Colloids and Surfaces A: Physicochem. Eng. Aspects 443 (2014) 331–337

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Hydrophobic coating of mica by stearic acid vapor deposition

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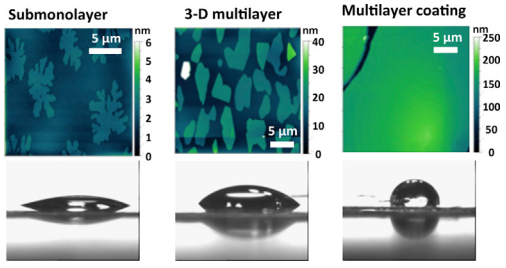
HIGHLIGHTS

- Self-assembled monolayers are formed on mica surface exposed to stearic acid vapors.
- Monolayer structures are always defective keeping the surface hydrophilic.
- Multilayer coatings form three-dimensional bilayer bulk-like structures.
- Hydrophobic coatings are obtained only from a multilayer coverage.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 September 2013
Received in revised form
11 November 2013
Accepted 20 November 2013
Available online 28 November 2013

Keywords:
Self-assembled monolayer
Atomic force microscopy
Stearic acid
Hydrophobic

ABSTRACT

We report on the preparation of thin films of stearic acid on mica by sublimation in air. We correlate their affinity to water (hydrophobic vs. hydrophilic character) to the morphology of the films as observed by Atomic Force Miscorcopy (AFM). Submonolayer and monolayer coverage exhibited hydrophilic character with dendritic shape defective self-assembled monolayer structures. With further exposure to stearic acid regular polyhedric multilayer three-dimensional structures formed on top of the monolayer, following the Stranski–Krastanov mechanism of growth. These structures were found to be compatible with a stearic acid bulk crystal structure. Coalesce of the structures generated a hydrophobic multilayer coating showing spiral growth. However, the multilayer coating was not homogeneous showing areas with only defective monolayer coating that still exposes bare mica.

1. Introduction

Stearic acid (STA, octadecanoic acid) is an 18-carbon chain saturated fatty acid found in many animal and vegetable fats and oils. Stearic acid is used in many industrial sectors to create protective coatings due to its amphiphilic character and low cost. For example, to avoid Mg corrosion [1], to prevent calcium carbonate particles adhesion [2] or to improve the compatibility of inorganic fillers with hydrophobic polymer matrices in flame retardants such as aluminum trihydrate and magnesium hydroxide [3]. In addition, its biocompatibility makes it ideal for the pharmaceutical industry, for example to be used in coatings to control drug delivery [4]. Stearic acid molecules form self-assembled monolayers (SAMs) triggered by its amphiphilic character, being able to produce hydrophobic coatings on top of hydrophilic surfaces [5]. STA coatings are usually created either by dry (exposure to vapors or aerosols) or by wet (immersion in solutions) processes. Dry processes are the most widely used in industry due to their lower cost and simplicity. In these processes, surfaces or particles are exposed to melted STA at temperatures ~100 °C [6]. Bulk properties of products coated in dry conditions have been extensively characterized [6]. However, most of the fundamental studies on the formation of SAMs and their structures have been focused on coatings created using

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http://dx.doi.org/10.1016/j.colsurfa.2013.11.031

wet processes [7,8]. The study of fatty acid films created in solution and transferred to surfaces using Langmuir–Blodgett techniques experienced an intense activity two decades ago [9,10]. In those studies SAMs were created at the air–water interface and then transferred to a surface. While the structures of films transferred to flat and well defined substrates such as mica, silica, gold, etc. were well established for films with a single type of molecules [9], the structure of films presenting mixtures of different molecules is still under debate [11]. Multilayer films are usually created by sequential transfers using this method. However, structures formed using this technique can be very different from the structures obtained using dry procedures due to the discontinuous character of the former and the continuous of the latter.

In this work, we study the formation of monolayer and multilayer STA films on mica surfaces exposed to STA vapors in ambient conditions, using a simplified experimental set up, and the correlation of the coatings' affinity to water (hydrophobicity/hydrophilicity) with their morphology. STA were prepared in a series of different temperatures and exposure times and studied with atomic force microscopy (AFM). The hydrophobicity/hydrophilicity character of the samples at the macroscale was determined by measuring the static contact angle of a water droplet deposited on the surface. A complete monolayer is expected to be the ideal coating to obtain the desired hydrophobic effect using the minimum amount of STA. In this configuration, STA molecules would be found closely packed and exposing their alkyl chains to the air. However, even on flat surfaces such as mica, SAMs exhibit a large amount of defects that can let water molecules to penetrate the layer, thus reducing its hydrophobic character [12]. On the other hand, the morphology at the nanometer level of the films may lead to water confinement [13], influencing the macroscopic affinity of the surface to water. Our results showed that the monolayer obtained by vapor exposure is not effective enough to obtain a macroscopic hydrophobic behavior, due to the presence of defects, and that hydrophobicity is reached only when a thicker multilayer film is obtained.

2. Experimental details

2.1. Materials and sample treatment

STA was purchased from Sigma–Aldrich (Grade I, nominal purity $\geq$ 98.5%). 1 cm^2 muscovite mica substrates (Grade V-4, SPI supplies) were freshly cleaved with adhesive tape and exposed to stearic acid vapors in air by sublimation of the as-received product. A laboratory glass vial containing 0.5 g of STA was placed on a hot plate and the temperature was measured using an electronic contact thermometer sensoterm II (JP Selecta, Barcelona, Spain) with an uncertainty range of $\pm$1 °C. Once the desired temperature for the current series was reached, the vial was covered with the fresh cleaved mica sample the desired amount of time. The separation between the surface of the melted STA and the exposed mica surface was of 10 cm. The sublimation rate of the STA was controlled by measuring the loss in mass of the initial 0.5 g of STA exposed during 15 min to different temperatures. The expected exponential Mass loss vs. T curve was found to start at around 85 °C with an initial loss of mass higher than 1% at this temperature. When the STA was exposed to temperatures above 170 °C, an irreversible change in the color of the STA remained inside the vial was observed, suggesting some kind of chemical modification. Taking into account these two observations our experiments were restricted within a range of temperatures comprised between 85 °C and 170 °C. Mica samples were exposed for 5, 10 and 15 min to STA heated at 90, 110, 130, 150 and 170 °C. A complete set of samples was prepared in five different days for statistical purposes. Once the exposure of the mica sample was complete, the coated mica samples were stored inside a desiccator for 24 h in order to leave enough time to the system to equilibrate its morphology.

2.2. AFM and contact angle measurements

AFM experiments were carried out using an Agilent 5500 AFM (Agilent Technologies, Santa Clara, USA). Images were taken at ambient conditions (RH $\sim$ 45%, $T \sim 22$ °C) using the Amplitude Modulation AFM (AM-AFM) in the repulsive mode [14] in order to minimize height artifacts [15]. Microfabricated silicon cantilevers with nominal force constants $k_c \sim 45$ N m^{-1} (PPP-NCHR, NanoAndMore GmbH, Darmstadt, Germany) were used. Contact angle measurements were performed after the AM-AFM measurements by depositing 3 μl of MilliQ water on top of the coated mica surfaces. The analysis of the drop shape was performed using an Easy drop standard apparatus (Kruss, Hamburg, Germany).

3. Results and discussion

Fig. 1 shows AM-AFM images of some of the coatings produced at different temperatures and exposure times. Images shown are representative of the most common structure found for each sample condition (temperature and exposure time) among the samples prepared in different days. In general, we distinguish between 4 kinds of coverage or morphology, submonolayer coating, in the form of islands of self-assembled monolayers (Fig. 1a, b and d), monolayer coverage (Fig. 1c), regular polyhedric three-dimensional structures (from here on we will name them *pillars*, Fig. 1e, f and g) and large multilayer structures (Fig. 1h and i). As mentioned above, the images are representative of the most common structures found for each condition and they do not have to be taken strictly. That means that, for example at 90 °C and 15 min of exposure times, pillar structures were also observed in two out of five samples measured. Samples prepared at 150 °C showed multilayer structures similar to what is shown in Fig. 1i. Above this temperature no regular structures appeared on the surface, only irregular agglomerates, covering partially the surface, were observed as shown in Fig. 3a.

The hydrophobicity of the coatings was explored by measuring the static contact angle of water droplets. In Fig. 2 the mean values of the contact angle measured on samples showing the different morphologies defined above are shown. Contact angle of 3 μl of MilliQ water droplets were measured in 5 samples showing the same morphology and the standard deviation of the mean is included in the figure as error bars. No quantitative information is intended from our static contact angle measurements because of the inhomogeneity of the samples, as observed by AFM. Our measurements give only qualitative information about the efficiency of the different structures in making the surface hydrophobic from a macroscopic point of view. The measurements revealed, as expected, that the increase in contact angle goes in unison with the increasing coverage of the mica substrate. However, only multilayer structures showed a contact angle value that could be considered as hydrophobic. In the following sections the different structures observed are analyzed in detail.

3.1. Submonolayer and monolayer

On samples prepared at the lowest temperature (90 °C), incomplete monolayers were usually observed, forming hydrophobic islands with irregular dendritic-like shaped edges (Fig. 1a and b) with an important presence of defects in the form of small holes. Dendritic-shaped islands have been previously observed on other SAMs, for example silanes on mica prepared from solution [16]. Such a fractal shape has been considered consistent with a 2D-diffusion-limited aggregation. In those cases, island growth