



## Affectability of Low Frequency Electrophoretically Deposited Patterns of WO<sub>3</sub> and TiO<sub>2</sub> Nanoparticles in the Presence of Modifier

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### PAPER INFO

#### Paper history:

Received 30 December 2014

Accepted in revised form 02 February 2015

#### Keywords:

AC electrophoretic deposition

TiO<sub>2</sub> nanoparticles

WO<sub>3</sub> nanoparticles

modifier

### ABSTRACT

In this work, the result of additives on electrophoretically deposited patterns of ceramic nanoparticles with totally different chemical composition in the case of using AC electrical field are studied. For this purpose, by the assistance of coplanar electrodes with an interelectrode gap size of 150 μm, heterogeneous AC electrical field was applied to the suspensions of TiO<sub>2</sub>-acetone and WO<sub>3</sub>-acetone in the presence and absence of Polyethylenimine (PEI) as an additive at the frequency of 1Hz. The results verified that whereas WO<sub>3</sub> nanoparticles tend to fill the gap once additive was not used, they show no tendency to enter it within the presence of PEI. However, TiO<sub>2</sub> nanoparticles that leave the gap once additive was not applied, fill it in the presence of PEI.

## 1. INTRODUCTION

Electrophoretic deposition (EPD) is one among the mixture processes in ceramic trade and have some benefits like short deposition time, desires straight forward equipment and pertinence to any solid that is offered within the variety of a fine powder [1,2]. EPD is based on the movement of charged particles suspended in liquid medium underneath the influence of associated degree an external electrical field and consequently deposition on the electrode of the other charge [2,3]. Classical EPD depends on continuous direct current (CDC) for deposition of particles however recently other forms of electrical fields like pulsed direct current (PDC) and alternating current (AC) are investigated [4-7]. Meanwhile applying the heterogeneous AC electric field by the utilization of coplanar electrodes with the interelectrode gap width of regarding 100 μm for deposition of ceramic nanoparticles have attracted the researchers attention [8,9]. Up to currently the impact of some parameters like voltage, concentration, time, frequency and addition of additives on the patterns of deposition are studied. Among these parameters the impact of additives was one in all the foremost dominant parameter [8-10]. So that at the frequency of 1 Hz, TiO<sub>2</sub> nanoparticles leaved the electrode surfaces and

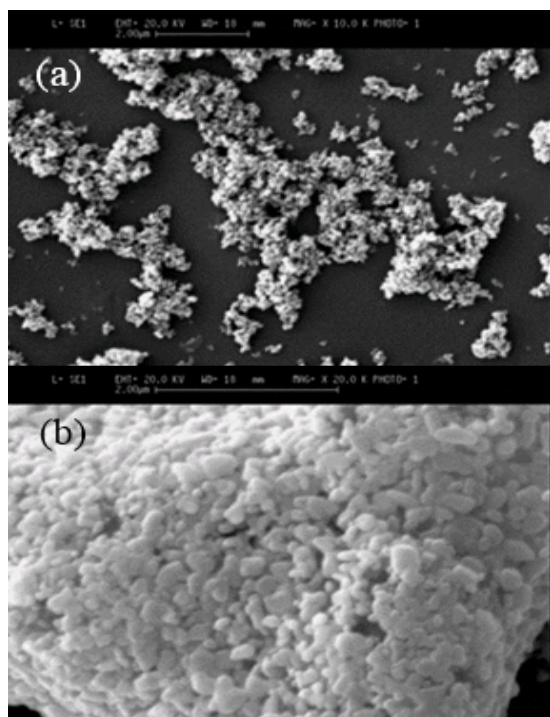
crammed the interelectrode gap in the presence of Dolapix as an additive. However addition of this additive to the suspension at 10 KHz, created the nanoparticles to create chain like pattern on the electric field into the gap. The mentioned results imply the notable result of additives on deposition patterns of TiO<sub>2</sub> nanoparticles at each frequencies[8,11]. However the effect of polymeric additive on electrophoretic deposition of various ceramic nanoparticles at a continuing frequency have not been investigated. Thus we tend to review the result of additives on deposition patterns of two sorts of ceramic nanoparticles with totally different chemical composition.

## 2. EXPERIMENTAL

The electrodes were fabricated by painting business gold paste on surface of borosilicate glass and firing it at 600 °C for 1hour and finally creating a notch on gold layer by laser beam which separates the surface into two coplanar electrodes with a gap size of about 150 μm. The TiO<sub>2</sub> (Art 813) and WO<sub>3</sub> (Art 8846) powders utilized in this analysis were purchased from Merck (Germany). The morphology of the powders which were studied by scanning electron microscopy (SEM, Cambridge S360) are shown in Figure 1. The SEM pictures reveal that particles of each powders are almost spherical in form with average particle size of 140 and 170 nm for TiO<sub>2</sub> and WO<sub>3</sub> nanoparticles, respectively.

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The polyethylenimine which the usage of it is common in EPD of ceramic particles [12], was purchased from Sigma Aldrich (US) and used as additive. It diluted in distilled water 4 times by proportion of 4:1 before usage (1 part PEI to 4 parts water).



**Figure 1.** SEM images of (a) TiO<sub>2</sub> and (b) WO<sub>3</sub> nanoparticles.

The individual suspensions of the TiO<sub>2</sub> and WO<sub>3</sub> nanoparticles were prepared in acetone (Merck, Art 13) at concentration level of 0.3 g L<sup>-1</sup> followed by 15 min ultrasonication. Next, to 10 mL of the above suspensions, 10 µL of diluted PEI was added and then suspensions were once more ultrasonicated for one more 15 min.

The Zeta potential of all four suspensions were characterized by employing a Malvern Zeta sizer (3000 HAS) and all samples were deposited on the coplanar electrodes by applying sinusoidal AC electric field at the frequency of 1Hz for 10min using a function generator (RIGOL DG1022). The peak to peak voltage of the applied wave was chosen to be 5V that was raised up to 37 V by amplifier (hp 6826 A). Finally the optical microscopy images of deposited patterns of all suspensions were obtained.

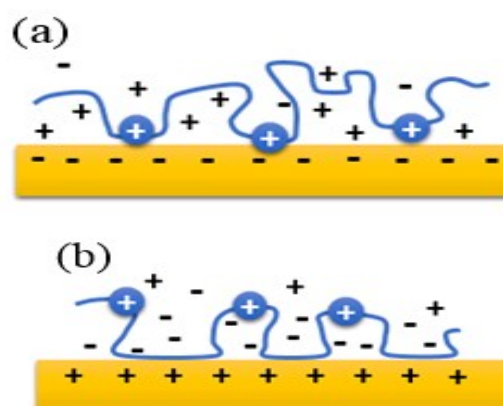
### 3. RESULT AND DISCUSSION

The Table 1 lists the measured average zeta potential of suspended nanoparticles in all told four suspensions. The information discovered that though PEI has raised the zeta potential values of TiO<sub>2</sub> and WO<sub>3</sub> nanoparticles, it has modified the sign of this parameter for WO<sub>3</sub> nanoparticles from negative to positive.

**TABLE 1.** The measured values for zeta potential of TiO<sub>2</sub> and WO<sub>3</sub> nanoparticles in the presence and absence of PEI.

Chemical composition of particles	Zeta potential for suspension without PEI (mV)	Zeta potential for suspension with PEI (mV)
TiO <sub>2</sub>	19.3	32.7
WO <sub>3</sub>	-25.4	39.8

Since the ionized PEI is positively charged and acts as a cationic polyelectrolyte [13], its conformation on the surfaces of particles with positive or negative charge is completely different. As Figure 2. shows, whereas PEI adsorbs via its charged half on the surfaces with negative charge (Figure 2. a) it adsorbs via uncharged polymeric backbone string on the positively charged surfaces (Figure 2. b) [14]. Therefore it is concluded that conformation of PEI on the surfaces of TiO<sub>2</sub> nanoparticles with positive zeta potential (meaning that particles are negatively charged), is simply like what is shown in Figure 2. (a) and for WO<sub>3</sub> particles that have negative zeta potential is like Figure 2. (b).

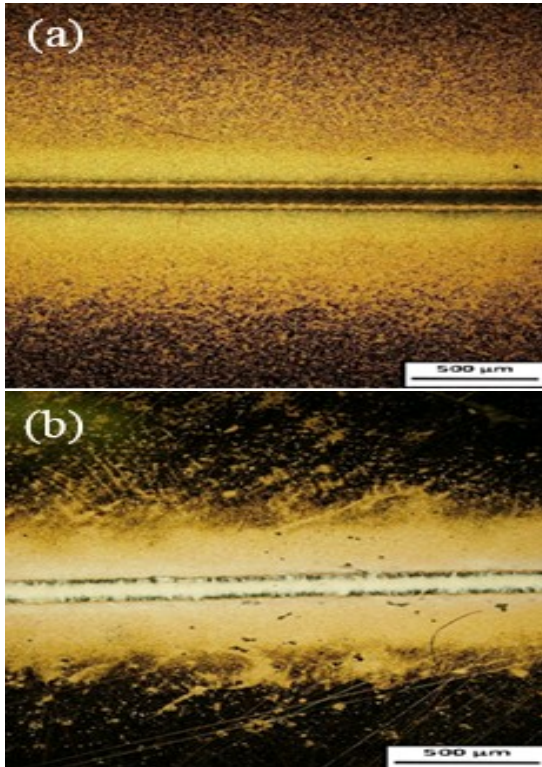


**Figure 2.** schematic representation of conformation of cationic polyelectrolyte on the surfaces of particles with (a) negative and (b) positive charge.

The deposition patterns of each powders at the pure state (without adding PEI) are shown in Figure 3. It is seen that particles of each powders deposited on some part of electrode surfaces close to the edge of the gap. However though WO<sub>3</sub> nanoparticles deposited into the gap, TiO<sub>2</sub> nanoparticles failed to have any tendency to enter it. We tend to according in our previous papers the doable mechanisms dealing with coping with filling the gap by ceramic nanoparticles at the frequency of 1Hz.

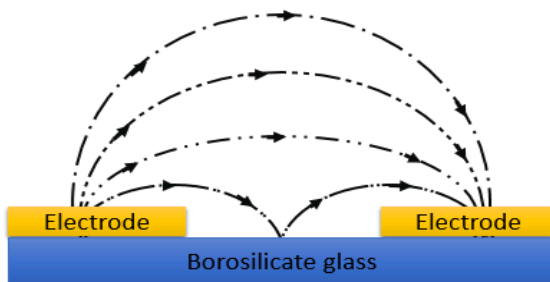
These mechanisms includes the result of unsteady state liquid flow and also the result of non-conductive substrate [8,15]. Since the primary mechanism (effect of unsteady state liquid flow) is a conductivity dependent effect, can not be used for justifying the mentioned leads to present study, as a result of measured conductivity of each suspensions of TiO<sub>2</sub> and WO<sub>3</sub> at pure states have the same value of 0.2 S Cm<sup>-1</sup>. However the second mechanism can be used to justify the phenomena. Supported this mechanism that has been

derived from numerical simulation of electrical field, glass surface works as a conductive substrate in the medium so the electrical field pattern deviates from one electrode toward the gap and from the gap to the adjacent electrode[15]. This prompt mechanism is represented in Figure 4. Therefore by applying electrical field, suspended particles respond to the field and follow the field lines and in keeping with Coulomb force, it is expected that this response for particles with high charge (meaning high zeta potential) is far greater.



**Figure 3.** Optical microscopy images of (a)  $\text{TiO}_2$  and (b)  $\text{WO}_3$  nanoparticles deposition pattern without adding additive.

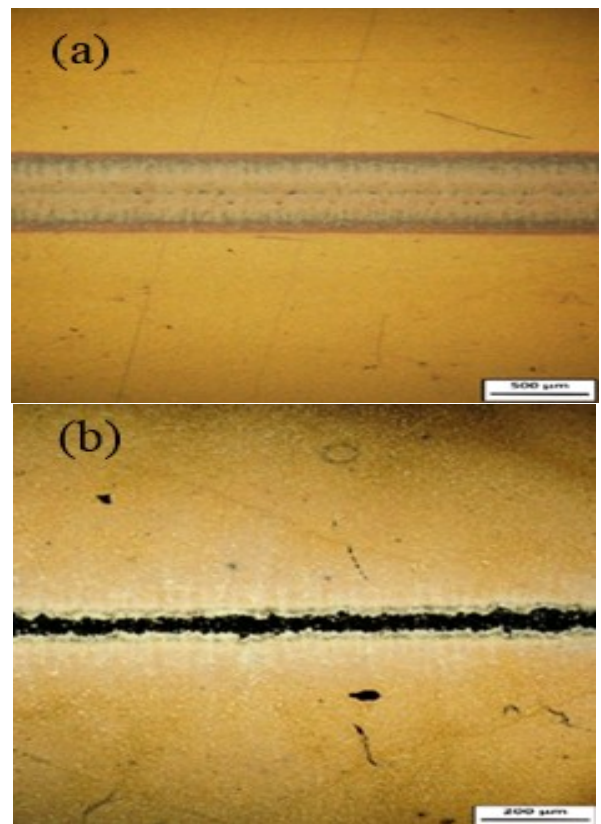
By considering the mentioned result and therefore the values of zeta potential listed in Table 1, filling the gap just by  $\text{WO}_3$  nanoparticles which have higher zeta potential compared to  $\text{TiO}_2$  nanoparticles is justified.



**Figure 4.** Electrical field lines by considering the gap as a conductive substrate.

Figure 5. represents the deposition patterns of  $\text{WO}_3$  and  $\text{TiO}_2$  nanoparticles in the presence of PEI. It is shown that PEI has changed the deposition pattern of each powders in several manner. In other words, although PEI created  $\text{WO}_3$  nanoparticles to leave the gap, enabled  $\text{TiO}_2$  nanoparticles to move in it. By increasing the zeta potentials of suspensions once adding PEI, it is expected that each particle ought to be ready to enter the gap. However Figure 5. (b) shows that  $\text{WO}_3$  nanoparticles did not. This observation indicates the existence of another mechanism.

By EPD of powdered glass specimen suspended in acetone under DC electrical field, a thick film deposition of the powder was occurred on the anode. Thus it will be concluded that glass particles get negative charge in the acetone (indicating they are positively charged) and also the conformation of PEI on the surface of it might be like what is shown in Figure 2. (b). So that according to description above, it seems that by applying the electrical field to the suspensions containing PEI, each  $\text{TiO}_2$  and  $\text{WO}_3$  follow the electrical field lines and move toward the gap. However whereas  $\text{TiO}_2$  nanoparticles would be deposited there, the electrosteric repulsion between  $\text{WO}_3$  nanoparticles and also the glass surface avoided the deposition of  $\text{WO}_3$  nanoparticles into the gap.



**Figure 5.** Optical microscopy images of (a)  $\text{TiO}_2$  and (b)  $\text{WO}_3$  nanoparticles deposition pattern in the presence of PEI.



#### 4. CONCLUSION

The addition of Polyethylenimine to the suspensions of TiO<sub>2</sub>-acetone and WO<sub>3</sub>-acetone had a major result on the surface charge of the particles. Additionally deposition behavior of TiO<sub>2</sub> and WO<sub>3</sub> nanoparticles beneath AC electrical field at 1Hz showed that PEI changed the deposition pattern of particles of both powders in different manner. In other words, whereas WO<sub>3</sub> nanoparticles fill the gap once additive was not used, show no tendency to move into it in the presence of PEI, however, TiO<sub>2</sub> nanoparticles that leave the gap when additive was not applied, fill it in the presence of PEI.

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