Coral-like nanostructures

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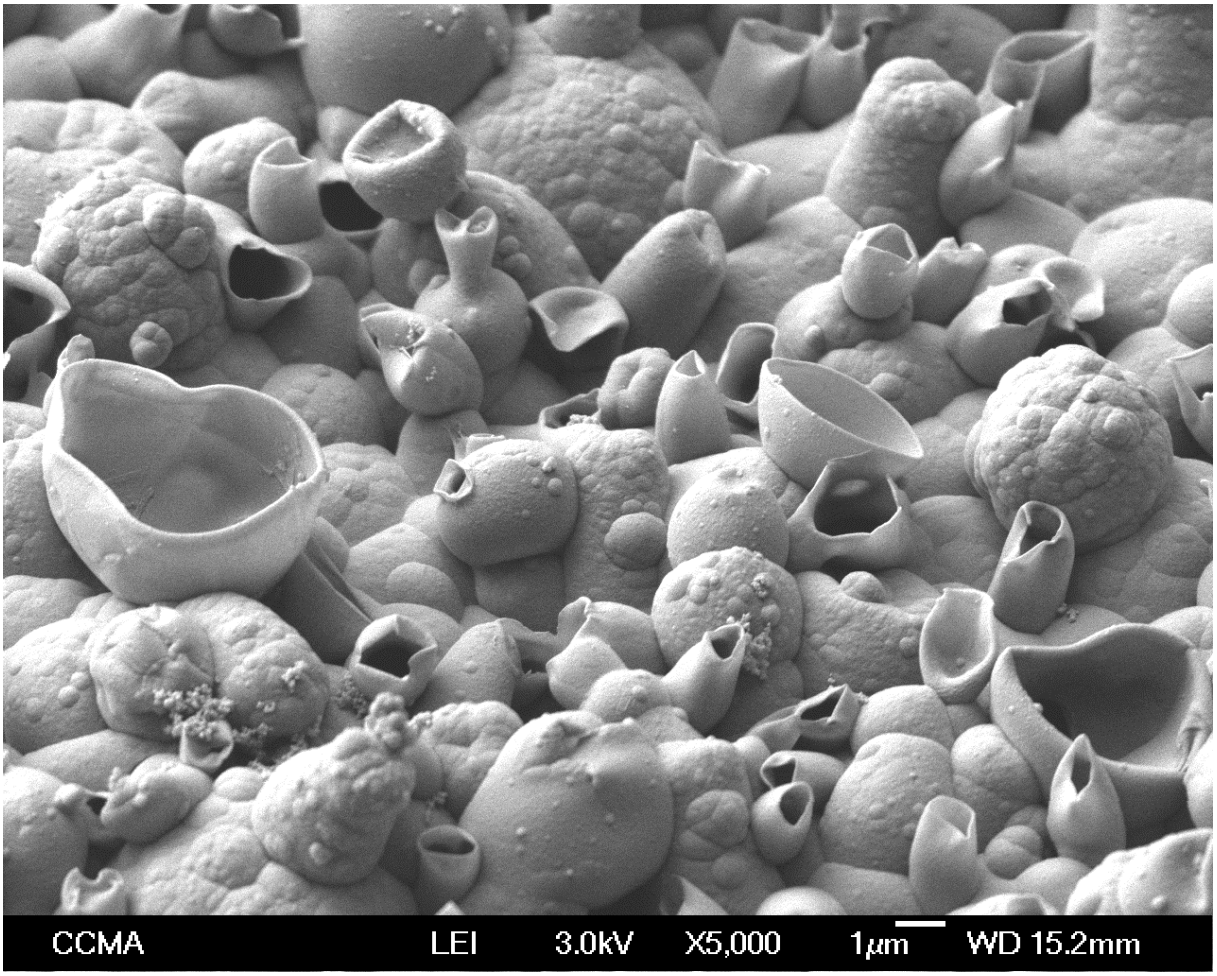

The design of nanoporous surfaces such as nanotubes with well-controlled dimensions (e.g. diameter, height, porosity) and shape (e.g. cylindrical, spherical) are fundamental in determining the relationship between geometrical parameters of such nanostructures and their ultimate surface properties [1]. The range of potential applications for these nanoporous surfaces is extremely vast. For example, nanotubular surfaces have been employed to encapsulate molecules, materials and even gases. Furthermore, additional applications are currently being explored in fields such as drug delivery and biomedical imaging, and nanocomposites built from these surfaces have potential use in catalysis, electrocatalysis, photocatalysis, batteries, supercapacitors, photovoltaics and sensors. The formation of porous structures such as nanotubes also provides an interesting approach towards controlling and manipulating surface hydrophobicity and water adhesion [2]. Air that is entrapped within these nanotubes has a significant impact on surface wettability, as explained in the Cassie-Baxter equation.

One of the most employed methods to produce ordered nanostructures is through the use of membranes, with anodized aluminum oxide (AAO) membranes being particularly popular [3].

With these membranes, it is possible to prepare ordered, vertically-aligned nanotubes. However, this process is difficult and long to perform and for each desired change in the nanotube parameter (height, diameter, etc.) it is necessary to employ another membrane. Templateless electropolymerization is an excellent alternative to producing porous, ordered nanostructures very quickly, such as nanotubes or nanocups. Towards this end, electropolymerization of pyrrole directly in water (H_2O) has been intensively studied in the literature [4]. With this method and depending on the electropolymerization method, H_2O causes the formation of different gases (O_2 and/or H_2) that are responsible for the porosity of the nanostructures. In this method, a surfactant is typically used to stabilize these gas bubbles during polymer growth.

Very recently, the possibility to obtain very ordered nanoporous structures such as vertically aligned nanotubes using a templateless electropolymerization approach but in organic solvent such as dichloromethane (CH_2Cl_2) and without surfactant was reported [5]. In this example, trace water (H_2O) present in solution was responsible for the formation of gas bubbles (O_2 and/or H_2) during electropolymerization, and as a consequence the formation of ordered porous structures. Since in this study no surfactant was employed, the monomer used has a significant role in stabilizing gas bubbles formed during polymerization and enabling polymer growth around them. Monomers derived from 3,4-phenylenedioxythiophene (PheDOT), 3,4-naphtalenedioxythiophene (NaphDOT) and thienothiophene were all found to be excellent candidates to develop porous nanofeatures. Moreover, the rigidity of the polymer was determined to be a key parameter. With this method, it was also possible to obtain parahydrophobic properties with extremely high water apparent contact angle (θ_w) and strong water adhesion.

Based on these previous results, in this contribution we wanted to investigate thieno[3,4-*b*]thiophene derivatives with highly rigid aromatic substituents such as pyrene. We have chosen pyrene as a substituent because it is an excellent electropolymerizable core, known to induce π-stacking interactions and therefore may significantly impact the ultimate surface topography. As an additional merit, pyrene is well-known for its fluorescence properties. With this selection, we have developed optical and multi-scales spatial (nano- and micro-meter ranges) and temporal (nanosecond to several days) studies of new highly structured and luminescent surfaces. Here we focus on the behavior of these structured surfaces upon stimuli (e.g. external perturbations by incubation with bacteria). Engineering new surfaces such as the ones reported here (highly ordered or structured and luminescent) has significant potentials for public health

issues such as bacterial infection as well as antibiotic resistance and tolerance. The originality of this project lies in our multidisciplinary approach, which combines innovative chemical and physical methods, green (sustainable) chemistry for the synthesis and in-depth characterization of these surfaces, as well as biochemical and biological methods.

First, we clearly demonstrate the significant influence of water content by saturating the solvent (CH_2Cl_2) with water and study the associated impact in surface morphology and properties. A dramatic change in the surface morphology is clearly observed after adding H_2O in the solvent, confirming the formation of a large volume of gas bubbles (O_2 and H_2) after this modification. Without water, the surfaces are extremely rough but no porous structures are observed. In contrast, with water addition, a large number of porous structures are present on the surface. Various substituents were tested, but the pyrene moiety clearly gives the best results. In the presence of H_2O, various porous structures are observed, such as nanotubes as well as open sphere/hemispheres, similar to those typical of natural coral reefs.

A decrease in the surface hydrophobicity is noted with the presence of these porous structures. These results can be explained using the Wenzel and Cassie-Baxter equations. Without water, the surfaces are more hydrophobic because of the extreme roughness. As a consequence, a large quantity of air can be trapped between a water droplet and the surface, leading to an increase in θ_w (up to 114°) which is possible following the Cassie-Baxter equation. By contrast, with water, the surfaces are more hydrophilic because water can enter and imbibe these porous features and a large amount of air is replaced by water (following the Wenzel equation).

Lastly, the fluorescence properties of aromatic substituents such as pyrene will be used for targeted applications such as the synthesis and characterization of antibacterial and antibiofilm surfaces, as well as for biosensitive coatings. In the first case, the surface results from the electropolymerization of aromatic molecules and the fluorescence will allow the colocalization of bacteria and surface nanostructures. For the biosensitive coatings, the surface will be *post*-functionalized by aromatic molecules and the luminescence of these molecules should vary in the presence of bacteria.

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