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Elaboration of thin colloidal silica films with controlled thickness and wettability

Élaboration de films minces de silice à épaisseur et mouillabilité contrôlées

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ABSTRACT

Silica films with controlled thickness and wettability have been formed by sequential adsorption of colloidal silica nanoparticles and a cationic polyelectrolyte (poly(allylamine hydrochloride) or poly(diallyldimethylammonium chloride)) was used as the binding agent. Whatever be the conditions used, the structure of films appeared dense and non-porous. Thicknesses varying from 12 to 430 nm and wettability varying from 5 to 60° were obtained when the pH or concentration of the silica solution was varied. Quartz crystal microbalance measurements evidenced the formation of regular and reproducible thin films mainly composed of silica nanoparticles. These films contained few polycations due to the formation of long-distance charge pairs between silica nanoparticles and polycations.

Mots-clés:
Auto-assemblage
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Polymères
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RÉSUMÉ

Des films de silice d'épaisseur et de mouillabilité contrôlées ont été formés par adsorption alternée de nanoparticules de silice colloïdale et d'un polyélectrolyte cationique (hydrochlorate de polyallylamine ou chlorure de polydiallyldiméthylammonium) utilisé comme liant. Pour toutes les conditions testées, la structure des films est apparue dense et non poreuse. Les films obtenus présentent des épaisseurs allant de 12 à 430 nm et des angles de contact allant de 5° à 60°, selon le pH ou la concentration de la suspension de silice. Des mesures de microbalance à cristal de quartz ont montré que la formation des films est régulière et reproductible. Les films obtenus contiennent principalement des nanoparticules de silice et peu de polycations, en raison de la formation de paires de charges à longue distance entre les premières et les derniers.

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1. Introduction

Due to the high surface to volume ratio, the incorporation of micro- and nano-particles can substantially increase the performance of initial materials. Inorganic particles such as gold, silver and silica are commonly used to obtain films having conductive [1], magnetic [2], optical [3], plasmonic [4], or hydrophobic and hydrophilic properties [5]. In particular, silica nanoparticles offer a potential building block to form ordered materials and composite structures. Thus, silica nanoparticles are employed in a wide range of applications, including biomedicine [6], optics [3] and paper industry [7]. However, the formation of films generally requires the use of another component possessing opposite charges. In this case, the two components can be self-assembled if the electrostatic forces are sufficient to overcome the other repulsive forces.

Different strategies have been used to prepare multilayer films incorporating nanoparticles. This includes deposition of natively oppositely charged nanoparticles [8,9] or of oppositely charged nanoparticles obtained by pre-deposition of polyelectrolytes on their surfaces [10–12]. Another interesting approach consists in the assembly of nanoparticles and oppositely charged polyelectrolytes [13,17–19]. This method has been used to prepare thin films with interesting optical [20] or sensing properties [21]. As an example, a multilayer film made of HgTe nanoparticles and a polymer showed strong emission in the near-infrared region allowing potential application in optoelectronics [22]. The photocatalytic response of multilayer films combining TiO_2 nanoparticles and polymers led to promising results for environmental applications [14,15]. The encapsulation of silica nanoparticles by polyelectrolytes was also used for the preparation of biocompatible microcapsules [11], antibacterial substrates [24] and superhydrophobic films that can be used as self-cleaning surfaces [23]. Liu et al. [3] reported the formation of nanostructured antireflective surfaces by deposition of monodispersed 120-nm-silica nanoparticles on a glass substrate by electrostatic attraction between negatively charged colloidal particles and positively charged polyelectrolytes.

Taking this literature into account, the present study aims at developing new dense composite thin films, with tunable size and wettability, made of silica nanoparticles and a cationic polyelectrolyte used as the binding agent. Growth of films was achieved by the alternate adsorption of negatively charged colloidal silica particles and positively charged polycations using the layer-by-layer technique [25]. Silica nanoparticles were assembled in alternation using two different polycations, PAH (poly(allylamine hydrochloride)), a weak polyelectrolyte and PDDA (poly(diallyldimethylammonium chloride)), a strong polyelectrolyte. The effect of other parameters including pH of the polycation solution and pH and concentration of the silica suspension, on the build-up of the composite films, was also investigated. These studies were carried out using dissipative quartz crystal microbalance (QCM), contact angle measurements, profilometry, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2. Experimental

2.1. Particles

Silica nanoparticles Bindzil 30/220 (30 wt% SiO_2 suspension in water, an average particle size of 20 nm and a specific surface area of 220 m^2/g) were purchased from Eka Chemicals AB. The stock silica suspension was diluted with 0.01 M NaCl up to desired silica concentrations ($[SiO_2] = 1$, 0.1, 0.01 g/L). The pH of SiO_2 dispersion (concentrated at 1 mg/mL) was 8.5 at 20 °C. The pH of the silica dispersion was adjusted to pH 4 by the addition of aqueous HCl.

2.2. Characterization of silica particles

Electrophoretic mobility and hydrodynamic diameter measurements were conducted on silica particles dispersed and sonicated in 0.01 M aqueous NaCl solution using a Malvern Zetasizer Nano ZS to determine their zeta potential and size distribution. It is generally considered that there are many silanol groups on the surface of SiO_2 nanoparticles, and the point of zero charge (PZC) is 2.1 for SiO_2. This makes the surface of SiO_2 nanoparticles negatively charged in aqueous solutions at a pH above 2.1 [26]. This was confirmed by our ζ potential measurements as a function of pH (Table 1). A negative ζ potential was obtained at all pH values investigated with the magnitude increasing from a value of −2.4 mV at pH 2.3 to a maximum value of −20.1 mV at pH 8.5. The size distributions of the silica suspensions in Table 1 are presented in percentage of intensity. They revealed the presence of two populations at all pH values investigated. However, the low size particles ($D_h = 23 \pm 5$ nm) are present in majority (Intensity ≥87% at pH 2.3 and 98% at pH 8.5).

2.3. Polyelectrolytes

Poly(diallyldimethylammonium chloride) solution (PDDA, 20 wt% in water, M_W 100 000–200 000) and poly(allylamine hydrochloride) (PAH, M_W 58 000) were purchased from Sigma Aldrich and used without further purification. Polyelectrolyte solutions were prepared at a concentration of 0.1 g/L with 0.01 M NaCl. The pH values of PDDA and PAH solutions were adjusted to 4 or 10 with dilute HCl or NaOH. PAH is a weak polyamine with a pKa value around 8.7 [27].

Table 1
Hydrodynamic diameter (D_h) and zeta potential of silica nanoparticles dispersed in 0.01 M NaCl solutions at different pH.

pH	D_h (nm) (% in intensity)[a]	Zeta potential (mV)
2.3	22 (87.6) 376 (12.4)	−2.4
4.0	26 (95.7) 171 (4.3)	−7.5
6.0	23 (98.2) 193 (1.8)	−19.6
8.5	23 (98.9) 263 (1.1)	−20.1

[a] Measurements uncertainty: ± 5 nm.

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