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Electrophoretic deposition of TiO_2 nanoparticles in viscous alcoholic media

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Abstract

In the present study, highly viscous alcoholic media, pentanol, hexanol and heptanol were used for electrophoretic deposition of ceramic (TiO_2) nanoparticles as a new approach in the EPD process. Optical and scanning electron microscopy of the obtained deposits at 50 V revealed that layers with a fairly uniform microstructure were obtained in pentanol and hexanol while the layer formed in heptanol suffered from lack of uniformity and did not cover the substrate even at higher voltages up to 200 V. It was also revealed by the atomic force microscope (AFM) studies that surface roughness of the deposited layers decreased with increasing suspension viscosity. This behavior was directly attributed to high viscosity of heptanol which strongly hinders particles movement through the media. The low dielectric constant of heptanol was also considered to decrease particle deposition.

Keywords: B. Microstructure-final; D. TiO_2; Electrophoretic deposition; Organic

1. Introduction

Titanium dioxide (TiO_2) is considered as an important n-type semiconductor [1] with potential applications in dye-sensitized solar cells (DSSCs) [2], sensors [3], photocatalysts [4] as well as optical and structural devices [5]. For most common applications of TiO_2, deposition of porous layers with high surface area and sufficient compactness and interconnection between nanoparticles is necessary.

EPD is a colloidal process based on the motion of charged particles in a suspension toward an electrode of the opposite charge under an applied DC electric field [6]. In the EPD process, the microstructure of the obtained deposit is a function of operational parameters such as voltage, suspension composition, and surface modifying additives. Among these parameters, suspension medium is regarded as a key factor affecting the deposition pattern [7].

Organic liquids with different molecular structures, viscosities and dielectric constants are expected to give rise to formation of different microstructures. Panigrahi et al. [8] studied the effect of organic solvents and charge inducing additives on the microstructure of electrophoretically deposited doped ceria micropowder. They obtained uniform deposits in butanol as a viscous medium while a porous microstructure was achieved in acetylacetone. In another study, Ghashghaie et al. [7] investigated the low frequency electrophoretic deposition of ZnO nanoparticles on co-planar electrodes in acetone and isopropanol. It was observed that uniform crack-free layers were obtained in isopropanol because of lower deposition rate in viscous media.

The mentioned studies indicate that heavy alcohols could be of high potential for being used as suitable vehicles in the EPD process. However, limited data is found in the literature about the application of highly viscous alcohols as suspension vehicles in the EPD process. Although electrophoretic deposition of TiO_2 in aqueous media has been widely studied for years [9,10], the application of organic media as suspension vehicles is a relatively recent approach [11]. Boccaccini et al. investigated the deposition of TiO_2 nanoparticles in acetylacetone using iodine as the dispersing agent. In another study, Dor et al. [12] investigated the effect of the type of organic solvent on the deposition pattern and density of the deposited layer.

In the case of alcoholic solvents, researchers have mostly focused on less viscous media and less attention has been devoted to heavy alcohols. In a recent study, we conducted a comparison between the patterns obtained in methanol and pentanol as two

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media with significantly different viscosities. We showed that a nonuniform porous layer was obtained in methanol, while deposition from the TiO_2/pentanol cell resulted in the formation of a relatively uniform microstructure [13].

In the present study, electrophoretic deposition of TiO_2 nanoparticles in pentanol, hexanol and heptanol as highly viscous organic media has been investigated. Considering the wide range of biological applications of TiO_2 [14], we tried to avoid common toxic dispersants such as iodine [15] and applied magnetic stirring for 24 h to prepare stable suspensions.

2. Experimental procedures

In the present work, TiO_2 nanopowder (Degussa P25) was used as the starting material. Two indium tin oxide (ITO) coated glass substrates were supplied from Kintec Company and used as the EPD cell electrodes.

Using pentanol, hexanol and heptanol as suspension medium, 6 g/l suspensions of TiO_2 nanoparticles were prepared without the addition of any surfactants. Each suspension was first sonicated for 15 min and then magnetically stirred for 24 h at 800 rpm. The prepared suspensions were then sonicated for 15 min to break up the remaining agglomerates.

Electrophoretic deposition was carried out within the voltage range of 10–200 V and finally the constant voltage of 50 V was chosen as the optimum potential. The anode and cathode electrodes with a fixed distance of 1 cm were connected to a regulated DC power supply (EICO 1030). The substrates were washed with distilled water and acetone and dried in air for 15 min.

In order to investigate the deposition pattern of deposited layers, an atomic force microscope (AFM, Dualscope/RasterscopeC26), a scanning electron microscope (SEM, Hitachi/S4160) and an optical microscope (Olympus/BX61) were employed. The zeta potential of TiO_2 nanoparticles was measured using a Malvern Zetasizer (3000 HAS, Malvern, UK). The stability tests for these three suspensions were performed in 10 ml graduated cylinders for 24 h and the volume of the sediment zone was finally measured.

3. Results and discussion

The optical microscope cross-section images of the TiO_2 film depicted in Fig. 1 (the white TiO_2 deposit zone and the uncoated area have been pointed by yellow and white arrows, respectively) show that layers with uniform thicknesses have been obtained in pentanol and hexanol, however, a nonuniform pattern was achieved in heptanol even at high deposition durations. Even increasing the voltage to 200 V did not result in the formation of an inclusive layer of TiO_2 nanoparticles on the entire ITO surface in heptanol.

The quality of the deposited layer obtained during the EPD process in a given medium is highly determined by the electrophoretic mobility of particles [12]. Based on the Henry equation [16], the electrophoretic mobility of particles suspended in a liquid medium is inversely proportional to the liquid viscosity while in direct relation with the zeta potential.

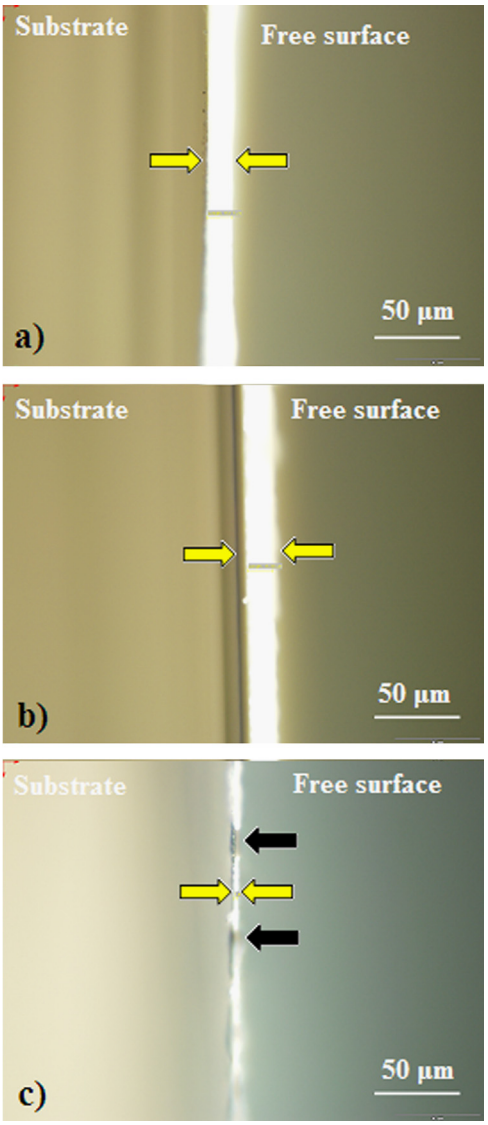

Fig. 1. Optical microscope cross-section of the layers formed at 50 V in (a) pentanol, (b) hexanol and (c) heptanol. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

In addition, the dielectric constant which explains the dissociation power of the medium plays a vital role in determining the surface charge of particles introduced by the zeta potential value [17]. The high viscosity (Table 1) of about 5.8 mPa s is the major factor that led to the decrease in electrophoretic mobility in heavy alcohols such as heptanol. In fact, such high viscosity value is nearly nine-folds of that of methanol as a common vehicle in EPD procedures. Another significant reason for immobility of particles in heptanol is its low dielectric constant that does not allow adequate charge dissociation in the medium surrounding the particles [16]. In this case, the electrophoretic mobility is not expected to be high enough to give rise to an uniform deposit as was observed for TiO_2 nanoparticles in heptanol.

Powers [17] proposed a dielectric constant interval of 12–24 for EPD experiments on alumina particles in organic media in which electrophoretically deposited layers were obtained. In this

Table 1
Physical properties and suspension parameters measured at different solvents [18].

Solvent types	Viscosity (mPa s)	Dielectric constant	Mobility (μm cm/V s)	Zeta potential (mV)	Particle size (nm)
Methanol	0.544	33	1.154	24	249
Pentanol	3.619	15.13	0.047	15.2	175
Hexanol	4.578	13.03	–	–	155
Heptanol	5.810	11.75	–	–	–

case, the electrophoretic mobility was not expected to be high enough to give rise to an uniform deposit, as was observed for TiO_2 nanoparticles in heptanol in the present work.

Powers interpreted that low dissociating power would not likely give rise to effective particle charging and on the other hand, using vehicles of high dielectric constant would lead to practical considerations including formation of the anodic film and Ohmic heating during the passage of current. The occurrence of electrochemical reactions resulting in hydrogen evolution and bubbling on the cathode electrode is the other challenging issue in EPD processing in case of highly conductive media [16]. As presented in Table 1, the dielectric constant of pentanol is lower than 12 (about 11.75) which can justify the formation of a nonuniform layer with dissipated islands based on Power's results.

The stability tests carried out in 10 ml graduated cylinders before deposition showed that the TiO_2 suspensions prepared in pentanol, hexanol and heptanol were stable for 24 h which is highly desirable for deposition. The possible charge bearing mechanisms on the surface of TiO_2 particles in alcoholic media has been investigated in detail elsewhere [19].

As a key fact, relatively low dielectric constant in the three viscous alcohols studied here (Table 1) indicates that this remarkable long-term stability observed for TiO_2 nanoparticles could not be merely a result of strong charge dissociation in the medium resulting in high zeta potentials. In the case of highly viscous media such as those studied in this paper, the slow movement of particles due to the strong viscous drag of the fluid is considered as a significant factor hindering agglomeration. In other words, as we discussed for ZnO nanoparticles [7], in fluids of higher viscosity the diffusion coefficient of suspended particles is significantly reduced which lowers frequent collision of particles and consequently decreases their chance to form aggregates. The remarkable difference between the viscosity of the mentioned heavy alcohols (pentanol, hexanol and heptanol) and methanol as an organic media with low viscosity is presented in Table 1. An important issue affecting deposition microstructure is the particle size and distribution within a given medium. According to particle size results (Table 1) and the size distribution curves (Fig. 2) obtained for TiO_2 nanoparticles dispersed in methanol, pentanol and hexanol, larger aggregates have formed in methanol compared with pentanol and hexanol.

The effect of fluid viscosity on the microstructure of the deposited layer was more closely studied using an atomic force microscope (AFM) for deposits formed in pentanol, hexanol and

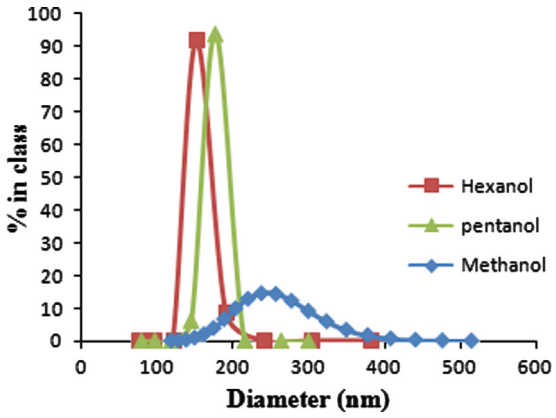

Fig. 2. Size distribution of TiO_2 nanoparticle aggregates in methanol, pentanol and hexanol.

methanol. As depicted by Fig. 3, the roughness of the layer obtained in methanol (Fig. 3a) is much higher than that of the layers formed in more viscous media, pentanol and hexanol (Fig. 3b and c). In addition to the higher deposition rate in methanol which is confirmed by the mobility value presented in Table 1, the agglomeration rate is also expected to be higher due to higher diffusion coefficient of particles in methanol compared with viscous media. At high diffusion rates, there is more opportunity for particle collisions and consequent agglomeration. The ultimate deposition of these agglomerates will give rise to a rough porous structure as depicted by the AFM image of Fig. 3a. In contrast, according to Fig. 3b and c, relatively uniform microstructures are observed to have formed in pentanol and hexanol as highly viscous media which is attributed to low deposition rate as well as small population of large agglomerates.

No matter for what reason, whether lack of surface potential on particles or a high drag force induced by a viscous fluid, the deposition trend is slow, the achievement of yield of deposition against time can clearly demonstrate the rate of the EPD process. As presented in Fig. 4, the rate of deposition decreases as the viscosity increases which is in accordance with mobility and zeta potential results.

Although suspension stability is a major prerequisite in electrophoretic deposition, it will not guarantee the quality of the final deposit without considering other effective factors. One of these parameters which has been rarely investigated in EPD-related studies is the method adopted to prepare the suspension. The SEM micrographs of Fig. 5 illustrate the deposition pattern of TiO_2 nanoparticles obtained in pentanol and hexanol from suspensions prepared by two different methods: Fig. 5a and c shows deposits obtained from TiO_2 suspensions prepared through ultrasonic agitation with no magnetic-stirring step in pentanol and hexanol, respectively, and the microstructure of layers formed in suspensions prepared by 24 h stirring followed by 15 min ultrasonic agitation is depicted in Fig. 5b and c.

A comparison between the microstructures obtained through different preparation methods shows that when preparation only includes ultrasonic agitation, a relatively nonuniform pattern containing large aggregates is formed. However, it can be clearly

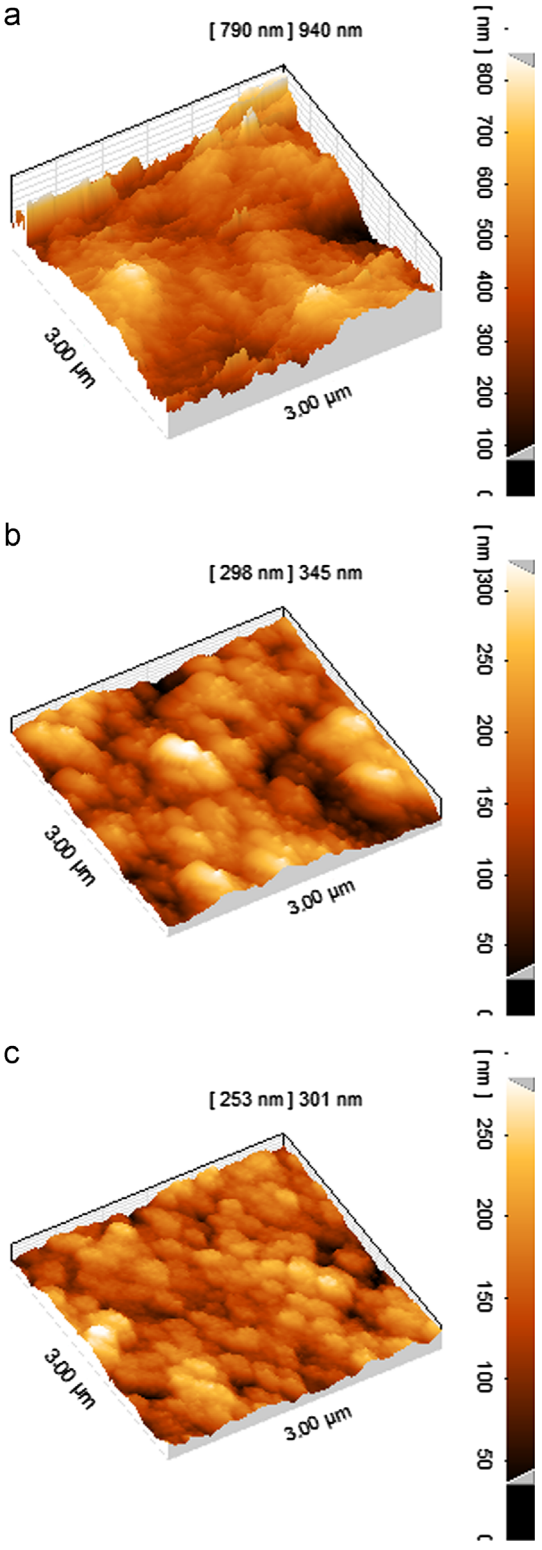

Fig. 3. AFM images for nanocrystalline TiO_2 films formed in (a) methanol, (b) pentanol and (c) hexanol.

observed that magnetic-stirring for 24 h has successfully eliminated the aggregates giving rise to an uniform layer in both pentanol and hexanol. The microstructure of the layers obtained from suspensions prepared by the latter procedure is depicted in Fig. 5e and f

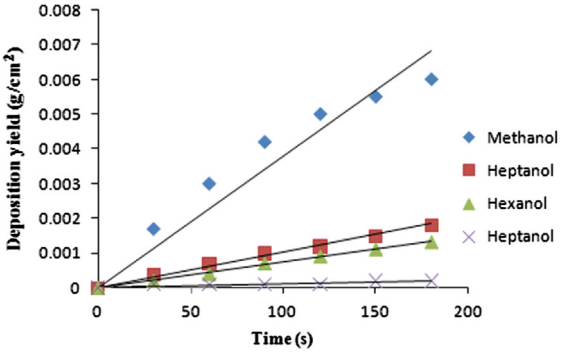

Fig. 4. Deposition yield versus time in four organic media for 6 g/l suspensions.

which exhibits a fairly uniform distribution of TiO_2 aggregates across the deposited film. As systematically investigated by Hecht et al. for Al_2O_3 particles [20], if a clustered system is sheared, clusters are broken up into pieces by the imposed shear. Hence, considering the toxicity of the common TiO_2 dispersants such as iodine, long-term magnetic stirring could be considered as a reliable alternative for suspension preparation in heavy alcohols.

According to the SEM micrograph of the surface microstructure of as-prepared TiO_2 films obtained in pentanol and hexanol (Fig. 5e and f), the layer formed in pentanol (Fig. 3e) appeared to be more porous containing large pores within its structure. Also, the compactness of obtained layers in heptanol and hexanol was determined by employing the packing density parameter. The particle packing density (packing ratio) is the ratio of the volume of the substantial parts (*Vs*) to the total volume of the packed powders (*V*). The packing density can be calculated as follows [21]:

$$P = Vs/V = M/At\rho \quad (1)$$

where M is the total mass (g), t is the thickness of the TiO_2 film, A is the deposited area and ρ is the density of the TiO_2 powder. According to Ref. [21], the density of rutile and anatase TiO_2 is 4.26 and 3.89 g/cm^3, respectively. The TiO_2 powder (P25) used in this work consisted of 70% anatase TiO_2 and 30% rutile TiO_2, and the density of the material was 4.00 g/cm^3. As a result, the packing density of a TiO_2 film fabricated using EPD in pentanol and hexanol is 42% and 45%, respectively.

4. Conclusions

The heavy alcoholic media, pentanol and hexanol, were found to be suitable media for electrophoretic deposition of TiO_2 nanoparticles to obtain uniform layers and appropriate interconnection between nanoparticles according to AFM and SEM studies. EPD in heptanol gave rise to the formation of a nonuniform layer unable to cover the whole substrate even at higher potentials. It was also observed that magnetic-stirring of the suspension for 24 h could effectively enhance the stability of suspension and resulted in uniform deposition in pentanol and hexanol.

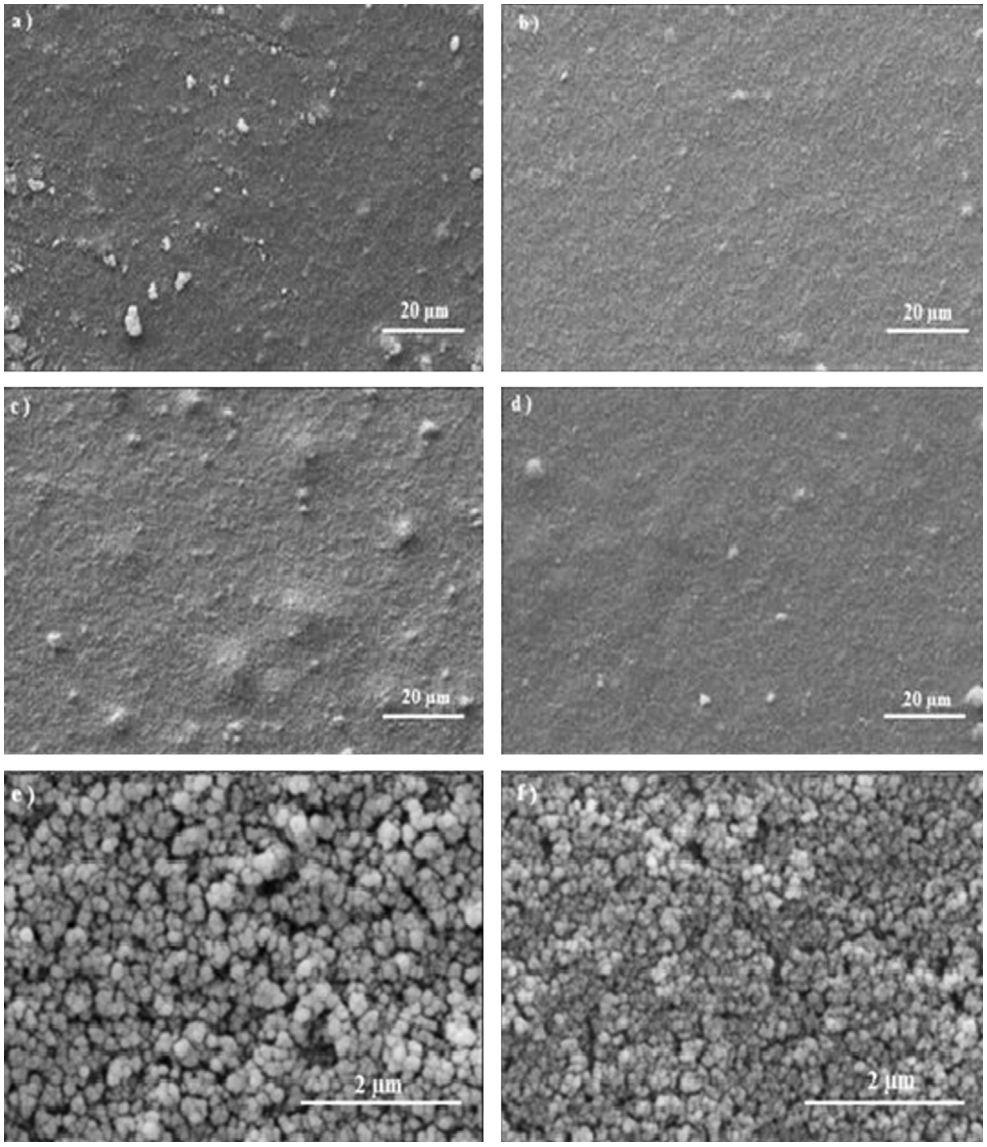

Fig. 5. (a)–(d) The SEM micrograph showing the effect of magnetic-stirring on the microstructure of layers obtained in pentanol (a,b) and hexanol (c,d). (e) and (f) The microstructure of EPD layers formed in pentanol and hexanol, respectively.

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