Title:

Chromatic Control of Multicolor Electrochromic Device with Localized Surface Plasmon Resonance of Silver Nanoparticles by Voltage-step Method

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Abstract

Inorganic electrochromic (EC) materials are of interest because of their many possible applications, including use in information displays. The multifunctional EC materials that enable control of multiple colors and color depth have considerable promise as candidates for full color EC display devices. In this research, we focused on Ag nanoparticles that exhibit various colors on the basis of their localized surface plasmon resonance (LSPR). Because the LSPR band depends on the size and shape of the nanoparticles, control of the morphology of Ag nanoparticles can lead to dramatic changes in color. In order to apply this color variation for display devices, we utilized here the electrochemical formation of size-controlled Ag nanoparticles using a voltage-step method that consists of an application of two successive different voltages. In order to improve the variation of colors of the EC cell, the effect of application voltages and their times on morphology of deposited silver were investigated. The relationship between the morphology of the deposited Ag nanoparticles and color of the EC cell was discussed, and then we successfully represented multiple coloration of the EC cell with various color depth.

Introduction

Today we obtain much of our information from color images in books, on TV, or on the internet. Therefore, display devices that facilitate our visual communication are indispensable for life. Electrochromism (EC), a phenomenon of reversible color change caused by electrochemical redox reactions of material, is one of the prime candidates for full color display devices because of its various advantages, such as multicolor representation, low operation voltages, memory effects, and high visibility under sunlight.¹⁻⁵

For full color representation in EC devices, realization of three primary colors, cyan, magenta, and yellow (CMY), has been expected.⁶⁻⁸ Multicolor EC systems, displaying more than two different colors in a single cell, have attracted attention because they have the potential to improve the resolution and color quality in full color EC displays.⁹⁻¹⁷ However, most of the inorganic EC materials (*e.g.*,

WO₃) exhibit only a single color change, and in most case, inorganic EC materials exhibit darkened and cold colors.^{3, 18-21} A system that enables control of multichromatic states using only one type of EC material has rarely been reported.

To address this issue, we recently demonstrated a novel multicolor EC device showing CMY three primary colors on the basis of an electrochemical Ag deposition mechanism (Scheme 1).²²⁻²⁴ The devices for reversible electrodeposition systems are basically composed of a pair of transparent electrodes with a gel electrolyte containing Ag⁺ ion between them. The application of a negative voltage to either one of the electrodes causes the Ag metal deposition on the electrode substrate to construct metal nanoparticles or thin film that alters the optical properties of the surface. The color of the devices can also be bleached by applying voltage for oxidation of the Ag deposition, leading to the initial state of transparent condition. The improvements of the highly reversible optical changes between transparent state and colored state will open-up new applications in information displays, light shutters, and variable reflectance mirrors.

The Ag nanoparticles electrochemically deposited on an electrode exhibit various optical states based on their localized surface plasmon resonance (LSPR).²⁵⁻³¹ As LSPR bands depend on the size and shape of the nanoparticles, morphological control of the Ag nanoparticles can lead to dramatic changes in color. In order to apply this color variation for display devices, we formed electrochemically size- and shape-controlled Ag nanoparticles by varying the surface morphology of the electrode and by using a voltage-step method, which consisted of the application of two successive different voltages (Fig. 1). In this method, the first voltage V_1 is applied for a very short time t_1 to initiate Ag nucleation. The second voltage V_2 is subsequently applied for a time t_2 to promote growth of the Ag nuclei. Because V_2 is more positive than the nucleation voltage, further nucleation is not induced during t_2 . Therefore, growth of the Ag nanoparticles and the resultant color of the device is controlled by changing the time for particle growth, t_2 .³²⁻³⁴ In our previous study, magenta and cyan color states were successfully observed when Ag was deposited on flat ITO electrode by using this voltage-step method and controlling the particle growth time of t_2 .²²⁻²⁴

Although the representation of multiple colors with various color densities is expected for practical realization of EC display devices, the method to control the color depth of Ag deposition-based EC cells using step-voltage has rarely been reported. The aim of this paper is to improve the variation in the colors of the EC cell by controlling the application conditions of step-voltages. The effect of the step-voltage parameters (*i.e.*, V_1 , t_1 , and V_2) on coloration of the Ag deposition-based EC device was investigated in detail. The optical property of the EC cell with flat ITO electrodes were measured during the application of step-voltage with various voltages and application times. In addition, the relationship between the morphology of the deposited Ag nanoparticles and the color of the EC cell are investigated by field emission scanning electron microscopy (FE-SEM) analysis.

Experimental

Materials

Silver nitrate (AgNO_3), copper chloride (CuCl_2), and lithium bromide (LiBr) were obtained from Kanto Chemical Co. Inc. Dimethyl sulfoxide (DMSO) was obtained from Sigma Aldrich Japan. Poly(vinyl butyral) (PVB, $\text{MW} = 10.0 \times 10^4$) was obtained from Sekisui Chemical Co. Ltd. These reagents were used as received. An indium tin oxide (ITO) electrode (Wuhu Token Sciences Co. Ltd., $<10 \, \Omega/\square$) was used after adequate washing with pure water and acetone.

Sample Preparation and Fabrication of Electrochromic Cells

The gel electrolyte for the electrochromic cell was prepared as follows: 50 mM of AgNO_3 as the electrochromic material, 10 mM of CuCl_2 as the electrochemical mediator,³⁵⁻³⁷ and 250 mM of LiBr as the supporting electrolyte and were dissolved in 10 mL DMSO. The Cu^{2+} ion in the gel electrolyte works as electrochemical mediator for the oxidation of the Ag deposition, accelerating bleaching speed of the device. The redox process of $\text{Cu}^{2+}/\text{Cu}^{1+}$ or $\text{Br}^{3-}/\text{Br}^-$ also work as the auxiliary electrochemical reaction, which prevent degradation of the EC properties of the device, against Ag deposition and dissolutions. Subsequently, 10 wt.% of PVB as the host polymer was mixed into this DMSO-based

electrolyte solution. The electrolyte thickening by adding PVB would suppress diffusion of the oxidized species generated on the counter electrode, improving coloration properties and bleaching responses of the devices. The electrochromic cell was constructed by sandwiching the PVB-based gel electrolyte between two flat ITO electrodes, maintaining an inter-electrode distance of 500 μm with a Teflon spacer. The relatively wide inter-electrode distance of 500 μm also improve coloration properties of the device by preventing the arrival of the oxidized species to electrodeposited Ag particles. The area of the cell was $1 \times 1 \text{ cm}^2$.

Apparatus

Chronoamperometric measurements were carried out using a potentiostat/galvanostat (ALS, 660A) equipped with a computer. Absorption spectra were recorded using a diode array detection system (Ocean Optics, USB2000). The Commission Internationale de l'Éclairage $L^*a^*b^*$ (CIE $L^*a^*b^*$) values of transmitted light of the cell were recorded using a photonic multi-channel analyzer (Hamamatsu photonics, PMA-12). The white point was defined as the tristimulus value of illuminant D₆₅. The surface morphology analyses of the Ag nanoparticles deposited on the electrodes were carried out using FE-SEM (JEOL JSM-6700F).

Results and Discussion

Effects of parameter, V_I

First, the effect of the initial voltage for nucleation of Ag (V_I) on the optical properties of the EC cell was investigated. Fig. 2 shows photographs of the EC cell during application of step-voltages with various V_I values. In the case of $V_I = -2.8 \text{ V}$, the cell is colored softly and shows very pale cyan after 20 s. The color change from magenta to cyan is observed by the application of $V_I = -3.0 \text{ V}$. This color becomes vivid with increase of V_I values. On the other hand, the hue is nearly independent of V_I , *i.e.*, during the application of various V_I values, the cell shows similar hues at the same application time of t_2 .

For quantitative characterization of these coloration properties, $L^*a^*b^*$ values were estimated from the transmittance spectra of the cell. Fig. 3(a) shows the time transitions of a^*b^* coordinates of the EC cell during the application of step-voltages with various V_I values. In the case of $V_I = -2.8$ V, the a^*b^* plots rotate in a clockwise direction with a small radius. The L^* values show a less of change, as shown in Figs. 3(b) and (c). When V_I is increased from -2.8 V, the track of a^*b^* plots show similar tendency of clockwise transition (Fig. 3(a)). On the other hand, the values of a^* and b^* increase and the tracks form large archs when V_I is increased. The L^* values also largely change with the increase of V_I . These results are in agreement with the color changes observed in Fig. 2. Therefore, V_I is effective for controlling the color depth.

Time transitions of the current were analyzed under an application of step-voltage with various V_I values. The currents observed in the nucleation process increase with an increase of V_I , as shown in Fig. 4(b). This indicates that the nucleation process is not limited by the diffusion of Ag^+ ions during this short application time ($t_I = 20$ ms). Fig. 4 also shows the charge amounts for the Ag deposition, calculated by subtracting the current for the charge of the electric double layer from that of the EC cell, according to the discussion in the Supporting Information (Fig. S1). Estimated charge amounts for the Ag nucleation process increase linearly with the increase of V_I (Fig. 4(d)). Therefore, the amount of deposited Ag and the number of nuclei are expected to increase depending on V_I .

Although the second voltage values are the same for all of the step-voltages, the currents and charge amounts measured in the particle growth process vary depending on V_I (Fig. 4(c) and (e)). This suggests that the increase in the number of nuclei (*i.e.*, the reaction areas for Ag deposition during the particle growth process), depend on the V_I values. The particle growth process reflects the changes in the nucleation conditions.

In order to investigate the mechanism for the appearance of color variation depending on V_I , as discussed above, FE-SEM analysis of the electrodeposited Ag nanoparticles was performed. Fig. 5 shows the FE-SEM images of deposited Ag nanoparticles by the application of step-voltages with various V_I values. The mean particle diameter and the particle densities are determined from Fig. 5

and summarized in Table 1 and Fig. 6. The density of the particles increases 1.5 times during the increase of V_1 from -3.6 V to -4.2 V (Fig.6 (b)). This increase in the number of the nuclei leads to the strong colors of the cell.

It is known that a size, shape, and connection of metal nanoparticles have a large effect on their LSPR band and resultant color.^{25,26,31,38} However, the mean particle diameters observed after 5 s do not indicate a large difference in the degree of growth, as shown in Fig. 6(a). The sizes of the Ag nanoparticles after application of V_1 are estimated from the charge amount and are similar for all the V_1 values, as shown in Table S1 in the Supporting Information. This indicates that the value of V_1 does not influence the nuclei size, and these nuclei are expected to grow uniformly under a low V_2 . In addition, most of the Ag nanoparticles are not connected with adjacent particles in any application conditions of V_1 . Therefore, V_1 has little effect on the size of the nuclei, and the dominant factor in determining the size, shape, or connection of deposited Ag is t_2 . This is the reason for the same hue of the cells at the same application time of t_2 .

In conclusion, the nucleation number, and the resultant depth of color, is well controlled by V_1 . Furthermore, the hue is controlled by only t_2 because V_1 does not have much influence on the particle size and the connectivity of the deposited Ag.

Effects of parameter, t_1

Changes in the application time of the first voltage (t_1) are expected to control the number of nuclei along with changes of V_1 . However, the color changes of the EC cell during the application of step-voltages with various t_1 values (Fig. 7) are significantly different in comparison with Fig. 2. When a step-voltage with a short t_1 (< 30 ms) is applied to the cell, the color changes from magenta to blue or cyan. Unlike the case in which V_1 is changed, the hue of the cell changes significantly as t_1 is increased. In the case of $t_1 = 50 \sim 100$ ms, the cell rapidly turns to purple. In addition, the cell shows only dark violet when $t_1 = 200$ ms.

Fig. 8(a) shows the time transitions of a^*b^* coordinates of the EC cell during the application of a

step-voltage with various t_l values. In the case of a short t_l of 10 ms, the b^* value increases within the first few seconds, and the a^*b^* plots rotate in a clockwise direction with a large radius. The rise of the b^* values observed earlier when voltage was applied, is determined with an increase of t_l . When t_l was 80 ms or longer, the b^* value decreases from the beginning of the voltage application. The track of a^*b^* plots are different between the times that are longer and shorter than 50 ms. This result indicates that t_l affects the hue of the cell significantly and short t_l values (< 20 ms) are effective for the appearance of magenta and cyan.

Fig. 9 shows the time transitions of the current during the application of a step-voltage with various t_l values. The current of the cell decreases with time and remains constant at -20 mA after 100 ms (Fig. 9(b)). This is characteristic current in diffusion-controlled deposition.³⁹ Therefore, the deposition process during nucleation transitions to diffusion-controlled mechanisms within about 100 ms. The charge amounts for Ag deposition during the nucleation process increases with an increase of t_l (Fig. 9(d)). However, unlike its relationship with V_l (Fig. 4(d)), the charge amount does not vary linearly with t_l . This is because the deposition rates are under the control of diffusion when t_l is long.

The charge amount measured during the particle growth process also varies as t_l is increased (Fig. 9(e)). However, the degree by which the charge amount increases is lower when t_l exceeds 50 ms. The particle growth process is influenced significantly by changes in the nucleation conditions. For long t_l values, the amount of deposited Ag and the number of nuclei are limited by the diffusion rate of Ag^+ ions. This is the cause for the small increase in charge amount observed when t_l is long, as shown in Fig. 9(e).

Fig. 10 shows the FE-SEM images of Ag nanoparticles deposited by the application of step-voltages with various t_l values. From these FE-SEM images, we analyzed the density of total particles, isolated particles, and connected particles (Table 2 and Fig. 11). The number of total Ag nanoparticles increases with an increase of t_l . However, in spite of the application of the step-voltage with 10 times longer t_l , from 20 to 200 ms, and a 5.6-fold increase in the charge amount, the density of Ag particles only increases by 10 % (from 7.04 to $7.74 \times 10^{10} \text{ cm}^{-2}$). This is due to the limited rate

of Ag deposition in the nucleation process by diffusion control, as discussed above. In addition, the growth of Ag nuclei progresses during the long period of t_1 and suppresses further nucleation. In contrast to the change in diameter associated with changes to V_1 , the estimated diameter after the application of V_1 increases as t_1 increases (Table S2 in supporting information). This indicates that the nuclei grow during t_1 , causing non-uniformity of particle size and particle connections.

Most Ag nanoparticles are not connected with the adjacent particles for $t_1 = 20$ ms, whereas the ratio of connected particles increases with the increase of t_1 (Fig. 11). The connected particles are shaped like nanorods. These anisotropic nanostructures have the LSPR band at longer wavelengths in comparison with nanospheres.^{25,26} The LSPR peak wavelengths observed after 5 s, shift to longer wavelengths (about 60 nm) as t_1 increases from 20 ms to 200 ms (Fig. 12). In addition, the absorption spectra broaden because of the wide distribution of size and shape of the Ag nanoparticles, resulting from the growth of nuclei and the connection of particles. For this reason, the hue of the cell varies and the cell shows dull colors as t_1 increases.

In conclusion, the increase of t_1 promotes the connection of particles and the resulting dull color representation. Therefore, a short t_1 is effective for the deposition of isolated particles and the appearance of vivid colors.

Effects of parameter, V_2

Finally, the effects of V_2 were evaluated. The colors of the EC cell during the application of step-voltages with various V_2 values are shown in Fig. 13. When a small growth voltage of $V_2 = -1.4$ V is applied to the cell, the color changes do not occur over entire area of the cell. Although -1.4 V is more negative than the critical voltage for particle growth (-1.3 V),²⁴ the cell does not change color after application of the second voltage. This is due to the re-dissolution of Ag nuclei by switching the applied voltage from V_1 to V_2 , which is more positive than V_1 . In the case of $V_2 = -1.6$ V, the cell shows a color change from magenta to cyan. Furthermore, the color of the cell becomes dull with the increase in V_2 . Therefore, a large V_2 value inhibits bright coloration.

The time transition of $L^*a^*b^*$ values of the EC cell during the application of a step-voltage with various V_2 values were also measured. In the case of $V_2 = -1.4$ V, the a^*b^* plots vary only slightly (Fig. 14 (a)). The L^* values also show little change, as shown in Figs. 14(b) and (c). When $V_2 = -1.6$ V, the a^* and b^* values show a large increase, and the a^*b^* plots rotate in a clockwise direction with a large radius. The L^* values also largely change when $V_2 = -1.6$ V. In addition, the values of a^* and b^* decrease and the plots, as shown in Fig. 14(a), form a small arch with the increase in V_2 . It is suggested that a large V_2 promotes dull and dark color representation.

The time transitions of the current by the application of a step-voltage with various values of V_2 were also measured. The currents and charge amounts observed in the nucleation process are similar in all step-voltages because the parameters of V_1 and t_1 are same (Figs. 15(b) and (d)). When the voltage is switched from V_1 to V_2 (20 ms), the instantaneous oxidation current was observed. This oxidation current increases depending on the decrease of V_2 , in other words, depending on the difference of applied voltage between V_1 and V_2 . This oxidation current is due to the discharge of the electric double layer and the re-dissolution of Ag nuclei by switching the applied voltage into a more positive value.³² When a relatively positive V_2 is applied, re-dissolution of part of the Ag nuclei occurs and the cell cannot change color, as shown in Fig. 13, for condition of $V_2 = -1.4$ V.

The current and charge amount measured in the particle growth process vary depending on V_2 , as shown in Figs. 15(c) and (e). The particle growth is accelerated during the application of a large V_2 .

Fig. 16 shows FE-SEM images of Ag nanoparticles deposited by the application of step-voltages with various V_2 values. When $V_2 = -1.6$ V, the deposited Ag nanoparticles are almost isolated, and do not connect with other particles. On the other hand, when $V_2 = -1.8$ V, most of Ag nanoparticles are connected with each other, and complex shapes are formed. This is due to an accelerated particle growth rate by the large V_2 , resulting in a dark and dull color representation.

All conditions for the electrodeposition of Ag discussed above, the device held its colored state during several periods (ex. magenta and cyan state kept its color for 4 s and 25 s, respectively) after the application of the voltage shut off. But the color gradually changed to transparent. This color

disappearance is caused by an effect of Cu^{2+} ions contained in the gel electrolyte which mediate the oxidation of the Ag deposition. In order to hold the device colors, it is necessary to maintain the size and shape of deposited Ag nanoparticles. The investigation for the keeping of the same color is now in progress. In present, it was confirmed that the device held its colored states for a longer period of time by a successive application of rectangular wave with appropriate duty rate after an application of voltage.

Conclusion

The effects of step-voltage parameters on the coloration of the Ag deposition-based EC cell were investigated. The optical properties of the EC cell with flat ITO electrodes were evaluated during the application of step-voltage using various voltages and application times. The number of nuclei, and the resultant depth of the cell color, is well controlled by the value of the first-voltage for nucleation, V_1 . Furthermore, V_1 does not have much influence on the particle size or the connection of deposited Ag. The hue is controlled by t_2 . The application time of the first voltage, t_1 , also influences the nucleation condition. The increase in t_1 promotes the growth of nuclei and the connection of particles, resulting in a dull color representation. The rate of particle growth and connection is accelerated by a large growth voltage of V_2 and leads to a dark and dull color representation. Therefore, a short t_1 and a small V_2 are effective for the deposition of isolated particles and the appearance of vivid colors. In summary, we successfully demonstrated the representation of multiple colors with various color depth by controlling the parameters of a step-voltage. The multifunctionality of this EC device is expected to be suitable for use in information display devices such as electronic paper and digital signage.

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Figure captions:

Scheme 1 Schematic illustration of the LSPR-based EC device with Ag deposition.

Fig. 1 Schematic representation of the voltage-step method. The first voltage V_1 is applied for a brief time t_1 to form nucleation sites. Application of V_1 is immediately followed by the application of a second voltage V_2 for a time t_2 . V_2 is more positive than the nucleation voltage and promotes particle growth without further nucleation.

Fig. 2 Photographs of the EC cell during the Ag deposition process under an applied step-voltage with various parameters of V_1 . $V_1 = -2.8 \sim -4.2$ V, $t_1 = 20$ ms. $V_2 = -1.6$ V, $t_2 = 0 \sim 20$ s.

Fig. 3 (a) a^*b^* coordinates, (b) $L^*a^*b^*$ three-dimensional coordinates, and (c) plots of L^* vs. V_1 of the EC cell during the Ag deposition process under an applied step-voltage with various V_1 values. $V_1 = -2.8 \sim -4.2$ V, $t_1 = 20$ ms. $V_2 = -1.6$ V, $t_2 = 0 \sim 20$ s.

Fig. 4 Time transition of deposition current during the application of a step-voltage with various V_1 values. (a) Currents observed during all reaction time. (b) Extended figure during the nucleation process. (c) Extended figure during the particle growth process. Charge amounts for Ag deposition during (d) the nucleation process (~ 20 ms) and (e) all deposition process (~ 20 s) by the application of a step-voltage with various values of V_1 . $V_1 = -2.8 \sim -4.2$ V, $t_1 = 20$ ms. $V_2 = -1.6$ V, $t_2 = \sim 20$ s.

Fig. 5 FE-SEM images of deposited Ag by the application of a step-voltage with various V_1 values. $V_1 =$ (a) -3.6 V, (b) -3.8 V, (c) -4.0 V, or (d) -4.2 V, $t_1 = 20$ ms. $V_2 = -1.6$ V, $t_2 = 5$ s.

Fig. 6 (a) Mean particle diameter, and (b) density of particles, as observed in Fig. 5.

Fig. 7 Photographs of the EC cell during the Ag deposition process under an applied step-voltage with various values of t_I . $V_I = -4.0$ V, $t_I = 10 \sim 200$ ms. $V_2 = -1.6$ V, $t_2 = 0 \sim 20$ s.

Fig. 8 (a) $a*b*$ coordinates, (b) $L*a*b*$ three-dimensional coordinates, and (c) plots of L^* vs. t_I of the EC cell during the Ag deposition process under an applied step-voltage with various values of t_I . $V_I = -4.0$ V, $t_I = 10 \sim 200$ ms. $V_2 = -1.6$ V, $t_2 = 0 \sim 20$ s.

Fig. 9 Time transition of deposition current by the application of step-voltage with various values of t_I . (a) Currents observed during all reaction time. (b) Extended figure during the nucleation process. (c) Extended figure during the particle growth process. Charge amounts for Ag deposition during (d) the nucleation process ($\sim t_I$ ms), and (e) all of the deposition processes (~ 20 s) by the application of step-voltage with various values of t_I . $V_I = -4.0$ V, $t_I = 10 \sim 200$ ms. $V_2 = -1.6$ V, $t_2 = \sim 20$ s.

Fig. 10 FE-SEM images of deposited Ag by the application of a step-voltage with various values of t_I . $V_I = -4.0$ V, $t_I =$ (a) 20 ms, (b) 100 ms, or (c) 200 ms. $V_2 = -1.6$ V, $t_2 = 5$ s.

Fig. 11 Number density of particles observed in Fig. 10.

Fig. 12 Absorption spectra of the EC cell during the Ag deposition process under an applied step-voltage with various values of t_I : (a) 20 ms, (b) 100 ms, and (c) 200 ms. $V_I = -4.0$ V. $V_2 = -1.6$ V, $t_2 = 5$ s. The peak wavelengths of these spectra are (a) 520 nm, (b) 550 nm, and (c) 578 nm.

Fig. 13 Photographs of the EC cell during the Ag deposition process under an applied step-voltage with various values of V_2 . $V_I = -4.0$ V, $t_I = 20$ ms. $V_2 = -1.4 \sim -2.0$ V, $t_2 = 0 \sim 20$ s.

Fig. 14 (a) $a*b*$ coordinates, (b) $L*a*b*$ three-dimensional coordinates, and (c) plots of L^* vs. V_2 of

the EC cell during the Ag deposition process under an applied step-voltage with various values of V_2 .
 $V_1 = -4.0$ V, $t_1 = 20$ ms. $V_2 = -1.4 \sim -2.0$ V, $t_2 = 0 \sim 20$ s.

Fig. 15 Time transition of deposition current by the application of step-voltage with various values of V_2 . (a) Currents observed during all reaction time. (b) Extended figure during the nucleation process. (c) Extended figure during the particle growth process. Charge amounts for Ag deposition during (d) the nucleation process (~ 20 ms) and (e) all deposition process (~ 20 s) by application of step-voltage with various V_2 values. $V_1 = -4.0$ V, $t_1 = 20$ ms. $V_2 = -1.4 \sim -2.0$ V, $t_2 = 20$ s.

Fig. 16 FE-SEM images of deposited Ag by the application of a step-voltage with various values of V_2 . $V_1 = -4.0$ V, $t_1 = 20$ ms. $V_2 =$ (a) -1.6 V and (b) -1.8 V, $t_2 = 5$ s.

Table captions:

Table 1 Mean particle diameter and density of particles, as observed in Fig.5.

Table 2 Number density of particles observed in Fig. 10.

Scheme1 Tsuboi et al.

Fig. 1 Tsuboi et al.

Fig. 2 Tsuboi et al.

Fig. 3 Tsuboi et al.

Fig. 4 Tsuboi et al.

Fig. 5 Tsuboi et al.

Fig. 6 Tsuboi et al.

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Table 1 Tsuboi et al.

V_I (V)	Mean particle diameter (nm) ^[a]	Density of particles (cm ⁻²)
-3.6	25.1±5.3	5.0×10 ¹⁰
-3.8	26.2±5.9	6.6×10 ¹⁰
-4.0	25.5±4.1	7.0×10 ¹⁰
-4.2	28.3±5.7	7.4×10 ¹⁰

^[a] average ± standard deviation

Table 2 Tsuboi et al.

t_I (ms)	Density of total particles (×10 ¹⁰ cm ⁻²)	Density of isolated particles (×10 ¹⁰ cm ⁻²)	Density of contacted particles (×10 ¹⁰ cm ⁻²)
20	7.04	5.19 [73.8%] ^[a]	1.85 [26.2%] ^[b]
100	7.42	2.19 [29.5%] ^[a]	5.23 [70.5%] ^[b]
200	7.74	2.63 [34.0%] ^[a]	5.10 [66.0%] ^[b]

^[a] Proportion of isolated particles to total particles. ^[b] Proportion of contacted particles to total particles.