

Methods for functionalization of microsized polystyrene beads with titania nanoparticles for cathodic electrophoretic deposition

S. Radice^{a,*}, P. Kern^{a,1}, H. Dietsch^b, S. Mischler^c, J. Michler^a

^a EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH 3602 Thun, Switzerland

^b Fribourg Center for Nanomaterials (FriMat), Department of Physics, Pérolles, CH 1700 Fribourg, Switzerland

^c Ecole Polytechnique Fédérale de Lausanne (EPFL), Lab. for Metallurgical Chem., CH 1015 Lausanne, Switzerland

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Abstract

Functionalization of colloidal particles based on the use of polyelectrolytes and heterocoagulation was combined with electrophoretic deposition (EPD), with the aim of depositing titania–polystyrene (TiO₂–PS) composite particles on Ti6Al4V substrates. The composite particles were obtained by heterocoagulation of TiO₂ nanoparticles on the surface of monosized polystyrene beads of 4.6 μm in diameter. Two alternative methods were developed for the preparation of the TiO₂–PS suspensions in organic fluids for cathodic electrodeposition. The first method was carried out in alkaline aqueous medium with the use of polyelectrolytes and intermediate control measurements of zeta potential, conductivity, and pH; the second one was carried out directly in the organic solvent used for EPD, typically isopropanol. Examples of deposits obtained by EPD in both suspensions and a comparative analysis between the two methods are presented.

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1. Introduction

In the present work, particle functionalization is considered for subsequent electrophoretic deposition (EPD), a simple and flexible technique for producing coatings and thick films [1]. In particular, cathodic EPD is interesting because it avoids uncontrolled anodization (oxidation) of the metallic substrate. EPD of polystyrene (PS) beads has mostly been investigated within the research fields of colloidal crystals and photonic stop-band materials, utilizing only nanosized or submicrometer PS beads [2–7]. Polystyrene beads can also be used as spacers in combination with inorganic particles, leading to porous coatings or materials after removal of the PS spacers by heat treatment. For example, Jia et al. prepared green samples by slip casting of aqueous suspensions of nano-ZrO₂-coated PS spheres

(∅ 1 μm) and sintered them at 1000 and 1400 °C for 2 h [8]. Hamagami et al. prepared ethanol suspensions with hydroxyapatite nanoparticles mixed with PS beads (∅ 3 μm) and used electrophoretic deposition to prepare macroporous coatings on titanium substrates [9]. The electrophoretic co-deposition of microsized PS beads combined with nanosized inorganic particles such as TiO₂ has great potentiality in the preparation of coatings with micropatterned surfaces combined with nanotopography, where the micropatterning is left by the microsized template and the nanotopography is given by the sintered inorganic nanoparticles. Such scale-resolved surface structuring is particularly relevant for biomedical applications, where specific combinations of micro- and nano-roughness were found to control cell adhesion and osteointegration of implant surfaces [10]. The fabrication of coatings with scale-resolved structuring by EPD starting from well-controlled particle functionalization remains a challenge.

Research activities on the functionalization of polystyrene beads include the use of polyelectrolytes and the concept of heterocoagulation (coagulation between oppositely charged par-

* Corresponding author. Fax: +41 33 228 44 90.

E-mail address: simona.radice@empa.ch (S. Radice).

¹ Current address: Hoffmann Neopac AG, Burgdorfstrasse 22, CH 3672 Oberdiessbach, Switzerland.

ticles or species due to electrostatic attraction). PS beads and polyelectrolytes have been widely investigated for the preparation of hollow particles [11–15] and functionalized particles in the field of biosystems and drug delivery [16,17]. Additionally, F. Caruso and co-workers have extensively reported on the functionalization of PS beads using polyelectrolytes and a layer-by-layer deposition process [18–23]. In particular, they compared the layer-by-layer coating procedure of PS beads using titania (TiO_2) precursors with that using TiO_2 colloidal nanoparticles [19], pointing out the advantages of the latter. The procedure using TiO_2 colloidal nanoparticles involved of PS particles as templates, on which layers of nanoparticles were deposited by the alternate adsorption of oppositely charged polyelectrolytes and nanoparticles, resulting in nanoparticle multilayer shells surrounding the template core. The authors used a variety of materials with the aim of producing hollow spheres. In particular, TiO_2 nanoparticles ranging from 5 to 50 nm and PS beads from 210 to 640 nm in diameter were used.

In this context, we report on the controlled functionalization and EPD of bigger particles (microsized instead of the nanosized particles commonly found in the literature). In particular, suspensions of TiO_2 -functionalized PS microbeads were prepared and used for cathodic EPD. The preparation of functionalized particles for cathodic EPD is constrained by specific requirements, such as the charge of the particles (positive, with the cathodic substrate negatively charged) and the suspension medium (organic solvent, avoiding the problem of gas evolution). Two parallel methods for the preparation of functionalized particles were developed and compared. In the first method, particles are mixed in ethanol and composite particles form by heterocoagulation; the second approach relies on the intermediate adsorption of polyelectrolytes in an alkaline aqueous suspension. In both cases, the suspensions obtained can be used for a controlled cathodic EPD of the composite particles alone, without any excess of TiO_2 nanoparticles.

2. Materials and methods

2.1. Preparation of suspensions

Carboxylate-modified polystyrene beads of 4.6 μm in diameter (<2% CV—coefficient of variation expressed as the standard deviation as a percentage of the mean diameter) in 4 wt% (3.8 vol%) water suspensions were purchased from Duke Scientific Corporation. TiO_2 spherical nanoparticles were available from a flame-synthesis process [24]. Polydiallyl dimethyl ammonium chloride (PDADMAC) solution with very low molecular weight ($M_w < 100,000$), 35 wt% in water, was purchased from Sigma-Aldrich Chemie GmbH. The solvents used were isopropanol puriss. p.a. (Fluka Chemie GmbH), deionized water 18.2 $\text{M}\Omega\text{ cm}$ (Milli-Q), and ammonium hydroxide solution puriss. p.a. NH_4OH , $\geq 25\%$ in water (Fluka Chemie GmbH).

In the procedures for preparation of the suspensions for cathodic EPD, control measurements and analysis techniques were employed: zeta potential and electrical conductivity measurements (ZetaSizer Nano Z, Malvern Instruments Ltd.); pH monitoring (color-fixed indicator sticks from Roth); particle-

size distribution analysis by dynamic light scattering at an angle of 90° (Alv 5000l, laser Coherent Inc., Nd: YVO_4 , 532 nm); and scanning electron microscope analysis (SEM Hitachi S-4800). Intervals of 20 to 30 min were used between two sequential steps of a procedure. Zeta potential, conductivity, and pH were measured at the end of each interval. Intermediate centrifugation steps of 10 min were carried out in a Hermle Z 300 centrifuge at 2000 rpm (equivalent to 560g).

2.2. Electrophoretic deposition

As substrates for EPD, Ti6Al4V disks of 18 mm in diameter and 2 mm thickness were used. The substrates were previously HF-etched to a surface roughness of $R_a = 0.1\ \mu\text{m}$, cleaned in an ultrasonic bath with water and ethanol, and, just before EPD, ultrasonicated with a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$) rinsed away by water and isopropanol. As counter electrode, a stainless-steel (316L) disk with an exposed area of $\sim 0.4\ \text{cm}^2$ polished with a 600 grit SiC paper delimited by a mask of Araldit was used. A special electrochemical cell of 5-ml volume was constructed in our laboratory for a controlled withdrawal of the sample from the suspension. The exposed area of the working electrode was $\approx 0.12\ \text{cm}^2$. The counter electrode was held at a fixed distance of 4 mm from the working electrode. Before the EPD, the cell was rotated to a vertical position so that the electrodes were immersed in the suspension. During the last 10 s of the EPD, the cell was turned back to the horizontal position so that the suspension was gradually removed from the exposed area of the sample. The rotation of the cell was achieved by means of an electric motor with a shaft rotating with a constant angular velocity of approximately 1 rpm (under load).

EPD experiments were performed at constant voltage supplied by a Xantrex XDC 300-20 Digital DC Power Supply. The applied voltages ranged from 100 to 300 V (from 250 to $750\ \text{V cm}^{-1}$), and the deposition time from 120 to 600 s. The current was measured by an ampere meter integrated into the circuit. The deposits were characterized by SEM.

3. Results

3.1. Preparation of TiO_2 -PS composite particles in suspension

Two parallel procedures for the preparation of suspensions in isopropanol with PS- TiO_2 composite particles are presented. The first procedure is based on the use of the cationic polyelectrolyte PDADMAC in water as preliminary medium and will be referred to as the PDADMAC procedure; the other one, carried out directly in isopropanol without the use of any polyelectrolyte, will be referred to as ISOPR procedure. A flow diagram summarizing both procedures is given in Fig. 1.

The first three steps of the PDADMAC procedure are: (1) 10-times dilution of a given volume of as-received PS suspension in deionized water; (2) addition of NH_3 to a final molarity of 3 mM NH_3 ; (3) addition of PDADMAC from a 1 mM KCl solution to a final molarity of 0.1 mM PDADMAC. The initial dilution was required for zeta potential measurements with

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