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Electrophoretic deposition of titania nanostructured coatings for photodegradation of methylene blue

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ABSTRACT

The suspensions of titania nanoparticles were prepared in different alcohols (methanol, ethanol, isopropanol and butanol) using polyethyleneimine (PEI) as dispersant. The results of sedimentation, conductivity, zeta potential, FTIR and thermal analysis showed that PEI macromolecules are protonated in the suspensions and then adsorbed on the particles enhancing their positive surface charge and so colloidal stability. Optimum concentration of PEI (PEI⁺) was lower in large molecular size alcohols due to its higher adsorption efficiency. PEI⁺ was 0.75, 0.5, 0.5 and 0.25 g/l in methanolic, ethanolic, isopropanolic and butanolic suspensions, respectively. Electrophoretic deposition (EPD) was performed at 60 V in different alcoholic suspensions. EPD rate was the fastest in the suspensions with PEI⁺ due to the highest mobility of particles. In contrast to the coatings deposited for 1 min from isopropanolic and butanolic suspensions, those deposited at same conditions from methanolic and ethanolic ones severely cracked during drying owing to their higher thickness and lower PEI contents (acting as the binder). The coatings deposited from methanolic and ethanolic suspensions with PEI⁺ had finer and rougher microstructures. The sintered coating deposited at 60 V for 10 s from ethanolic suspension with PEI⁺ had crack-free microstructure with the thickness of $\approx 130 \mu\text{m}$. This coating degraded $\approx 24\%$ of methylene blue from its aqueous solution (30 ml with the concentration of 5 mg/l) within 2 h under UV illumination. Photodegradation of MB on the surface of titania coating obeyed the first order kinetics law.

1. Introduction

Titania in its anatase form has relatively high photocatalytic activity resulting in its extensive applications as photovoltaic cell [1–3], photocatalytic degradation of organic pollutants [4,5], sensors [6,7], self-cleaning [8,9] and antibacterial [10,11] materials. Titania nanoparticles has high photocatalysis efficiency for the degradation of pollutants due to the extremely high specific surface area. However, the recovery and reuse of such nanoparticles from the industrial effluents after the completion of photocatalysis process are very difficult. If titania nanoparticles used for photocatalytic degradation of pollutants are not removed from the treated water stream, they can lead to serious toxicity to environment and human being. One way to overcome this problem is the immobilization of photocatalyst nanoparticles on the supporting materials [12]. Several methods have been used to immobilize photocatalyst particles on the supporting materials such as sol-gel [13–16], chemical vapor deposition (CVD) [17], spray pyrolysis [18] and thermal spray [19,20]. Electrophoretic deposition (EPD) is a colloidal processing method which has been extensively used to deposit

ceramic particles on the metallic substrates [21]. EPD is a two step process: in the first step, charged particles dispersed in an appropriate solvent move toward the oppositely charged electrode under the influence of an applied electric field (electrophoresis step); in the second step, they deposit on the substrate and form a particulate layer on it (deposition step). EPD has several advantages such as simplicity, need to low cost equipments, deposition of uniform coatings on the substrates with complex shapes, fast processing rate and ability to control the thickness and microstructure of coatings by simple adjustment of EPD parameter like voltage and time [21]. The coatings with interconnected porosity are obtained after drying the solvent present between the particles in wet EPD deposits. The porous EPD coatings have relatively high surface area beneficial for photocatalytic applications. So, EPD is an attractive technique for deposition of titania photocatalyst coating on the metallic supports [22–31]. Usually, organic solvents like alcohols [29–31] are used for the preparation of EPD suspensions. Water encounters electrolysis at relatively low applied electric fields resulting in the generation of hydrogen and oxygen gases at cathode and anode, respectively [32]. On the other hand, the surface charge of

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particles and so their colloidal stability is lower in organic solvents due to their less dielectric constant. So, the addition of an effective dispersant is essential for the preparation of non-aqueous suspensions with high colloidal stability.

In this work the EPD of titania coatings on 316 L stainless steel substrates was carried out using different alcoholic suspensions containing polyethyleneimine (PEI) as dispersant. The optimum composition (type of alcohol and concentration of PEI) of suspension was determined by the results obtained for the characterization of suspensions as well as coatings. Finally, the photocatalytic degradation of methylene blue dye on the surface of optimum coating was investigated in the aqueous solution.

2. Experimental

2.1. Preparation and characterization of suspensions

Anatase phase titania nanopowder with primary particles size in the range of 10–30 nm was used in this work. The powder was also characterized by SEM (FE-SEM-Mira3 TESCAN) and XRD (Philips X'Pert MPD) analysis. Different alcohols (methanol, ethanol, isopropanol and butanol) and polyethyleneimine (PEI, Across Organic, MW: 60,000 g/mol) were used as solvents and dispersant, respectively. The suspensions were prepared by adding the titania powder (10 g/l) into the alcoholic solutions of PEI (0, 0.1, 0.25, 0.5, 0.75 and 1 g/l) followed by their stirring and ultrasonic dispersing for 24 h and 10 min, respectively.

Sedimentation test was used to investigate the effect of PEI on the colloidal stability of titania particles in alcoholic suspensions. The suspensions with different contents of PEI were poured into the 40 ml test tubes and allowed to settle for 30 days in the resting condition.

The electrical conductivity of alcohols and their corresponding suspensions was measured as a function of PEI concentration using a conductivity meter (Inolab, WTW series, Cond 720). FTIR (Shimadzu Co) and thermal analysis (TG/DTA; STA 504; Bahr) were performed on the as-purchased titania powder and those extracted from different alcoholic suspensions with 1 g/l of PEI. The samples for FTIR and TG/DTA analysis were prepared by centrifuging the suspensions (6000 rpm, 5 min) followed by washing the sediment powders by 3 repetitive washing/centrifugation operations with deionized water and their drying at 120 °C for 24 h. The zeta potential of particles was measured in the suspensions with different concentrations of PEI using Malvern instrument (HS C1330–3000). Prior to zeta potential measurement, the suspensions were diluted based on the method described in Ref. [33].

2.2. Electrophoretic deposition

Both substrate and counter electrodes were the 316 L stainless steel plates with the dimensions of 1 mm × 20 mm × 40 mm. The electrodes were separated by 1 cm in EPD cell. The surface area of electrodes exposed to suspensions was 20 mm × 30 mm and remainder covered by polymeric adhesive tape. Electrophoretic deposition (EPD) was carried out at 60 V using a D.C power supply (HY30002E; Huayi Electronics Industry Co.). The in situ kinetics of deposition and current density were recorded during EPD using a high accuracy balance (GR-200 A&D co.) and digital multimeter (model: 289 True RMS, Fluke), respectively, based on the method presented in Ref [30]. The effective voltage across the suspensions at any moment ($V_{eff,t}$) was calculated according to the following equation:

$$V_{eff,t} = R_{sus} i_t \quad (1)$$

Where R_{sus} is the resistance of suspension and i_t is the current passing through it at moment t . R_{sus} was determined according to the Ohm's law by dividing the applied voltage (60 V) to current passing through the EPD circuit at start point ($t = 0$ s).

2.3. Characterization of coatings

The microstructure of coatings was observed by SEM (FE-SEM-Mira3 TESCAN) at both low and high magnifications. Considering the results obtained from the characterization of suspensions and coatings, the ethanolic suspension with 0.5 g/l of PEI was selected as the optimum suspension. The coating for photocatalysis studies (optimum coating) was deposited at 60 V for 10 s from optimum suspension and sintered at 600 °C for 1 h. The microstructure of optimum coating was observed by SEM at low and high magnifications before and after sintering. The cross section SEM image was also taken from the optimum coating after its sintering.

The substrate covered by optimum coating (surface area: 2 cm × 3 cm) was immersed in the aqueous solution of MB (volume: 30 ml and concentration: 5 mg/l). Prior to UV illumination, the solution was equilibrated with the coating in the darkness box for 1 h. Then the coating was illuminated with UV light for different times using an ultraviolet lamp (wavelength: 380 nm and 400 W) placed in the distance of 20 cm from it. To monitor the photocatalytic degradation of MB, the solution was analyzed by UV-Vis spectrophotometer (OPTIZEN 3220) after different periods (0, 15, 30, 45, 60, 90 and 120 min) of UV illumination. The concentration of MB with respect to its initial concentration (C/C_0) as a function of illumination time was calculated using the Lambert-Beer law at wavelength of 665 nm (characteristic peak of MB).

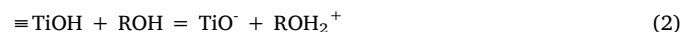
3. Results and discussion

3.1. Characterization of suspensions

The SEM image and XRD pattern of titania nanopowder are shown in Fig. 1. As the SEM image shows, the powder is composed of nanometer sized primary particles (≈ 10 –35 nm) stick to each other to form coarser agglomerates. The XRD pattern only shows the characteristic peaks of anatase verifying the absence of any other major phase in the powder.

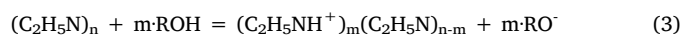
Fig. 2 shows the photographs of suspensions after the sedimentation test for 30 days. As can be seen, the colloidal stability of all alcoholic suspensions increases considerably with PEI addition into them.

The electrical conductivity of alcohols (without titania) and their corresponding suspensions (with 10 g/l of titania) as a function of PEI concentration is shown in Fig. 3. As can be seen, in the absence of PEI, the conductivity of all alcohols increases as 10 g/l of titania powder is added into them. Ceramic particles acquire negative surface charge in the pHs above the point of zero charge (PZC). The pH of alcohols is above the PZC of titania (5.8). So, titania particles acquire negative surface charge in alcohols according to the following reaction (the surface of oxide particles is hydrated):



The conductivity of alcohols increases due to the generation of free ROH_2^+ ions as titania powder is added into them.

The conductivity of all alcohols increases with the concentration of PEI. PEI has the chemical formula of $(\text{C}_2\text{H}_5\text{N})_n$ where n depends on its molecular weight. PEI has basic characteristics due to the lone pair electron on the nitrogen atoms. PEI can be partially protonated in alcohols according to the following reaction:



Where m denotes the number of nitrogen atoms protonated in the alcohol. The generation of $(\text{C}_2\text{H}_5\text{NH}^+)_m(\text{C}_2\text{H}_5\text{N})_{n-m}$ (it will be denoted by H^+ PEI in the rest of paper) and RO^- ions increases the conductivity of alcohols with PEI addition. The tendency of alcohols for proton donation increases with decreasing its molecular size (the equilibrium constant for autoprotolysis reaction ($\text{ROH} + \text{ROH} = \text{ROH}_2^+ + \text{RO}^-$) is

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