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Electrophoretic deposition of titania–carbon nanotubes nanocomposite coatings in different alcohols

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Abstract

The suspensions of titania nanoparticles in different alcohols (methanol, ethanol and butanol) were prepared using triethanolamine (TEA) as a dispersant. The optimum concentration of TEA was 16.67, 8 and 0.33 mL/L in methanol, ethanol and butanol, respectively. Two component suspensions of titania (20 g/L) and carbon nanotubes (CNTs) (0.1, 0.2, 0.5 and 1 g/L) were prepared in different alcohols without and with optimum concentration of TEA. The finer and positively charged titania nanoparticles were heterocoagulated on the surface of coarser and negatively charged CNTs and generated the titania–CNT composite particles with the net positive charge. In the presence of TEA, titania nanoparticles completely covered CNTs surface due to their higher positive surface charge. At same CNT concentration, the deposition rate was faster for suspensions with TEA additive due to the faster mobility of the composite particles. The photocatalysis efficiency of coatings for methylene blue degradation increased as CNTs were incorporated in their microstructure.

Keywords: Alcohol; Carbon nanotubes (CNTs); Coatings; Electrophoretic deposition (EPD); Titania nanoparticles

1. Introduction

Titania nanostructured coatings and thin films have attracted considerable attention due to their applications in photocatalysis,[1] air and water purification,[2] bacterial and fungus resistance coatings,[3] biomaterials[4] and sensors.[5] Carbon nanotubes (CNTs) have high potential for application in biomedical and functional devices due to their nanomorphology and exceptional mechanical and electrical properties.[6] By combining titania nanoparticles and CNTs, it is possible to prepare the titania–CNTs composites with modified mechanical and photocatalytic properties. The combination of TiO_2 and CNTs can yield more active sites for photocatalytic degradation. Electrophoretic deposition (EPD) is a colloidal processing method which has been extensively used to prepare the nanostructured ceramic coatings.[7–10] EPD is a two-step process: in the first step the charged particles dispersed in the suitable liquid migrate toward the oppositely charged electrode under the effect of an applied electric field. In the second step they deposit on the electrode forming a relatively dense layer of particles there.[7] EPD is a versatile process offering various advantages such as simplicity, need to low cost equipments, short formation time, ability to deposit even coatings on the substrates with complicated shapes and controlling the microstructure of deposit by simple adjustment of deposition parameters such as voltage and time.[7] Using water as the suspending medium is limited in EPD due to its electrolysis at relatively low applied electric fields; this leads to the generation of hydrogen and oxygen gases at the cathode and the anode, respectively, yielding the poor quality deposits.[11] Thus usually organic solvents such as alcohols are preferred as the suspending medium in EPD.[12–14] EPD has been used extensively to deposit single phase titania[12,13,15–17] and CNT[8,10] coatings as well as TiO_2–CNTs nanocomposite coatings.[18–20] EPD also has been used to deposit other ceramic–CNTs nanocomposite coatings such as SiO_2–CNTs,[21] hydroxyapatite–CNTs,[18,22–25] Fe_3O_4–CNTs[26] and MnO_2–CNTs.[27,28] The uniform dispersion of CNTs in the matrix of ceramic particles leads to the ceramic–CNTs nanocomposites with modified properties; this

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can be achieved by EPD from the well dispersed colloidal suspension of ceramic particles as well as CNTs in an appropriate medium. The charge generated on the surface of particles in non-aqueous solvents is usually very low; so the use of an efficient dispersant is essential to prepare the well dispersed colloidal suspension of ceramic particles and CNTs in alcoholic suspensions. Functionalized CNTs are more dispersible due to ionizable functional groups at their surface. Triethanolamine (TEA) is an organic compound which can be used as the dispersant to increase the surface charge and colloidal stability of particles in non-aqueous media.[12,13] In this work the EPD of titania nanostructured coatings and titania–CNTs nanocomposite coatings from different alcoholic suspensions have been studied. The effect of triethanolamine as a dispersant on the EPD process and the properties of obtained coatings have been investigated.

2. Experimental

2.1. Titania single phase coatings

Suspensions preparation. Triethanolamine (TEA) was added at different concentrations (0, 0.167, 0.33, 1.33, 4, 8 and 16.67 mL/L) into different alcohols (methanol (99.99%, Merck), ethanol (99.8%, Merck) and butanol (99%, Merck)); then 20 g/L of titania nanoparticles (Degussa P25, 21 nm) were added into them. These suspensions were magnetically stirred for 24 h and ultrasonically (Sonopuls HD 3200, 20 kHz; Bandelin Co., Berlin, Germany) dispersed for 10 min. The electrical conductivity of suspensions was measured against TEA concentration by conductivity meter (Cond 720, WTW series; Inolab, Weilheim, Germany). The zeta potential of titania nanoparticles was measured in different alcoholic suspensions with various concentrations of TEA (Malvern Instrument, 3000HS, Worcestershire, U.K.).

Electrophoretic deposition. The plates from 316 L stainless steel with the dimension of 1 mm × 20 mm × 40 mm were used as the substrate as well as counter electrodes in EPD cell. Only 20 mm × 20 mm of electrodes surfaces was exposed to suspension and remainder insulated by polymeric adhesive tape. The distance between the electrodes was 1 cm in EPD cell. Electrophoretic deposition was performed at 60 V using a laboratory power supply (HY30002E; Huayi Electronics Industry Co., Hangzhou, Zhejiang, China). The current density during EPD was recorded by digital multimeter (289 True RMS; Fluke, Everett, WA). The wet (W_{wet}) weight of deposits was measured immediately after depositon (GR-200, A&D Co., Tokyo, Japan). The immersion weight of deposits (W_{im}) was recorded *in situ* according to the method described in Ref. 13. During *in situ* deposition weight measurement, the voltage was applied for 6 min and then switched off for 2 min. Wet density of deposits prepared at 60 V from different alcoholic suspensions containing various concentrations of TEA was measured according to the Archimedes' principle:

$$\rho_{wet} = \frac{W_{wet}}{Vol_{wet}} \quad \text{and} \quad Vol_{wet} = \frac{W_{wet} - W_{imm}}{\rho_{Alcohol}} \tag{1}$$

where Vol_{wet} is the wet volume of the deposit and $\rho_{Alcohol}$ is the density of alcohol (methanol: 0.792 g cm^{-3}, ethanol: 0.789 g cm^{-3} and butanol: 0.81 g cm^{-3}).

The kinetics of EPD follows the Hamaker equation:[29]

$$\frac{dw}{dt} = \mu \cdot c \cdot A \cdot E \tag{2}$$

where dw/dt is the deposition rate, μ is the electrophoretic mobility of particles, c is the concentration of suspension, E is the applied electric field and A is the deposition area.

Sarkar and Nichelson[30] introduced an efficiency factor (f factor or sticking parameter) to take into account that not all the particles which reach to the substrate electrode are incorporated in it ($0 \leq f \leq 1$):

$$\frac{dw}{dt} = f \cdot \mu \cdot c \cdot A \cdot E \tag{3}$$

In our previous work[13] it was found that actually all the particles reaching the substrate electrode are incorporated in it. However, particle detachment from deposit into the suspension also occurs dynamically at their interface during EPD. The rate of particles detachment from the deposit into the suspension determines the value of f factor:

- When no particle detachment occurs from the deposit into the suspension at their interface: $f = 1$.
- When all the particles incorporated in the substrate detach into the suspension: $f = 0$: no deposition occurs.

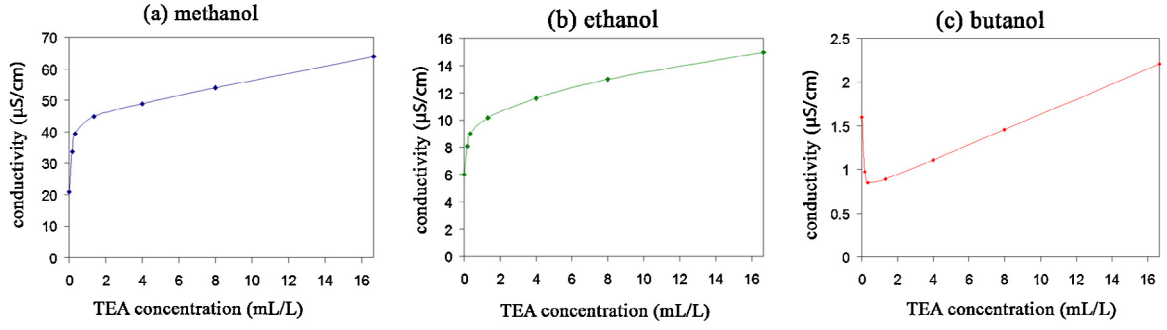

Fig. 1. Electrical conductivity of 20 g/L suspensions of titania nanoparticles as a function of TEA concentration in different alcoholic suspensions: (a) methanol, (b) ethanol and (c) butanol.