

Deposition of TiO₂ nanoparticles in surfactant-containing aqueous suspension by a pulsed DC charging-mode electrophoresis

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A pulse electrophoresis method was designed for depositing TiO₂ nanoparticles on a metal substrate inside an aqueous suspension. The suspension was prepared by mixing the commercially available nanometer-sized TiO₂ powders (P25, Degussa) with an organic surfactant in water. A suspension with relatively high concentration (30 wt%) is stable for a few months; therefore it was not necessary to place an additional mixing during the deposition process. In the range of 2.5 to 40 Hz, the pulse direct current (PDC) charging type electrophoretic with a maximum applied voltage of 54 V (50% duty cycle) could narrow the particle size distribution or dispersity of TiO₂ particles depositing on the surface of a stainless steel electrode. The morphology of the TiO₂ nanoparticles layer deposited by PDC charging-mode was finer than those was deposited by a direct current (DC) charging mode.

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1. Introduction

Deposition or coating of nanoparticles on various types of solid surface had given a great impact on current ceramics technology and its application. Nano ceramics material such as TiO₂ has been recognized for its beneficial characteristic in becoming strong oxidizing agent which most organic compounds can be oxidized to carbon dioxide at ambient temperature and pressure.¹⁾ As a result, coating of TiO₂ on complex shape's filter material such as stainless steel will give a great promise for air and water purification.²⁾ Instead of enhancing the purpose of the metal filter, the advantage of TiO₂ as corrosion protective material also made it a suitable candidate for metal coating.³⁾ Electrophoretic deposition (EPD) or electrophoresis is known to be one of the promising methods to form a ceramic layer from a particle suspension. In comparison with other methods of depositing nanoparticles such as dip coating and spin coating,^{4),5)} EPD has the advantages of low application cost, high deposition rate and less particle wastage, which is always preferable. During EPD, charged particles dispersed or suspended in a liquid medium are attracted and deposited onto a substrate surface of opposite charge under the influence of an electric field.^{6),7)}

Deposition conducted using an aqueous suspension has a few issues compared to a non-aqueous suspension such as bubble formation due to the electrochemical process therein.⁸⁾ However, a deposition process using an aqueous medium is very important due to its environmental acceptability. Thus, this approach has been selected in this study. Unfortunately, the organic surfactant

(dispersant) which plays a key role in dispersing and suspending nanoparticles in an aqueous or non-aqueous suspension moves together with the deposit particles during deposition process hence it brings in non-uniform particle size and it creates saturated layer on the vicinity of the electrode. As a result, wide particle size distribution will deposit on the surface of the substrate and non-uniform particle size could not be obtained.^{6),9),23)} These drawbacks also cause transient chemical or physical barrier layers during transporting of particles and ions onto the electrode surface^{4),10),11)} which halt the particles that are moving towards the electrodes and reduce the deposition rate.

EPD method by pulse direct current (PDC) has been reported to be suitable for depositing oxide and carbide particles.^{14),18),21)} Furthermore, this method can achieve transportation leading selective particle growth in a uniform size.^{7),13),15),16),20)} However, most of the methods developed by previous workers were independence of particle stability and were absolutely a need agitation. In general, an additional mixing operation (e.g. agitation and stirring) is necessary during EPD since the stability of a suspension cannot be maintained for a long of operation without a surfactant or a highly Brownian motion (if they are electrostatic stabilization). This condition makes a comparative study between the charging modes (pulse vs non-pulse) and the effect on the deposition rate as well as the morphology of deposited particle layer still unclear and requires a further investigation.

In the present study, an electrophoresis technique with PDC was designed to deposit TiO₂ nanoparticles inside a high concentration and stable suspension onto submillimeter metal wire. A high-stability particle suspension will allow us to investigate the relation between charging-mode and the morphology of the deposit particles under no influence of additional mixing

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involved during particles deposition. Furthermore, one may expect that the pulse-mode charging electrophoresis can provide size-selective deposition by selecting the particles with a smaller size (or narrower size distribution) inside the high-stability particle suspension.

2 Experiment methods

2.1 Preparation of bath media

Bath media were prepared using a surfactant-assisted TiO_2 suspension ($\text{TiO}_2\text{-SA}$) from TAM Network Co., Ltd., Tokyo. A milky white color suspension consisting of P25–Degussa TiO_2 particles was stable although the suspension was kept for several months. The TiO_2 nanoparticles used in this study were bead-milled with a selective surfactant in order to make the combination of TiO_2 -surfactant become a stable suspension. No agitation was conducted in this study. The weight ratio of TiO_2 to the surfactant as received was 1 to 60 with 30 wt% of TiO_2 particles. Bath media with different concentrations were prepared by diluting the received suspension with ultrapure water to obtain 15 and 7.5 wt% of TiO_2 . Prior to the deposition process, the media were sonicated for 20 min to avoid fouling on the wall surface. The particle size distribution of each medium was measured using a dynamic light scattering (DLS) analysis (Malvern Instruments, HPPS 5001).

Stainless steel wire (SUS316) with 250 μm diameter was used as a substrate, which was placed as a cathode and treated in a pretreatment stage. The substrate in this stage was submerged in sulfuric acid (0.1 M) at 50°C and was sonicated for 10 min. It was then rinsed with water for 5 min and sonicated in acetone for 2 min. An aluminum plate with a dimension of $50 \times 15 \text{ mm}^2$ was used as a counter electrode (anode). Both electrodes were then submerged into TiO_2 -SA suspension.

2.2 Particle deposition and heating

Each electrode was submerged into the prepared media with a 3 cm distance at $26 \pm 2^\circ\text{C}$. A pH probe was placed in the bath to monitor the pH value before and after deposition. Electrophoretic deposition (EPD) with DC voltage up to 54 V was applied during the deposition. An in-house built circuit, cali-

brated with digital electrometer (Keithley Instrument Inc., Keithley 617) and an oscilloscope (Texttronix Inc., TDS 2002B), was used to control the pulse current and to measure the current density. The frequency of each pulse cycle, was varied from 2.5 to 40 Hz was kept constant for each bath. A data logger (Graphtec Corp., GL200) was used to record in-situ outputs of the average current density from the cathode. Pulse time intervals or frequencies were controlled by a field-effect transistor (FET), being assisted by an optical coupled. These combinations between the working electrophoretic bath and the circuit enable determine actual speed and altitude of each pulse during the deposition. The detail of the whole apparatus is illustrated in **Fig. 1**.

The deposition process was conducted up to 5 min by using PDC. For comparison, another deposition process was conducted by applying a continuous direct current (DC) and an isolated reference substrate was placed inside the media without applying any voltage.

The deposited substrate was heated to 550°C for 4.5 h with a heating rate of 2.5°C/min in a furnace to evaporate any organic or volatile components. Temperature above this point was not desirable because of the possible transformation of the anatase phase in the TiO₂ particles will transformed to the rutile phase,⁵⁾ which would cause substrate contamination¹⁹⁾ and grain growth.²²⁾ Grain growth, cause the change in mechanical property and weaken the adhesion force of deposit ceramic layer.

2.3 Characterization

Crystal phase characteristics of the TiO₂ films deposited on the substrate after heating were determined using X-ray diffraction (XRD) (X-ray diffractometer, Rigaku Co.). The film morphology was characterized using field emission scanning electron microscopy (FE-SEM) (JEOL Ltd., JSM 6335F). Energy dispersive spectroscopy (EDS) (JEOL Ltd., JED-2200F) was used to detect metal element in the substrate components such as Ti, Fe, Cr and Ni on the deposited surface.

3. Results and discussion

3.1 Particle size distribution

Diluting of as receive TiO_2 -SA makes particles agglomerated,

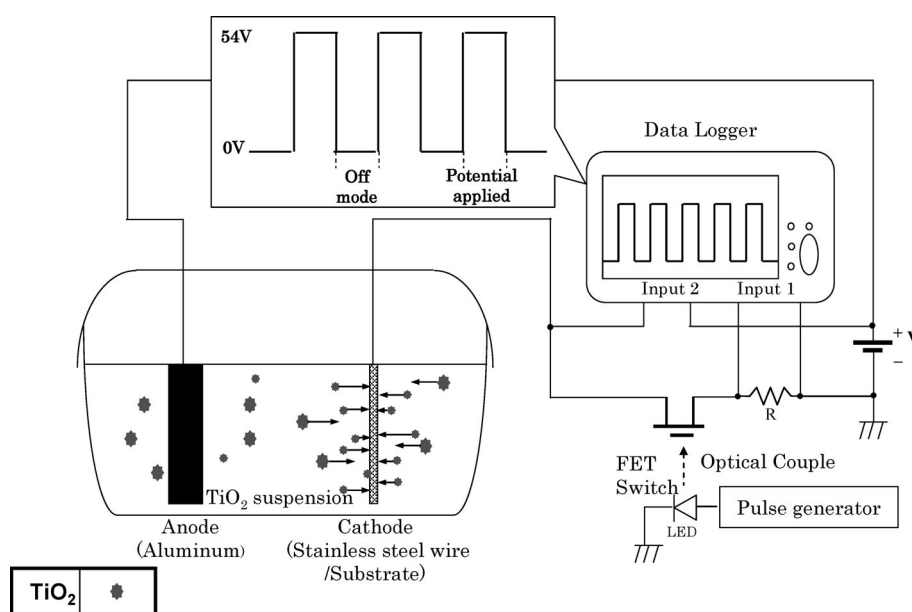


Fig. 1. Schematic illustration of pulse circuit generator and working electrophoretic bath.

because reduction of surfactant per volume decreases due to the dilution of the medium and a slightly increase in the pH from 2.79 to 3.24. A plot of the particles intensities versus the size at different concentrations, displayed in Fig. 2, shows that the concentration at 30 wt% have smaller particles size than those at 15 and 7.5 wt%. Dilution during deposition is necessary, since it plays an important role in the study of particle deposition rate. Particles with various sizes deposit at different rates depending on the volume fraction of solids in the suspension. Particles deposit at an equal rate only if the suspended particles have a uniform surface charge and so diluted that they can deposit at their individual electrophoretic mobility.³⁾ In this study, suspension dilution was conducted at their critical or adequate values so that no agitation was needed during the deposition.

3.2 Current density

Figure 3 shows the current density versus the deposition time. The observed current density in Fig. 3 during the DC charging mode shows particle deposits and surfactant interference surrounding the substrate area. Similar phenomena have also been reported for non-conductive nanoparticles such as α -Y₂Si₂O₇.¹⁰⁾ The decrease in the current density with the deposition time from 0.1 to 0.02 A/cm² indicates that TiO₂ particles, which are non-conductive reduce the substrate conductivity as they screening the substrate surface. Unfortunately, the surfactant, bonded to the TiO₂ surface goes together with the deposit particles during deposition hence creates saturated cloud of surfactant-covered TiO₂ particles at the substrate vicinity. The density of the saturated cloud increase as more particles and surfactant move to the substrate vicinity. Under this condition, high concentrations of the particles and the surfactant surrounding the electrode area lower

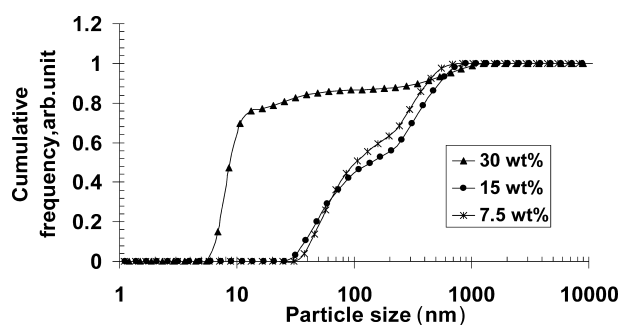


Fig. 2. Cumulative particle size distribution of different media concentrations from dynamic light scattering (DLS) analysis shows suspended particle size reduce as dilution conducted from 30 to 15 and 7.5 wt%.

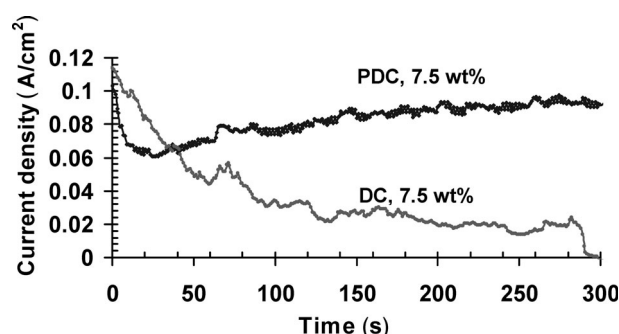


Fig. 3. Current density comparisons as different charging technique is applied during EPD. TiO₂ concentration was kept at 7.5 wt% with 40 Hz time interval during the deposition.

as the deposition goes on. However, most of the particles and the surfactant screen only the substrate surface but do not directly contact the surface thus creating a packed transient cloud as deposition goes on. These surfactant-covered TiO₂ particle cloud or the particles remaining in the suspension also prevent the incoming deposit particles from approaching the substrate and hence decrease deposit rate.

This situation can be avoided once the PDC charging mode is conducted. Higher deposition rate in conductivity decrease indicates the suspended particles deposit faster than the DC charging mode during deposition. As deposition time goes on, current density will slowly become flat for a few seconds and suddenly start increasing. The increasing on current density is due to the continuously interaction by ion or deposited particles at the substrate surface. During this condition, the diffusion of particles cloud slowly occurred due to osmosis and electro-osmosis phenomena thus give some space at the electrodes vicinity. These spaces give more opportunity to water molecule and TiO₂ particles getting contact with substrate surface hence increase the current density after several minutes of EPD. The phenomena can be well understood if we focus on electro-osmosis and osmosis phenomena during deposition process.^{12),17)} These phenomena could not be observed when PDC charging mode is conducted at a higher suspension concentration, i.e. at a smaller agglomerate size (Fig. 4). By combining these two figures, we can make a hypothesis that water and particles contact at the substrate surface occurred back after several minutes only at the PDC charging mode. Electro-osmosis or osmosis phenomena could not be observed if stirred or agitated bath is conducted.

Figure 4 shows current density behavior as bath concentration increase from 7.5 to 15 and 30 wt% when the PDC charging mode is applied. The decrease on current density can be ascribed to the low water contains at higher concentration. A small amount of water contains inside the bath limit the particles and ion movement surrounding the electrodes hence lower the contact with the electrode surface thus made the current density slowly decrease.

3.3 Surface morphology

From the observation on dried TiO₂ deposit substrate (Figs. 5(c) and 5(d)), it is clear that particles with size a distribution less than 100 nm was deposited either by using the DC or PDC charging mode. However, the PDC charging mode yields finer grain and a more homogenous surface due to higher instantaneous current density at each pulse than that by DC charging mode. Figures 5(a) and 5(b) show the treated substrates without any deposit

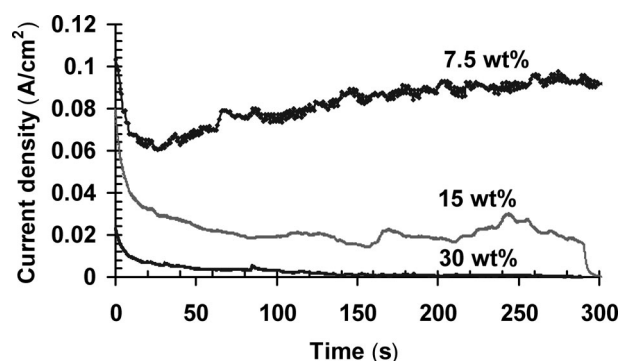


Fig. 4. Current density comparisons as media concentration increase by using PDC charging mode at 40 Hz.

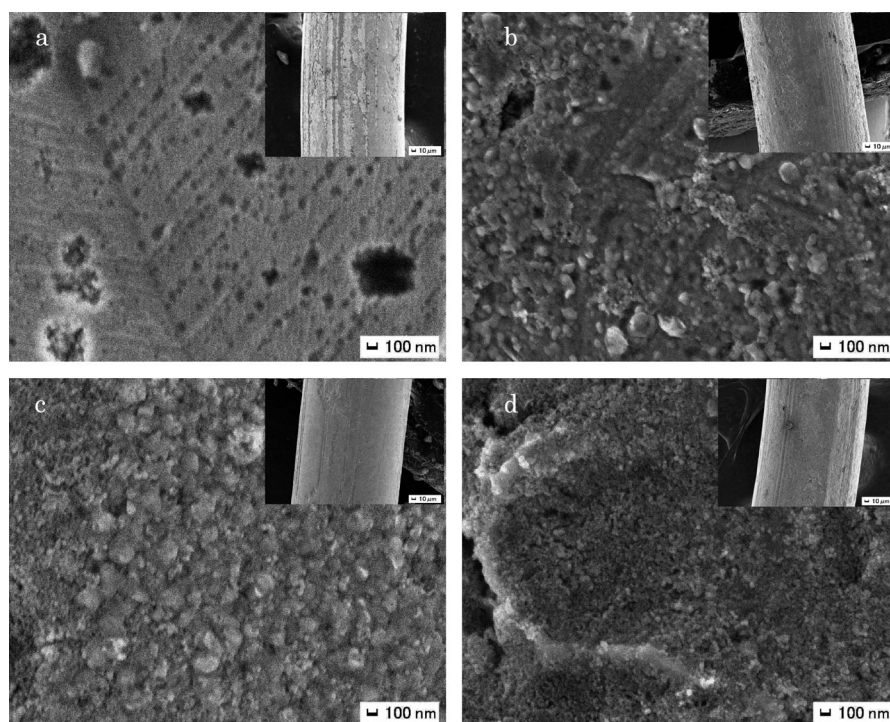


Fig. 5. FE-SEM image on (a) Treated substrate (before deposition), (b) Fully submerge substrate (without voltage apply), (c) TiO₂, 7.5 wt% deposited by DC charging mode and (d) TiO₂, 7.5 wt% deposited substrate by PDC charging mode, 40 Hz. Image of the whole substrate (10 μ m scale) was on the top right of each picture.

layer and the reference substrate, respectively.

When the potential was applied in PDC charging mode, all particles were attracted to the substrate surface due to different surface charge. However, isolate primary particles which have smaller size, i.e higher mobility, deposited faster than the agglomerate particles. In this condition, the vicinity of the substrate was suddenly congested with the surfactant and TiO₂ particles. The off-mode (no voltage applied) condition gives a more space at the substrate vicinity due to the osmosis. In this condition water molecules move towards substrate vicinity, while some particles move in the opposite way. Clouds of surfactant and TiO₂ particles were slowly scattered due to water penetration, thus give a more space at the substrate vicinity. When the potential was restored after the off-mode stage, smaller or isolated primary particles tend to be deposit first than agglomerate particles due to their low resistance. By increasing the pulse interval time up to 40 Hz, agglomerated particles which have higher resistance will not have enough time to be deposit compare with smaller or isolated primary particles.

3.4 Element analysis

A further analysis on the same sample by EDS revealed that the PDC charging mode at 40 Hz interval was more favorable because it gave higher TiO₂ deposit than by the DC charging mode. An EDS analysis showed that the concentration on Fe, Cr and Ni atoms normally available in an ordinary stainless steel material decrease as TiO₂ particles were deposited onto the substrate surface (Fig. 6 and Table 1). The decrease of the X-ray energy peak on the substrate elements was due to the TiO₂ particles that covered the substrate surface as deposition occurs. Fully submerged substrate, which acts as reference, showed deposit of TiO₂-SA particles even when no potential was applied.

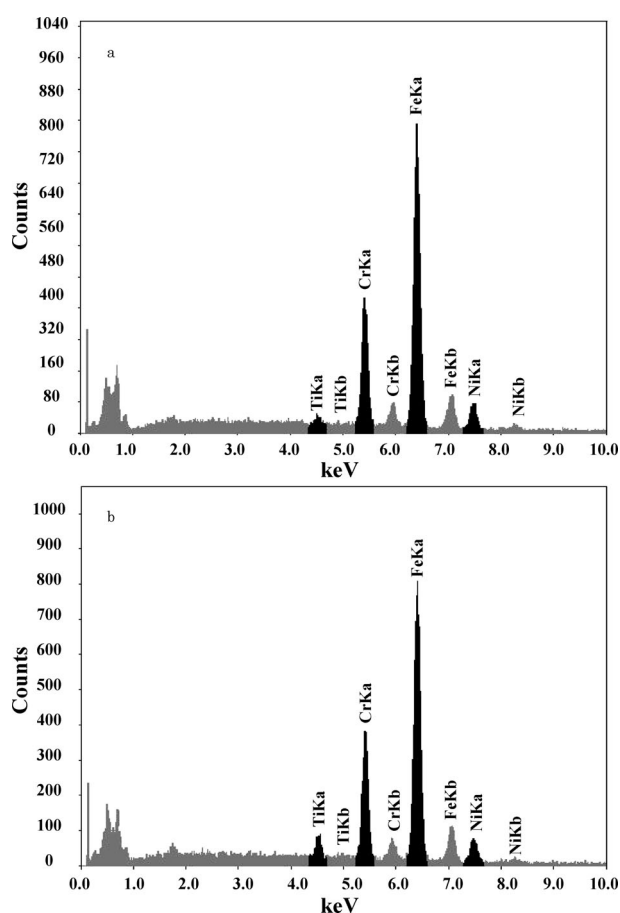


Fig. 6. EDS analysis on selected element peak from substrate surface by (a) DC charging mode and (b) PDC charging mode.

From the EDS analysis shown in Figs. 6(a) and 6(b), the intensities of the Fe, Cr and Ni atom were clearly decrease, and especially so as the charging mode was changed from DC to PDC.

Table 1. Comparison on X-ray Energy Peak Percentage at Selected Element by EDS

Substrate/K value	Ti	Fe	Cr	Ni
Treated substrate	0	67.50	22.45	9.52
Fully submerged substrate (without applied potential)	0.96	65.14	23.14	10.22
Deposit by DC EPD	2.71	65.99	21.46	8.99
Deposit by pulse DC EPD	4.7	68.32	16.26	10.21

The increase in the Ti intensity as charging method was changed shows that the PDC charging mode deposits more TiO_2 particles than the DC charging mode. Other peaks such as $\text{TiK}\beta$ and $\text{FeK}\beta$ were not taken into analysis, since they arose from undesired orbital while an X-ray energy peak less than 1 keV was negligible and considered as a noise or overlapped elements.

Further experiments with high concentration suspension produced thicker TiO_2 particles deposits but as the concentration reaches to 30 wt%, agglomerated TiO_2 particles, which are undesired products, packed together on substrate surface. The deposited agglomerate TiO_2 particles even though they gave a high concentration in the TiO_2 deposit; it gives a surface of low quality and particles adhesion due to crack formation after the heating process (**Fig. 7(a)**). Cracking was reduced at 15 wt%, but

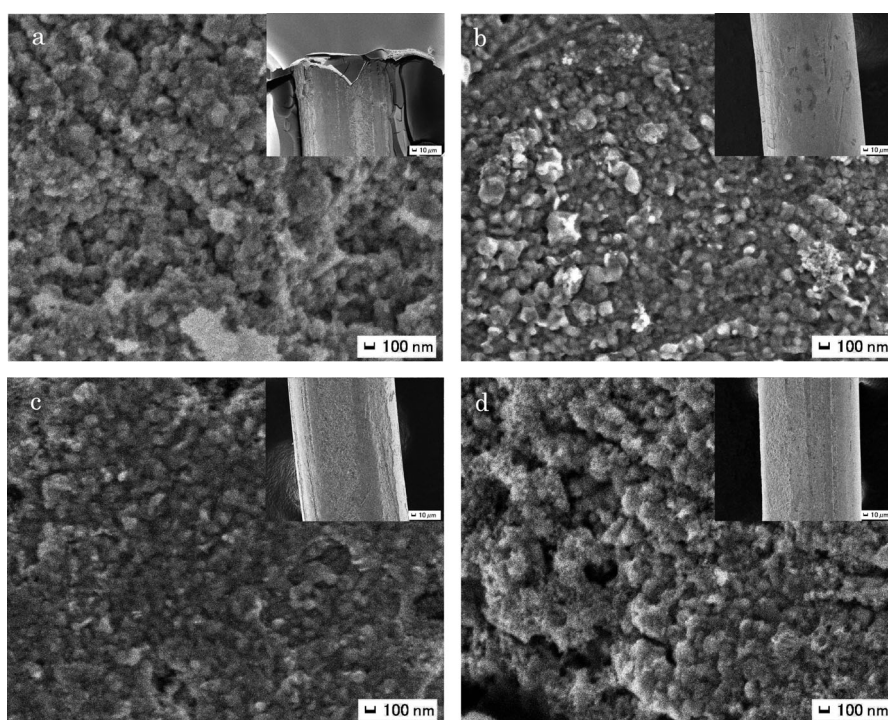


Fig. 7. FE-SEM image on deposit TiO_2 particles by PDC charging mode with different concentration and frequency (a) 30 wt% at 40 Hz (b) 15 wt% at 40 Hz, (c) 7.5 wt.% at 10 Hz and (d) 7.5 wt% at 2.5 Hz. Image of the whole substrate (10 μm scale) was on the top right of each picture.

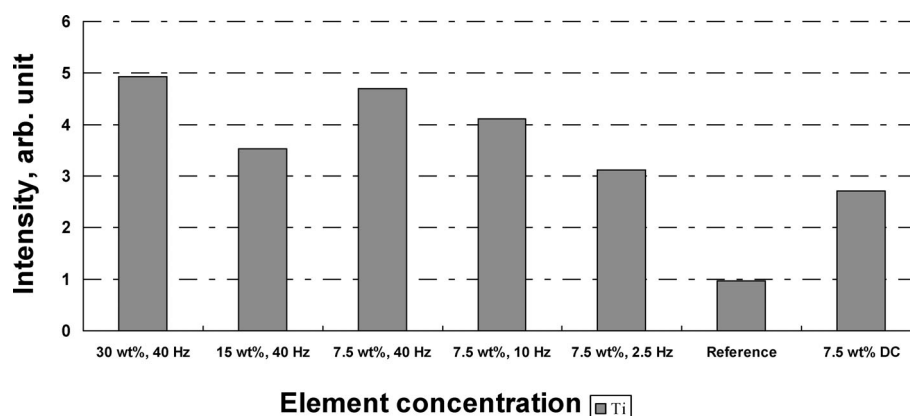


Fig. 8. Comparison on titanium concentration by EDS in various particle concentration and interval time deposit. The reference (no potential applied) was compare between the PDC and DC charging mode.

it still was not be comparable with 7.5 wt%, which was conducted at the same frequency.

3.5 Comparison of the selectable EPD methods

Pulse interval time or frequency of deposition plays an important role in this study, since lower pulse interval time or lower frequency will not only makes agglomerate particle deposit but also low particle concentration. A further analysis by EDS (Fig. 8), indicates that the number of particles deposit onto substrate surface was slightly decreased as the bath concentration was diluted from 30 to become 15 and 7.5 wt%. The intensity of Ti is plotted in Fig. 8 versus the charging method and various types of suspension concentration. As for fully submerge substrate (reference), even though covered with TiO₂ particles, the concentration of the deposit particles was much lower than those with the DC charging mode and PDC charging modes.

By maintaining the concentration of the bath media and increasing the frequency, the number of deposit particles increased with the frequency increased from 2.5 to 40 Hz. When PDC charging was conducted at 40 Hz, the concentration of deposit particles become high as the 30 wt% of bath concentration is conducted. However observation on SEM image shows crack-free surface thus these result makes EPD with 7.5 wt% at higher frequency was more favorable.

4. Conclusion

It is possible to deposit high stable TiO₂ particles suspension in an aqueous suspension under an influence of a surfactant by applying PDC charging mode electrophoresis. The mode of applying voltage during EPD can be manipulated as a driving force in controlling a selected particle size. The size distribution of the deposit particles can be tailored by varying the EPD frequency in the PDC charging mode.

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