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Nanoparticles Covered Surfaces for Post-functionalization with Aromatic Groups to Obtain Parahydrophobic Surface with High Water Adhesion (Petal Effect)

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Abstract

Numerous exceptional properties can be observed in nature. Among these properties, parahydrophobic feature is of interest. This property describes material with high adhesion with water such as rose petals or gecko foot. Such kind of surface presents a real potential for applications in the field of water harvesting systems. In this work, we report a new synthetic strategy to mimic this property. Here, we combine three strategies in one. First, a monomer is electropolymerized in order to form the starting structured surface. Then, nanoparticles are grafted on the surface to increase the structuration and consequently to create the reactive surface. Finally, the grafted surface is post-functionalized (Huisgen reaction) with various aryl alkynes to control the surface chemistry and energy. This strategy allows to reach surfaces with both very high hydrophobic properties ($\theta = 140^\circ$) and high water adhesion. This work also includes the surface wettability, roughness and morphology investigation in order to study the impact of the starting monomer structure and post-functionalization on the surface properties.

Keywords: conductive polymers, nanostructures, click chemistry, superhydrophobic, adhesion

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1 Introduction

The observation of natural species provides the scientific community a permanent and inextinguishable source of inspiration. For example, in the domain of surface wettability, natural phenomena reveal the possible total wetting or non-wetting of a liquid on a substrate. One of the most popular examples is the lotus leaves, for which the water has almost no contact with the leaves[1,2]. Such kinds of surfaces are described in the literature as superhydrophobic. Other examples of natural superhydrophobic surface are known such as *Echeveria*, taros and rice leaves[3,4]. Other natural surfaces are extremely hydrophobic but with extremely high water adhesion. Such kind of surfaces were described by Marmur as parahydrophobic and is also known as petal effect[5–8]. This effect was observed for examples on rose petals, gecko feet or peach skins[9–11]. These properties have potential applications in water collection even in arid environment or for example in oil/water separation[12–14].

Observation of natural surfaces has revealed two key parameters in the control of surface wettability: the surface energy and the surface morphology/roughness. Hence, researchers have developed various strategies to control these parameters[15–17]. Mainly, the strategies can be classified in two categories: the top-down and the bottom up approaches. Electropolymerization was found to be an excellent method to develop new surfaces with controlled wettability in one step[18–21]. The approach combining the monomer structure with electropolymerization parameters can offer the possibility to fully tune the surface morphology and wettability. The main drawback of this approach is the necessity to synthetize a wide range of monomers to diversify the prepared surfaces. The synthesis part is generally the more expensive and time consuming part of the work. A smart alternative for this part is the possibility to prepare a single monomer suitable for additional reaction that can be functionalized after electropolymerization. Because the

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functionalization is performed after the polymerization, this approach is described as a post-functionalization. Numerous reactions are now known and currently used for post-functionalization[22], for example the thiol-ene reaction[23], the Staudinger Vilarassa reaction[24] and the Diels-Alder reaction[25]. The most popular example of post-functionalization reaction is the Huisgen reaction[26] and more precisely the modification was described simultaneously by Sharpless and Meldal in 2002[27,28]. The azide-alkyne cycloaddition mostly described as the click chemistry spearhead has been extensively studied. More particularly, this reaction has been reported to covalently graft alkyl, aryl or perfluoroalkyl chains in order to prepare highly hydrophobic surfaces[29–31]. In order to increase even more the hydrophobic feature of the surface, this reaction has also been studied to covalently graft nanoparticles on the surface[32]. It is now well known that the grafting of particles on surface is an efficient way to increase the roughness and area of the surface[33,34]. A simple and elegant example is the use of carbon nanoparticles covered surfaces[35–37]. Superhydrophobic and superoleophobic surfaces were prepared by grafting flame synthesized carbon nano-particles on surfaces. That approach using flame synthesized nanoparticles is efficient but the formed surfaces are not suitable for surface post-functionalization. The use of functional nanoparticles is a smart alternative.

Nanoparticles suitable for the Huisgen reaction (bearing azido groups) are commercially available and can be grafted on surface using the Huisgen reaction. The functionalization can change the surface morphology and increase the number of functionalizable groups by increasing the functional surfaces. Here, in order to enhance the surface properties, we report a three-step strategy using the Huisgen reaction (Fig. 1). This strategy includes the electropolymerization, the grafting of nanoparticles and hydrophobic modification. The surfaces properties are then studied including wettability, surface roughness and surface morphology.

2 Materials and methods

2.1 Synthesis

All the used monomers (PEDOT-C_1-Alkyne and PEDOT-C_4-Alkyne) were synthetized following procedures reported in the literature. All yield and spectroscopic data were consistent with reported values[38].

2.2 General procedure for electropolymerization

In a glass cell containing a solution 0.1 M of tetrabutylammonium perchlorate (Bu_4NClO_4) in anhydrous acetonitrile, 0.01 M of monomer was inserted. Three electrodes were put inside the solution. A 2 cm^2 Gold plates (purchased from Neyco), glassy carbon rods, and Saturated Calomel Electrodes (SCE) were used as working, counter, and reference electrodes, respectively. The three electrodes were connected to an Autolab potentiostat (Metrohm). Before each experiment, the solution was degassed under argon. After the deposition, the samples were cleaned in three different acetonitrile solutions in order to remove the remaining salts.

2.3 General procedure for PEDOT surface modification

The PEDOT-C_n-N_3 (C_1 and C_4) substrates were modified as following: the substrates were immersed in 50/50 water/THF solution (5 mL). 100 mg of $CuSO_4$ (0.6 mmol), 100 mg of sodium ascorbate (0.5 mmol) and 100 mg of alkyne (from 0.98 mmol to 0.49 mmol depending on the used alkyne) were then added. The mixture was shaken for 3 h. The substrates were then successively washed 3 times with water and 3 times with ethanol and dried.

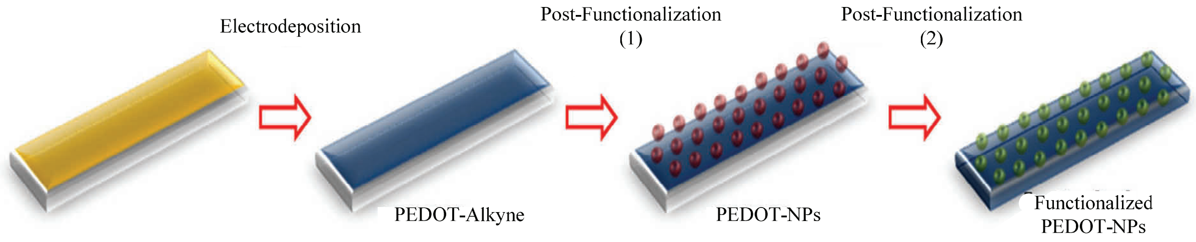

Fig. 1 Concept of the post-functionalized nanoparticle grafted surface elaboration.