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Electrophoretic deposition of nanoscale TiO_2: technology and applications

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The importance of titania (TiO_2) as the main component of photocatalytic and photovoltaic devices or its employment in sensors, biomedical coatings and as anticorrosion or antioxidation agent, is highlighted by the increasing number of systems in which titania is being widely used. Many of the attractive applications of TiO_2 require the manufacture of thin (and thick) films and layered structures . In this regard, electrophoretic deposition (EPD) has gained increasing attention over the last years to process TiO_2 nanoparticles (n-TiO_2) for production of a variety of TiO_2 layers, films and coatings. This review compiles the different aspects involved in the fabrication of TiO_2 coatings by EPD of n-TiO_2, first focusing on the general aspects of the deposition process and the parameters involved, and considering further the specific requirements for given applications. The recent advances achieved are discussed and avenues for future research and innovations on the EPD of n-TiO_2 are highlighted.

1. Introduction

Titania (TiO_2) in its different crystalline forms is one of the most widely used ceramic materials in applications as varied as self-cleaning glazing [1], water purification [2], sensors [3], photocatalyst and photovoltaics [4,5], corrosion protective coatings [6], bactericide surfaces [7], and coatings for biomedical applications [8–11]. The reasons why titania is being so effectively used in all these fields reside in its high chemical durability, thermal stability, relatively high hardness, wear resistance, and/or photocatalytic properties (derived from its bandgap (3.06 eV for rutile phase and 3.23 eV for anatase phase) which is close to the energy of photons of visible or ultraviolet light, i.e., $E < 3.5$ eV) [12,13]. For most of these applications, and due to their specific requirements, titania in the form of coatings or thin (and thick) films is often needed.

Among many other coating technologies used to produce titania coatings, such as chemical vapor deposition (CVD) [14], physical vapor deposition (PVD) [15], sol–gel [16,17], plasma spraying [18], or tape casting [17], the electrophoretic deposition (EPD) technique has emerged as one of the most promising technologies due to its versatility, simplicity, and low cost [19]. Moreover, EPD can be carried out under normal conditions of temperature and pressure, in contrast to CVD, PVD, or plasma spraying, which require the use of gases, high temperature, and/or pressurized systems [14,15,20]. If compared to sol–gel processes, which can also be carried out at room temperature, EPD presents the possibility of using environmentally friendly precursors and solvents, while the sol–gel process requires organic precursors (titanium isopropoxide $Ti(O^iC_3H_7)_4$ for the specific case of titania) [16]. In the case of tape casting, high solid contents are required and the inorganic phase must be combined with a polymeric component in high concentration [21]. In the case of EPD, solid contents as low as 0,01 wt.% [22] or as high 70 wt.% [23], can be employed for the fabrication of inorganic coatings. The simultaneous deposition of organic [24,25] and inorganic [26,27] materials (in the desirable ratio) is also possible, which leads to the facile fabrication of organic–inorganic composite coatings [28]. This last point, and the fact that EPD can be performed in water at room temperature, is of great importance in the field of biotechnology and biomaterials because it enables the combination of titania with other organic (biomolecules) or inorganic materials [9,28–30]. Finally, EPD is a very convenient technique for the controlled assembly of nanoparticles, thus, being a versatile processing tool in nanotechnology to obtain nanostructured coatings and self-standing nanoscale films [31].

EPD is based on the motion of charged particles in suspension under the influence of an electric field towards an oppositely charged electrode to form a dense, coherent, and homogeneous coating. The set up required consists of simple equipment usually including a power supplier, a multimeter to record current density, a vessel containing the suspension to be deposited (EPD

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cell) and two conductive electrodes namely a working electrode (substrate to be coated) and a counter electrode. One of the major advantages of EPD is the possibility of adjusting the set up to the substrate requirements, which implies that substrates with different shapes and sizes can be coated [32]. Comprehensive review papers on the fundamentals and applications of EPD are available [19,26,33–36]. Traditionally, EPD has been carried out using organic solvents instead of water, mainly due to the low voltage at which water electrolysis occurs [37], which leads to bubble formation at the electrode-suspension interface and, consequently, to non-homogenous coatings and substrate corrosion. However, in terms of cost efficiency and due to environmental concerns, water based suspensions are preferred over organic solvents. In order to overcome the problems arising from water decomposition, different approaches have been followed, such as the employment of pulsed current (or voltage) EPD or alternating current EPD (AC-EPD). The advantages of these methods have been previously summarized in different papers by Neirinck et al. [38], Ammam [34], Chávez-Valdez and Boccaccini [36] Yoshioka et al. [39] and Besra et al. [40].

Considering the many innovative applications of titania and the enhanced properties that can be achieved by the employment of nanosized materials (particle size <100 nm), many efforts have been devoted to the study and development of nanoscale titania (nano-TiO_2) coatings by electrophoretic deposition. It is apparent that the field of EPD of nano-TiO_2 is continuously expanding which has motivated us to prepare the present review. Indeed, the number of publications per year reporting on titania coatings by electrophoretic deposition has increased more than eight times in the last 14 years (from 2000 to 2013), according to a search using the keywords “electrophoretic deposition” and “titania” in Web of Science®.

This review compiles and comprehensively discusses previous investigations on EPD of nano-titania covering specific aspects of the processing of titania coatings and thin/thick films highlighting the conditions of EPD processing in relation to the final applications. Moreover, perspectives for the further expansion of the field of EPD of nano-TiO_2 addressing challenges and exploring new applications are also discussed.

2. General aspects of nano-titania coatings by EPD

Generally, the final application potential of a given material acts as the driving force for its research and development. This implies that each different application requires different characteristics of the final material (in the case of coatings it could be for example thickness, adhesion to substrate, surface roughness or porosity) that should be achieved by controlling the different parameters during the process. In addition, in the specific case of coatings obtained by EPD, it is important to understand how the different parameters involved in the EPD process (the ones related to the suspension preparation as well as the parameters governing the electrophoretic process itself) can affect the deposition of nanoparticles independently of the final application. Clearly, for successful EPD, stable and well-dispersed nanoparticle suspensions are required, which include the selection of suitable solvents and/or additives. In this first section, relevant TiO_2 suspension systems are discussed considering the type of solvent and EPD parameters used, the employment of different stabilizing agents and the co-deposition of TiO_2 nanoparticles with other entities. In addition, approaches involving deposition under AC, pulse current (voltage) or under the influence of magnetic fields are described. Table 1 summarizes the main characteristics of the most applied systems according to the literature, showing the type of titania nanopowders and solvents used, the EPD mode employed (DC, AC, or pulse EPD), the use of additives or the co-deposition of titania with other organic or inorganic particles.

2.1. Influence of the suspension and EPD parameters

The first model describing the kinetic of EPD was proposed by Hamaker and Verwey in 1940 [41]. This model linearly correlates the mass deposited during the process (m) with the particles concentration in the suspension (C), the electrophoretic mobility of the particles (μ_e), the electric field applied (E), the deposition area (A), and the deposition time (t) through the following equation:

$$m = C\mu_e EAt \tag{1}$$

Despite the linear relation between m and t, the parameters related to the suspension (i.e., concentration of the particles and electrophoretic mobility) are of special importance since they determine the colloidal stability of the particles and have a great influence on the final quality of the coatings.

Due to the limited voltage range allowed for aqueous suspensions, numerous studies have been done on EPD of titania using different organic solvents. The employment of different alcoholic media has been studied by different authors [42–44], focusing on the influence of pK_a values, vapor pressures, viscosities, or dielectric constants of the alcohols on both the suspension stability and the final quality of the coatings. In this sense, Farrokhi-Rad and Ghorbani, [42] studied the deposition of titania nanoparticles with an average size of 5 nm (Sigma–Aldrich Corporation, USA) using methanol, ethanol and butanol in the presence of triethanolamine (TEA) as a dispersant, and reported that the lower the pK_a of the alcohol, the higher the absolute value of zeta potential, which implies higher stability of the particles. Considering the deposition yield, the lowest rates were obtained for the butanolic system, regardless of the voltage and deposition time. The reason for the lower deposition yield with this solvent relies on its low dielectric constant ($\epsilon = 17.51$) compared to methanol ($\epsilon = 32.63$), and ethanol ($\epsilon = 24.55$). This implies a low dissociation power of the solvent leading to a lower electrophoretic mobility. It was also observed that at low voltages the mass deposited per area is governed by the electrophoretic mobility of the particles, while at high voltages the deposit resistance becomes more significant. Regardless of the optimum TEA concentration to stabilize the particles in the different alcohols, only slightly higher porosity due to the lower rearrangement of particles, was observed when increasing the voltage from 5 to 60 V.

In related investigations, Sadeghi et al., [43,44] studied the influence of methanol, ethanol, 1-propanol, butanol, pentanol, hexanol, and heptanol on the EPD of titania P25 . P25 is a common commercially available TiO_2 nanopowder (Evonik Industries) of 21 nm in diameter, which is a mixture of anatase and rutile polymorphs. In the study involving simple alcohols, i.e., methanol, ethanol, 1-propanol, and butanol, the authors observed that there was a critical concentration of titania above which the coatings suffered cracking and that crack formation was affected by the viscosity of the solvent. It was observed that for higher viscosities, the solid content in the starting suspension that led to crack-free coatings was higher (3 g/L for methanol ($\eta = 0.544$ mPa s) and 8 g/L for butanol ($\eta = 3.0$ mPa s)) [43]. In the case of higher alcohols, i.e., pentanol, hexanol, and heptanol, it was also observed that the viscosity of the dispersion media plays an important role in the colloidal stability of the particles while the quality of the final coatings was confirmed to be affected by its dielectric constant. The high viscosity values of the three solvents studied (3.619, 4.578, and 5.810 mPa s for pentanol, hexanol, and heptanol, respectively), were seen to lower the diffusion coefficient of the suspended particles which resulted in a reduction of the rate of collision between particles and, therefore, resulted in decreased agglomerate formation. As a result, the parti-