an ultraviolet—visible (UV—vis) spectrophotometer (V-550, Jasco Corporation, Tokyo, Japan). The morphology and elemental maps of titanium-based nanoparticle products were characterized using transmission electron microscopy (TEM) (JEM-2100Plus, Japan Electronic Co., Ltd., Tokyo, Japan) with energy-dispersive X-ray spectroscopy (EDS) (JEOL, JED-2300T & Gatan, GIF Quantum ER). These products were also characterized using Raman spectroscopy (NRS-1000, Jasco Corporation, Tokyo, Japan). The particle-size distribution of titanium-based nanoparticles was determined based on TEM images using ImageJ 1.42 image analysis software.

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Notes
The authors declare no competing financial interest.

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