The major influence of the substrate nature on the formation of nanotubes with high water adhesion using a templateless electropolymerization process

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ABSTRACT

Inspired by nature, the development of nanotubes on surfaces is an excellent way to control both surface hydrophobicity and water adhesion. Among the methods used in the literature, nanotube arrays can be deposited very quickly using a templateless electropolymerization process. Naphtho[2,3-*b*]thieno[3,4-*e*] [1,4]dioxine (NaphDOT) was found to be an excellent monomer to obtain nanotubes in organic solvent and without surfactant. It allows the stabilization of gas bubbles produced from trace water. Here, we show how the substrate nature can affect the surface morphology and wettability. Three different substrates are used (gold as noble substrate and stainless steel and nickel as noble substrate oxidizible in the range of the monomer) as well as two electropolymerization methods (constant potential and cyclic voltammetry). We show that depending on the electropolymerization method, the substrate nature can highly affect the formation of nanotubes because of surface oxidation. Hence, for the formation of nanotubes on non-noble substrate it could be envisaged in the future to add a sub-layer in order to avoid surface oxidation.

1. Introduction

In nature, it is known that superhydrophobic properties characterized by extremely high water apparent contact angles (θ_w) and low water adhesion [1] allows to species to resist to wetting by water during rainfalls [2], to slide on water surface [3] or to clearly see in foggy environments [4]. Following the Cassie-Baxter equation [5], superhydrophobic properties can be obtained if surface structures or roughness are able to trap a high amount of air between the substrates and water droplets. Moreover, it was shown that the presence of two-dimensional surface structures (usually micro and nano) allows to reach superhydrophobic properties with high robustness [6,7]. However, other natural substrates such as gecko foot [8], rose petals [9] as well as desert plants [10,11] possess both extremely high θ_w and high water adhesion allowing to capture small water droplets even in hot environments. This particular surface property, also called para-hydrophobicity by Marmur [12], is also possible using the Cassie-Baxter equation if solid-liquid interface is very important. For example, beetles are able to move underwater because their moving induces a mechanical control of gas bubbles trapped inside their legs [13] while other species use this air to breathe underwater [14].

Hence, controlling the formation of surface structures and the surface energy is fundamental to prepare substrates with extremely high water adhesion [15,16] As observed for example in nature on gecko foot [8], the presence of one-dimensional nanostructures such as nanofibers, nanowires or nanotubes can lead to extremely high water adhesion. Controlling water adhesion is also fundamental for various potential applications in water harvesting [17,18], underwater locomotion [13], oil/water separation membranes [19], anti-icing coatings [20] or in biosensors [21].

In particular, vertically aligned nanotubes are excellent candidates thanks to the presence of air trapped inside the nanotubes. Vertically aligned nanotubes can be fabricated using anodized aluminum oxide (AAO) membranes but the process is difficult to implement and needs several steps. Indeed, the cylindrical pores of AAO can be filled by different materials and after membrane dissolution densely packed nanotubes can be obtained [22–24]. For example, inspired by gecko foot, Jiang et al. reported this process to produce densely packed polystyrene nanotubes. The substrates displayed extremely high θ_w up to 162° but also extremely high water adhesion. Other methods to produce vertically aligned nanotubes in one-step exist but are highly

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dependent on the substrates or on the materials deposited. For example, anodization can produce nanotubes but especially on titanium substrates [25]. Chemical vapor deposition (CVD) can also produce different nanostructures surfaces as nanowires or nano-sheets but nanotubes were especially reported using carbon-based materials [26–28]. Hence, the methods to prepare vertically aligned nanotubes in one-step with the possibility to control their formation are limited.

Nanotubes can also be obtained by a one-step and templateless electropolymerization process [29–34]. Shi et al. was the first to report the formation of nanotubes by electropolymerization of pyrrole in water. In their process, a surfactant was added to stabilize gas bubbles (H_2 or O_2) produced *in-situ* during the electropolymerization process. Previously, it was shown that the use of naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxine (NaphDOT) as monomer (Scheme 1) can be used to form nanotube arrays in organic solvent and without any surfactant [35–38]. Because, the formation of nanotubes needs the appearance and stabilization of gas bubbles on the working electrode, the formation and characteristics of the nanotubes is probably highly dependent on the working electrode nature. Here, to study its effect three different metals (gold, stainless steel and nickel) were used as working electrode. Gold was chosen as inert and reference substrate. Stainless steel and nickel were chosen because they can be oxidized but in a potential range close to that of the monomer. Because, the formation of nanotubes is also highly dependent on the deposition method, two different deposition methods (cyclic voltammetry and constant potential) were also chosen.

2. Materials and methods

2.1. Electrodeposition experiments

The monomer NaphDOT was synthesized using a procedure reported in the literature [35]. For each experiment, 0.01 of NaphDOT was added to an electrochemical cell containing 10 mL of anhydrous dichloromethane and 0.1 of tetrabutylammonium perchlorate (Bu_4NClO_4). Three electrodes were inserted inside the solution. A 3 cm^2 plate of different metals (gold, stainless steel and nickel) was used as working electrode. A carbon was used as working electrode while a saturated calomel electrode (SCE) was used as reference electrode. The three electrodes were connected to an Autolab potentiostat (Metrohm) and the electrodeposition experiments were monitored with the GPES software. The solution was degassed under argon. Then, the monomer oxidation (E^{ox}) potential being highly dependent on the metal substrate used as working electrode, E^{ox} was determined for each metal by cyclic voltammetry. After, the monomer was electropolymerized by cyclic voltammetry from -1 V to E^{ox} at a scan rate of 20 mV s^{-1} and using different number of scans. The monomer was also
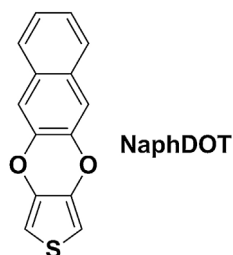
electropolymerized at constant potential and using different deposition charges (Qs).

2.2. Surface characterization

The surface hydrophobicity was characterized by measuring water apparent contact angle (θ_w) using a DSA30 goniometer (Krüss). The values are the mean of five measurements using 2 μL water droplets. Then, the water adhesion was characterized using the tilted-drop method. In the process, a 6 μL water droplet is placed on the substrate and the substrate is inclined until the droplet moves. The advancing (θ_{adv}) and receding contact angles (θ_{rec}) and by deduction the hysteresis H = $\theta_{adv} - \theta_{rec}$ are determined just before the droplet moving. The maximum contact angle if called sliding angle (α). If the water droplet does not move even for $\alpha = 90°$ the substrate is extremely sticky.

3. Results and discussion

Gold substrates were chosen as noble and reference electrode while stainless steel and nickel substrates were used as non-noble substrates but with an oxidation potential in the range of the monomer oxidation potential. Indeed, the oxidation of stainless steel and nickel substrates was determined by cyclic voltammetry in Bu_4NClO_4/dichloromethane starts at around 1.7 V *vs* SCE.

Then, the monomer NaphDOT was introduced in the solution. The monomer oxidation potential (E^{ox}) of NaphDOT on gold and in Bu_4NClO_4/dichloromethane was found to be around 1.78 V *vs* SCE. E^{ox} was found to be the same using nickel substrate and higher (1.97 V) using stainless steel. Hence, the monomer oxidation is more affected on stainless steel.

Different deposition methods can be used for electropolymerization. Here, two different deposition methods were chosen because the surface morphology is expected to be highly modified.

3.1. Electropolymerization at constant potential

First, the electropolymerization was performed at constant potential (E = E^{ox}) and using different deposition charge (Qs). Indeed, as previously demonstrated [39], using high constant potential two reactions are possible:

n Monomer → Polymer + 2 ne$^-$ + 2 nH$^+$

$2H_2O$ (trace water) → O_2 (bubbles) + 4H$^+$ + 4 e$^-$
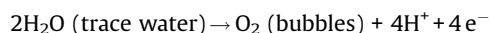
SEM images obtained on inert gold substrates and for different deposition charges (Qs) are given in Fig. 1. Extremely ordered and densely packed nanotubes were observed. Moreover, the formation of nanotubes was obtained in the first instance of the polymerization. The seeds are formed instantaneously (for Qs = 12.5 mC cm^{-2} the size of the seeds is extremely low ($\phi \approx 70$ nm, h ≈ 100 nm)) and after the size of the nanotubes increases with Qs (for example, for Qs = 100 mC cm^{-2} the size of the nanotubes become very high (h above 1 μm)). Throughout the increases in Qs, the density of tube like structures decreases as more and more of them appear to be closed on the top. Moreover, they are also more and more inclined.

The wettability measurements (Table 1) show that the water apparent contact angle (θ_w) decreases when the deposition charge (Qs) increases from 130.0° for Qs = 12.5 mC cm^{-2} to 75.2° for Qs = 200 mC cm^{-2}. The exceptional results obtained for Qs = 12.5 mC cm^{-2} can be explained by the extremely high air fraction in contact to water droplets due both to the high number of vertically

Scheme 1. NaphDOT monomer used to obtain nanotubes.