Full Length Article

Superhydrophobic brass and bronze meshes based on electrochemical and chemical self-assembly of stearate

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ARTICLE INFO

ABSTRACT

The preparation and characterization of superhydrophobic membranes formed on metal meshes (brass and bronze) by coating from stearic acid is presented. The membranes were prepared by two methods: electrolysis and acid etching. The electrolysis process is a one-step method performed by anodizing the mesh in ethanol solutions of stearic acid. Stearic acid concentration, support electrolyte concentration and electrolysis time were systematically varied. Nanostructures, including nanotubes, are induced on the metallic filaments. Analysis by FTIR, XRD, XPS and SEM of surfaces and precipitated material indicate that formed nanostructures are assemblies of metallic stearates on the surface (copper and/or zinc stearates). Superhydrophobicity (contact angles larger than 150°) was only achieved (in the electrolysis method) in cases where the formation of nanotubes was observed. On the other hand, the acid etching process is a two-step method: immersion of the meshes in acid solution of $CuCl_2$ or $FeCl_3$, oxidizing the surface with formation of inorganic salts nano crystals, followed by immersion in stearic acid solution. Organic nanostructures (nanoribbons and/or nanopetals) were observed after the second step. Superhydrophobic surfaces (contact angles between 150 and 170°) were obtained for all the membranes.

Both kind of membranes (electrolysis and etching) resulted effective in oil-water separation.

1. Introduction

The non-wetability properties of metallic surfaces are receiving increasing attention in connection with several applications, such as corrosion resistance, anti-icing surfaces, self-cleaning surfaces, separation of fluids and filtering [1–7]. In these applications, it is central to obtain superhydrophobic surfaces, usually defined as those displaying water contact angles (WCA) larger than 150° and *sliding angles* (α) lower than 5 degrees [5,8]. Superhydrophobic effect is inspired by the naturally occurring lotus leaf phenomenon, where water roll-off is due to the micro-nano hierarchical structure which provides self-cleaning properties to the surface [9]. In material science, these features can be obtained by controlling the composition and structure at micro-nano scale [10] and many research efforts are permanently done to develop simple and less expensive methods to produce superhydrophobic surfaces.

In particular, to obtain superhydrophobic surfaces on metal surfaces or substrates is of high importance, not only in corrosion resistance but also in separation membranes and industrial filters. Most of the methods for converting hydrophilic to superhydrophobic metal surfaces are based on creating organic coatings on the surface by several approaches, including electrospinning [11], spin-coating [12] or grafting [13]. From a methodological point of view, these methods are typically referred as *two-step methods* since presenting a first step of modifying the metal surface by chemical attack in order to favour the formation of adsorption sites, followed by a second step of depositing the organic material. In fact, one common path to obtain superhydrophobicity consists in an acid oxidation of the metal substrate, followed by immersion in a solution which reacts chemically or electrochemically to produce the adsorption/deposition of organic material. Binding sites are produced at the first step by oxidation [14,15]. For instance, Liu et al. [14] made superhydrophobic stainless steel meshes by immersion

during 15 s in a solution of HCl 0.5 M and $CuCl_2$ 1.5 M (acid etching) followed by immersion in 0.1 M stearic acid ethanolic solution.

On the other hand, *one-step* methods are gaining more relevance [16–18]. Huang et al. [19] have developed a simple *one-step* electro-chemical process based on the anodization of a copper surface in ethanolic stearic acid solution. Concerning the use of stearic acid, Feng et al. [13] reported fabrication of superhydrophobic surfaces by grafting stearic acid onto roughened aluminum. Recently stearic acid was used to hydrophobize cellulose membranes [20]. Thus, the use of stearic acid appears as very promising for the case of many substrates. Hence, for metallic substrates, one-step anodization of stearic acid solutions appears as an interesting alternative. However, characterization of the whole chemical reactions, identification of sub-products of electrolysis, determination of conditions for inducing different morphological structures (nanotubes, nanobelts, nanopetals, etc.), are open issues, not clarified yet.

Additionally, membranes for applications in filtering and oil-water separation do need to satisfy specific requirements related to robustness, flexibility and fluidization of a mobile phase through them. Flexible metallic meshes made of brass or bronze are the most common materials for those applications. In some cases copper [21] or stainless steel meshes must be used [2,22], although costs increases in comparison to brass and bronze meshes.

Therefore, the aim of the present work is to investigate a protocol for obtaining superhydrophobic surfaces which is based on combining the following issues: (i) substrates based on metallic meshes; (ii) exploring brass and bronze meshes; (iii) deposition of stearic acid, using two-step and one-step methods, which are compared. The single-step method is based on an electrochemical process, where a central target is the identification of experimental conditions to form micro-nano structures, such as nanotubes and nanopetals. For the two-step method, acid etching followed by adsorption of stearate was selected.

2. Materials and methods

2.1. Chemicals

Stearic acid (HSt) was provided by Y-TEC (YPF Technology, Argentina). Anhydrous lithium perchlorate ($LiClO_4$) was from Baker Analyzed (J.T. Baker™, USA). Hydrochloric acid (37%), copper (II) chloride and iron (III) chloride were provided by Merck™ (Germany). All solvents were of analytical quality. All reagents were used as purchased. Bronze meshes (porous diameter $\approx 77\,\mu m$) and brass meshes (porous diameter $\approx 77\,\mu m$) were provided by Sueiro & Hijos (Ciudadela, Provincia de Buenos Aires, Argentina). These meshes are typically used in several oil-water and waste-water separation processes at industrial levels.

2.2. Preparation of membranes by electrolysis

Based on the method described by Huang et al. [19], an electrochemical process to produce stearate-brass meshes was developed. Electrolysis was performed on solution of stearic acid in ethanol (EtOH). The concentration of stearic acid was varied in the range 10^{-2}–10^{-1} M. $LiClO_4$ (10^{-3} and 10^{-2} M) was used as inert electrolyte in order to increase the electrical current, hence reducing electrolysis time. A copper surface was used as the cathode. Brash meshes with porous diameter $\approx 77\,\mu m$ determined by SEM and strand thickness $\approx 33\,\mu m$ (mesh 200) were used as the anode. The stoichiometric Cu/Zn relationship in the mesh was about 4, determined by EDS. The geometrical-macroscopic area (**A**) of the mesh immersed in solution was 3 cm × 2 cm. The area of the metal mesh, estimated from SEM, is about 0.7**A**. The distance between electrodes, **d**, was fixed to **d** = 3 cm. Electrolysis was performed using a Zurich DF1730SB5A electrical source. The voltage applied between electrodes (**ΔV**) was fixed to the maximum allowed value (30 V) in order to provide enough electrical

current. The electrical current (**I**) was determined with a UNI-T UT60E tester and varied by changing the concentration of $LiClO_4$ (**I** between 10 mA and 100 mA). Electrolysis time (**Δt**) was typically 10 min, although some essays were performed changing the time in the range from 10 to 180 min (at 0.001 M $LiClO_4$) in order to analyze its influence on the surfaces. The macroscopic electrical density charge (**σ**) that is transferred during electrolysis was calculated as $\sigma = \frac{I\Delta t}{0.7A}$.

2.3. Instrumentation

Measurements of water contact angle (**WCA**) were performed using a KSV CAM 200 Optical Contact Angle Meter. Calibration was performed with a magnetic stainless steel sphere (4 mm diameter). The sliding angle (**α**) is defined as the minimum angle from the horizontal which is required for water drops to roll. Measurements of **α** were performed trigonometrically by determining the minimum altitude for a water droplet to start rolling. Distilled water was used for all **WCA** and **α** measurements. All determinations were performed at room temperature ($\approx 25\,°C$) and ambient pressure (≈ 1 bar). The volume of the water droplet was 15 μL and angles (**WCA** and **α**) were registered after one minute since drop deposition on the surface. No variation with the droplet volume was detected in the range 10–20 μL, which is the range suggested by the provider of the instrument for **WCA** determinations. For a given sample, **WCA** was measured in ten different sites on the surface (and for each site, **WCA** values at the left and right sides of the drop were recorded). The standard deviation for the whole set of twenty determinations on each sample was about 3%, which is larger than the error of one determination (1%).

Surface morphology was analyzed using a Field Emission Scanning Electron Microscope (FESEM; Zeiss Supra 40 Gemini). Infrared spectra (ATR) were recorded using Nicolet 8700 equipment. X-ray photoelectron spectroscopy (XPS) experiments were carried out with a SPECS instrument. Spectra were acquired using a monochromatic Al Kα (1486.6 eV) operating at 100 W and 10 keV. The spectrometer is equipped with a dual anode Al/Ag X-ray source, and a hemispherical electron energy analyzer. Binding energies (BE) are referred to adventitious C1s emission at 284.8 eV. Measurements were carried out on dry samples using a conducting double stick carbon tape. The vacuum chamber pressure during the analysis was $< 5 \times 10^{-9}$ mbar. Atomic force microscopy (AFM) images were acquired to characterize surface topography. A Bruker Multimode 8 SPM (Santa Barbara, CA, USA) and NanoScope V Controller (BillericaSanta Barbara, CMA, USA) were used. The image analyses were performed using Gwyddion version 2.46 (Brno, Czech Republic) and Nanoscope version 9.1 software (Santa Barbara, CA, USA). The AFM images were acquired in the intermittent mode using silicon tips with a spring constant of $1–5\,Nm^{-1}$ and a resonance frequency in the range of 60–100 kHz. Areas of typically 50 μm × 50 μm were scanned. For each AFM image, a reference plane (mean plane) was defined and a Z-axis, perpendicular to that plane, was considered, where $Z = 0$ was on the plane. Z-values were calculated from the images in a discrete manner, where Z_j was defined as the height of the j-pixel from the mean plane. That is, Z is a discrete stochastic variable. Positive Z-values are associated to protrusions above the mean plane, while negative Z-values, to depressions below the plane. The average surface roughness (R_a) of each AFM image was determined as the average deviation of height values from the mean plane, when considering N pixels in a given image: $R_a = \frac{1}{N}\sum_{j=1}^{N}|Z_j|$ ($N = 262{,}144$).

2.4. Preparation of membranes by etching followed by adsorption of stearic acid

Bronze meshes (the same used for electrolysis) were immersed into a 1.5 M $CuCl_2$ and 0.5 M HCl aqueous solution for different times (15, 30, 45, 60 and 90 s). After that time the meshes were rinsed