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Towards the development of superhydrophilic SiO_2-based nanoporous coatings: concentration and particle size effect

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ABSTRACT

Superhydrophilic nanoporous coatings were prepared from layer-by-layer assembled silica nanoparticles (SiO_2) and a polycation. As expected, concentration of silica dipping suspension and particle size are closely related to thickness of the obtained multilayer films. However, wettability might not to be mainly governed by coating thickness as usually reported on literature; instead, superficial homogeneity should be carefully considered. It was found that if a uniform nanoporous structure is obtained, superhydrophilic behavior is observed and, at least for the studied system, increases in coating thickness are not followed by improvements on wetting performance. In turn, for obtaining uniform structures, the usage of dipping suspension with a hypothetical minimum silica nanoparticles concentration is mandatory. Below such critical value, stacking defects along the coating surface are observed and the manifestation of superhydrophilicity is inhibited. As an additional feature, low refractive indices of multilayer coatings resulting from nanoporosity was found to provide good antireflection (AR) properties.

1. Introduction

Coatings design with extreme wetting characteristics have the potential to inspire an entire research field focused on manipulating the interaction between liquids and solids. Nevertheless, the interest in fine-tuning wettability of solids particularly upraised after a wide acceptance that liquid spread control can be simply achieved through small changes in surface roughness and chemistry [1]. Superhydrophobicity, superhydrophilicity and super-wetting are probably the most popular topics concerning the wetting field, in which efforts have been directed to elucidate the correlation between liquid penetrating (or suspending on) phenomena and complex geometry surfaces [2–7]. Antifogging, self-cleaning and bacteria-resistant surfaces are but a few of the practical applications that could be enabled by the promotion of superhydrophobic [8–11] and superhydrophilic [12–15] behavior; the latter showing itself as the studying subject of the present work.

Superhydrophilic surfaces (normally described on which water contact angle is $< 5^\circ$ within 0.5 s or less) have gained notoriety especially due to their antifogging effect, which prevents light scattering of transparent substrates by the almost instantaneous spreading of condensed water droplets. Nonetheless, besides such trendy antifogging feature, other interesting properties like easy-cleaning, anti-reflective and biocompatibility have also been attributed to the superhydrophilic state [16,17].

Regarding superhydrophilic surfaces, two basic strategies have been approached in the literature. The first is based on the use of photochemically active materials such as titanium dioxide (TiO_2) that exhibit superhydrophilicity after exposure to UV or, with proper chemical treatments, visible radiation. However, although much progress has been made, TiO_2-based coatings typically lose their super-wetting properties when placed in dark environment, been limited to *outdoor* applications [18–21]. The second strategy involves the use of texturized surfaces to induce super-wetting properties. Early theoretical work by Wenzel [22] and Cassie-Baxter [23] suggest that it is possible to enhance wetting properties with water by introducing roughness at the right scale. Based on this concept, it was demonstrated that both lithographically textured [24] and micro -nanostructured surfaces might exhibit superhydrophilicity [25–27].

Electrostatic layer-by-layer assembly (LbL) is a versatile technique based on the alternated adsorption of oppositely charged polyelectrolytes and/or inorganic nanoparticles on solid substrates to build-up ultrathin multilayer films [28]. Previous studies have reported the utility of LbL assembly in the preparation of nanostructured coatings which, with optimized processing conditions, have the potential to be employed in the manufacturing process of superhydrophilic surfaces [29–32]. Nevertheless, it seems to be a consensus that the relation between processing parameters and performance of coatings is still not

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completely understood and need to be systematically investigated for each individual system.

In the current work, superhydrophilic assembled silica nanoparticles coatings were prepared via LbL assembly technique. The influence of concentration and particle size on topography, wettability, structural and optical properties have been discussed. Up to now, there is just a reduced number of studies concerning superhydrophilic SiO_2-based coatings resulting in a lack of experimental information and, thus, divergences on literature. In this context, this study contributes to consolidating a robust technical background for this important and captivating research field.

2. Experimental details

2.1. Materials

Poly(diallyldimethylammonium chloride) (PDDA, Mw = 200, 000–350,000, 20 wt% aqueous solution); poly(acrylic acid) (PAA, Mw = 250,000, 35 wt% aqueous solution); colloidal silica nanoparticles Ludox® SM (30 wt% SiO_2 suspension in water, 7 nm average diameter) and Ludox® TM-40 (40 wt% SiO_2 suspension in water, 22 nm average diameter) were purchased from Sigma-Aldrich. Standard microscope glass slides were employed as substrates. Deionized water purified in a Millipore Milli-Q® system was exclusively used in all aqueous solutions and rinsing procedures.

2.2. Multilayer assembly process

Prior to the deposition process, glass substrates were immersed in a slightly boiled *piranha solution* (3:1 98% H_2SO_4:30% H_2O_2 mixture) for 20 min, rinsed with copious amount of water and dried under N_2 flow. *Warning: piranha solution reacts violently with organic materials and should be handled carefully*. The deposition process is consisted of immersing the substrates repetitively into different aqueous solutions. Sequential adsorption of multilayer coatings were performed in freshly cleaned glass slides assisted by an automated dipping unit; immersion time for all polymers and nanoparticle suspensions was fixed in 15 min. Each deposition step is followed by a rinse step of 2 min to remove the non-adsorbed material on surface. The pH of all dipping solutions were adjusted with NaOH or HCl (0.2 M) to a value defined by zeta potential measurements (to be discussed).

The multilayers were composed of two main blocks. First, *adhesion layers* were used to improve binding of the polymer-nanoparticle system to the substrate. In this stage, two (PDDA/PAA) bilayers were deposited. PDDA was employed as the cationic solution (0.1 wt%) and PAA as the anionic solution (0.1 wt%).

For the *body layers*, fifteen (PPDA/SiO_2) bilayers were deposited. PDDA (0.1 wt%) was once more employed as the cationic solution. For the anionic solution, the two differently sized SiO_2 nanoparticles (7 nm and 22 nm) prepared in various concentrations (0.01, 0.03, 0.05 and 0.1 wt%) were used. All specimens were identified as following: (PDDA/SiO_2 (y) x%), where y refers to the nanoparticle size and x refers to the concentration of SiO_2 suspension employed in the preparation of each specimen.

The as-prepared coatings were dried at room temperature and calcinated at 500 °C for 4 h. Calcination step is responsible for removing the organic part and enhancing mechanical stability through formation of siloxane bridges. Preparation protocol of the superhydrophilic coatings is schematically illustrated on Fig. 1.

2.3. Characterization

Stability of colloidal silica nanoparticles were evaluated by zeta potential measurements in a Zetasizer Nano ZS (Malvern) equipment over a wide range of pH values. Contact angle measurements were carried out at ambient temperature in a CAM 200 (KSV NIMA) equipment using 1 μL water droplets as indicators. Contact angle values were calculated from the digital video files captured by a CCD camera. Topographical information and root-mean-square roughness (RMS) values were determined by atomic force microscopy (AFM) using a NanoScope V (Bruker) equipment operating under *soft tapping in air* mode. Thickness and morphological properties of the coatings were evaluated from the scanning electron microscopy (SEM) images obtained by a Magellan 400 L (FEI) equipment. Transmittance measurements at normal incidence were performed using a Cary 50 Probe UV–visible spectrophotometer (Varian) operating in visible light range. For each analysis, more than three measurements were performed and the average value is reported.

3. Results and discussions

Probably, the two most fundamental factors to create functional multilayer coatings based on nanoparticles are (1) control over z-direction placement and (2) control over the aggregation level. The LbL process by itself provides the ability to place each layer in a fine-tuned manner whereas the manipulation of assembly conditions (nanoparticles size, concentration and solution pH) provides the control over nanoparticle aggregation.

3.1. Colloidal silica stability

It is well-known that colloidal SiO_2nanoparticles have a negative character due to the presence of silanol (−OH) groups on their surface; however, there is still no satisfactory method to determine the surface charge of small particles in aqueous solution. The common practice is to determine the electric potential at a location away from particle surface, in a region named slipping or shear plane. The potential measured at this plane is called *zeta potential* and can be closely related to the suspension stability [33]. Since the surface charge of particles brought into contact with water are normally pH-sensitive [33,34], colloidal 7 nm and 2 2 nm SiO_2 nanoparticles stability was evaluated by zeta potential measurements over a wide range of pH values as shown in Fig. 2.

According to the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory, highly stable colloidal systems are characterized by high zeta potentials, whereas low zeta potentials indicate less stable systems. It is widely accepted that zeta potential values of ± 30 mV are enough to promote stable water suspensions [35].

Intuitively one can infer that the presence of randomly shaped agglomerates in LbL dipping solutions might result in a deleterious effect over the control of the deposition process. From Fig. 2, stable suspensions of both 7 nm and 22 nm SiO_2 nanoparticles can be prepared in the range of pH 8 to 10. On the other hand, since PDDA is considered as a strong polycation the degree of dissociation of its ionic groups is nearly pH-independent [36]. Concerning the stability window of both colloidal nanoparticles and the PDDA pH dissociation independence, seems to be obvious that the most suitable assembly condition is precisely between pH 8 and 10; thus, for sake of simplicity, pH 9 was fixed for all dipping solutions.

3.2. Topographical analysis

The wetting behavior of a surface is determined by both its chemistry and micro-nanotexture. It is believed that, for a given chemical composition, increasing the roughness of a surface might enhance its hydrophilicity or hydrophobicity, depending on the wettability of the material in the smooth state. This phenomena is described by Wenzel's model [22] and is mathematically shown in Eq. (1)

$$\cos\theta_e^W = r\cos\theta_e \tag{1}$$

where $\theta_e{}^W$ is the apparent water contact angle on a rough surface; θ_e is