

Influence of the monomer structure and electrochemical parameters on the formation of nanotubes with parahydrophobic properties (high water adhesion) by a templateless electropolymerization process



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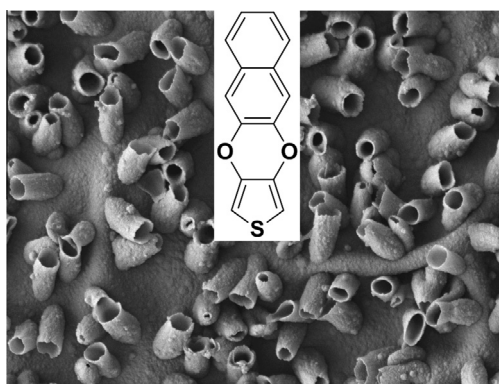
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HIGHLIGHTS

- Formation of nanotubes by electropolymerization (templateless).
- The substrates with nanotubes display extremely high water adhesion.
- Presence of nanotubes highly dependent on monomer structure and electrochemical parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

Controlling the formation of surface nanostructures and nanotubes in particular is extremely important for various applications in electronic devices for energy systems, biosensing but also for the control of water adhesion. Here, we use a direct (without template) electropolymerization process to produce vertically aligned nanotubes. Different monomers are tested as well as different solvents, electrolytes and electrodeposition methods. We show that naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxine (NaphDOT) is the best monomer to obtain these nanotubes while dichloromethane has to be used as solvent for their formation. The surfaces with nanotubes display both extremely high apparent contact angles ($\theta_w = 142.7^\circ$) and high water adhesion even if the nanotubes are made of intrinsically hydrophilic polymers and are not densely packed.

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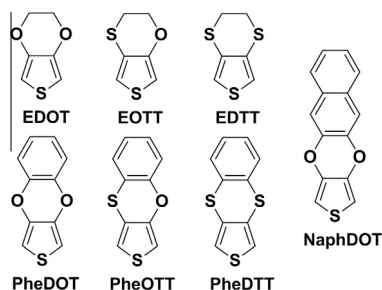
1. Introduction

Inspired by phenomena present in nature, the possibility to reach superhydrophobic (i.e. extremely low water adhesion) but also parahydrophobic properties (i.e. extremely high water adhe-

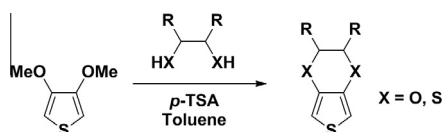
sion) by the presence of surface structures have opened a large range of potential applications of these materials in waterproof textiles, water transportation and harvesting, microfluidic devices or oil/water separation membranes [1–3]. Characterized by extremely high water contact angle (θ_w) and low water adhesion or hysteresis (H), superhydrophobic properties are present in numerous species of plants and animals such as the famous lotus leaves [4,5]. One of the easiest way to produce superhydrophobic proper-

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Scheme 1. Monomers studied in this work.

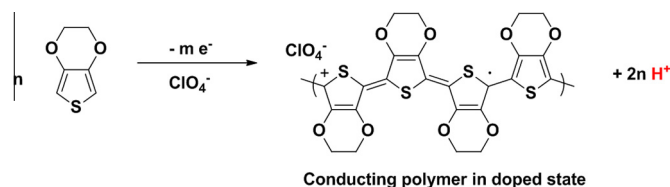


Scheme 2. Synthetic way to monomers.

ties is to combine both the presence of surface structures at a nano- and microscale with low surface energy materials (fluorinated materials for example) [6,7]. However, other species having surfaces with high θ_w but high H (parahydrophobic properties) [8] such as the gecko foot, rose petals or peach skin which are able to capture water droplets or to walk on vertical substrates [9–11]. Here, both the surface hydrophobicity and water adhesion can be controlled with the shape and the characteristics of surface structures as well as the surface energy of the materials present in these structures [12–13].

Using conducting polymers, different strategies have been developed for controlling the shape and the dimensions of nanostructures not only in solution but also on substrates [14]. For example, rambutan-like [15], dandelion-like structures [16] as well as square [17] and star-shaped structures [18] were reported by self-assembling during polymerization of aniline in solution and using different experimental conditions. Superhydrophobic properties were obtained after deposition of this nanostructures on substrates by spin coating, dip-coating or spray-coating. Otherwise, the growth of nanostructures directly on substrates is also possible. For example, this is possible by preferential growth [19], grafting [20], plasma polymerization [21], vapor phase polymerization [22] and electropolymerization [23–29]. The technique allowing the widest possibilities in the surface structure control is probably electropolymerization. In this technique, a monomer in an electrolytic solution is oxidized to induce in one-step the polymerization and the deposition on the resulting conducting polymer on the working electrode. The surface structures are then highly dependent on the electrochemical parameters [23] and also the monomer structure [24–29]. The monomers of the 3,4-ethylenedioxythiophene (EDOT) family are among the most exceptional monomers for their polymerization capacity, opto-electronic properties and the possible formation of various surface structures such as spherical nanoparticle, nanofibers, nanosheets, flower-like structures and cauliflower-like structures [24–29]. It is also possible to graft a substituent on the monomer structure in order to modify the surface hydrophobicity or oleophobicity. For example, superhydrophobic or superoleophobic properties were reported using fluorinated or hydrocarbon chains [24–27], but also much higher water adhesion (parahydrophobic properties) using branched hydrocarbon chains or aromatic groups [28–29].

It is also possible to produce vertically aligned nanotubes by electropolymerization using hard templates such as anodized alu-



Scheme 3. Schematic representation of electropolymerization process.

minum membranes which are very often used in the literature [12,30,31]. It is also possible to obtain nanotubes very quickly in one-step by electropolymerization and without any template. Shi et al. were the first to report this possibility by electropolymerization of pyrrole in water and with a surfactant [32–34]. The authors showed that the surfactant allows the stabilization of H_2 or O_2 bubbles produced during electropolymerization process. Previously, it has been shown that the electropolymerization of naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxine (NaphDOT), a highly rigid monomer obtained by grafting a naphthalene moiety on EDOT, can lead in dichloromethane and without surfactant to the formation of vertically aligned nanotubes with parahydrophobic properties [35]. Indeed, the electropolymerization releases H^+ , which can lead to H_2 bubbles in organic solvent. In our study, in order to better understand the formation of nanotubes and the role of the monomer, solvent, electrolyte and of the electropolymerization method, we have synthesized and studied in the same conditions all the monomers shown in Scheme 1 differing by the presence, or not, of aryl groups (phenyl or naphthalene) directly grafted on the 2- and 3-position, or by the replacing of one or two oxygen atoms by sulfur ones. In addition, the monomers were electropolymerized in different solvents, electrolytes and using different electrodeposition methods in order to study their influence on the nanotube formation.

2. Materials and methods

2.1. Monomer synthesis and characterization

2-mercaptoethanol, 1,2-benzenediol, 2,3-naphthalenediol, 2-mercaptophenol, benzene-1,2-dithiol, 2,3-naphthalenediol, 2,3-dihydrothieno[3,4-*b*]-1,4-dioxine (EDOT) and 2,3-dihydrothieno[3,4-*b*][1,4]dithiine (EDTT) were purchased from Sigma Aldrich. The other monomers were synthesized by transesterification of 3,4-dimethoxythiophene with the corresponding reactant [36,37] (Scheme 2). More precisely, 2.5 g of 3,4-dimethoxythiophene, 2 eq. of the corresponding reactant and 0.5 g of *p*-toluenesulfonic acid monohydrate (0.15 eq.) were added to 120 mL of toluene.

Table 1

Scan ranges used for the electropolymerization by cyclic voltammetry.

Monomer	Solvent	Scan range
EDOT	Acetonitrile	–1 V to 1.38 V
	Dichloromethane	–1 V to 1.64 V
EOTT	Acetonitrile	–1 V to 1.28 V
	Dichloromethane	–1 V to 1.58 V
EDTT	Acetonitrile	–1 V to 1.27 V
	Dichloromethane	–1 V to 1.67 V
PheDOT	Acetonitrile	–1 V to 1.45 V
	Dichloromethane	–1 V to 1.68 V
PheOTT	Acetonitrile	–1 V to 1.23 V
	Dichloromethane	–1 V to 1.51 V
PheDTT	Acetonitrile	–1 V to 1.26 V
	Dichloromethane	–1 V to 1.49 V
NaphDOT	Acetonitrile	–1 V to 1.47 V
	Dichloromethane	–1 V to 1.80 V

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