Enzyme biocatalyst route to superhydrophobic surfaces on microstructured poly (ethylene terephthalate) film

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ABSTRACT

A tunable and green enzyme biocatalyst route to develop superhydrophobic surfaces on microstructured poly (ethylene terephthalate) (PET) films by the tailoring of the micro- and nano scale hierarchical structures is described. Upon the aminolysis of PET films with hexamethylenediamine, the primary amine groups are covalently attached onto the PET surfaces and microstructured pattern is formed. The binding of citrate-stabilized Au nanoparticles onto the PET surfaces via the covalent bond between the gold nanoparticles and the primary amine groups introduced on the PET surfaces was followed spectroscopically. The biocatalytic enlargement of the Au nanoparticles using the enzyme-generated H_2O_2 as reducing agent for the reduction of $AuCl_4^-$ at the attached Au nanoparticle seeds on the PET surfaces was followed by spectroscopic means and atom force microscopy (AFM). The AFM experiments indicated that micro- and nano scale hierarchical structures were tailored by the enzyme biocatalyst route. Superhydrophobic surfaces with water contact angles as high as $158.6 \pm 2.0°$ was achieved upon the chemisorption of 1-octadecanethiol as low surface energy material. This route can be potentially applicable to superhydrophobic PET-based microfluidic devices with reduced friction surfaces.

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1. Introduction

Superhydrophobic surfaces, characterized by water contact angles larger than 150° and tilt angles less than 5°, have recently attracted extensive attention for their potential industrial applications including self-cleaning surfaces, anti-adhesive coatings, microfluidic devices with reduced friction surfaces, and many others [1–5]. Inspired by natural systems including the lotus leaf, which accomplish self-cleaning superhydrophobic surfaces through the generation of combined micro- and nano hierarchical structure of the surface and the low surface energy material covered on the structure, researchers have made impressive efforts to prepare similar artificial superhydrophobic surfaces. Various methods, such as plasma etching and polymerization, chemical vapor deposition, electrodeposition, sol–gel, solidification, phase separation, and deposition of nanoparticles, have been developed for the preparation of superhydrophobic surfaces on various substrates, including polymers, metal and semiconductors [6–12].

Poly (ethylene terephthalate) (PET), representing a cheap, chemically stable, and nontoxic materials for diverse technological applications, for example the microfluidic devices, has been intensively studied especially on the surface functionalization [13,14]. Interestingly, regular micro scale patterns on the surfaces of PET films were reported to form upon aminolysis treatments, during which amines attacked the electron

deficient carbonyl carbon where chain scission and amide formation occur [15,16]. Although PET represents an attractive material for the applications in microfluidic devices, for which the superhydrophobic surfaces are very important, the report on the construction of superhydrophobic surface on PET film is scarce, particularly under mild conditions. Superhydrophobic coating films prepared on PET substrate using Al_2O_3 the sol–gel chemistry was reported [17]. Furthermore, superhydrophobic surface from a PET substrate via selective oxygen plasma etching followed by plasma-enhanced chemical vapor deposition using tetramethylsilane as the precursor has been obtained [18]. Although these methods work well for the preparation of superhydrophobic surfaces with high contact angles and low sliding angles, tunable and green methods are still highly desired.

The synthesis and enlargement of particles using enzyme biocatalysts and biological structures of high complexity is an emerging area in nanobiotechnology. Micrometer-long Au metallic wires exhibiting heights and widths in the region of 150–250 nm were fabricated from dip-pen nanolithography patterned "biocatalytic lines" using Au nanoparticle (NP) functionalized glucose oxidize as "ink". The enzyme-generated H_2O_2 acted as reducing agent that stimulated the reduction of $AuCl_4^-$ at the Au nanoparticle seeds associated with the enzyme. The biocatalytic growth process of nanoparticles was tunable with the biocatalytic "development" time-interval [19,20]. Similarly, Ag nanowires were prepared using alkaline phosphatase produced p-aminophenol as reducing agent for Ag^+ [19,20]. Furthermore, the exposure of the fungus *Verticillium* sp. to an aqueous solution of $AuCl_4^-$ resulted in the reduction of the salt to gold nanoparticles [21]. Also, cell extracts from the

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lemongrass plant yield, in the presence of $AuCl_4^-$, single crystalline gold nanotriangles and nanoprisms [22]. We conceived that the enzyme biocatalyst route for the enlargement of particles is a tunable and green way to fabricate surfaces with tailored hierarchical architecture in micro- and nano scales.

Our goal here is to develop superhydrophobic surfaces based on the tailoring of the micro- and nano scale hierarchical structures on microstructured PET films for potential microfluidic device-based applications. In contrast to previous studies, here we adopted a tunable and green enzyme biocatalyst route for the construction of the superhydrophobic surfaces. We also showed that the enzyme biocatalyst route is a rapid and versatile method to construct superhydrophobic surfaces on various substrates.

2. Materials and methods

2.1. Materials

PET films (Mylar®, DuPont) with thickness of 100 μm were obtained from DuPont. Cetyltrimethylamonium chloride, glucose oxidase and $HAuCl_4$ was purchased from Aldrich and used without further purification. β-D(+) glucose and sodium citrate with AR purity obtained from Shanghai Chemical Reagent Company of China and used as received. Other reagents were purified by conventional methods. All the water used in this work is distilled and deionized water.

2.2. Instruments and measurements

Transmission electron microscopy (TEM) analysis was performed on a JEM-1200EX TEM operating at 200 kV in bright field mode. UV–vis spectra were carried out with a UV–vis Shimadzu UV-2055 spectrometer using quartz cuvettes. Atomic force microscope (AFM) measurements were performed in the tapping mode under ambient conditions using a commercial scanning probe microscope, Seiko SPI3800 N, equipped with a silicon cantilever, nanosensors, typical spring constant 40 N/m. Scanning electron microscope (SEM) were performed on Jeol, JSM-35C. The contact angle of the samples toward distilled water was measured by the sessile drop technique using contact-angle measurement equipment, model KRUSS DSA 10-MK2.

2.3. Aminolysis reaction of PET substrates [15,16]

PET film was cut to 1×2 cm samples. The samples were cleaned with acetone, ethanol and triple-distilled water using ultrasonication for 15 min and dried in a dessicator before aminolysis. The aminolysis reactions were carried out in tubes. PET samples were added to tubes containing 10 mL of 10% hexamethylenediamine solution in i-propanol, which were previously thermostated in an oil bath at 65 °C. Moderate agitation was used during the reaction. The PET samples were removed from the solution after the desired reaction time, washed with methanol, and then dried in vacuum at room temperature for at least 8 h.

2.4. Preparation of Au-NPs seeds [23]

In a 250 mL round-bottom flask equipped with a condenser, 100 mL triply distilled water was added. After boiling, 4.12 mL of 10 mg/mL $HAuCl_4$ was added with vigorous stirring. Rapid addition of 11.57 mL of 38.8 mM sodium citrate to the boiling solution resulted in a color change from pale yellow to burgundy. Boiling was continued for 10 min; the heating mantle was then removed, and stirring was continued for additional 15 min. The UV–vis spectrum exhibits a characteristic plasmon band at 520 nm. The diameter of the particles, measured from TEM images, was 16 nm ± 2 nm.

2.5. Attachment of Au-NPs onto the aminolised PET substrates [24]

The aminolised PET substrates were immersed into the citrate-stabilized Au Au-NPs for desired reaction time. The PET substrates that included the Au-NPs films were rinsed with water.

### 2.6. Biocatalytic enlargement of Au-NPs on the PET substrates [25]

In a 250 mL growth solutions consisted of 2×10^{-4} M $HAuCl_4$ in 0.01 M phosphate buffer, pH = 7.2, 2×10^{-3} M cetyltrimethylamonium chloride (CTAC) and 3×10^{-3} M β-D(+) glucose with 50 μg mL^{-1} glucose oxidase (GOx). For the catalytic growth of the Au-NPs, Au-NPs attached PET substrates were then soaked in the above-described growth solution. The experiments were performed at ambient temperature (30 ± 2 °C). The absorbance features of the resulting modified PET substrates were recorded in water.

2.7. Chemisorption of 1-octadecanethiol on the gold-coated PET substrates

Control PET samples were prepared by sputtering deposition Au on pristine PET. The sputter-coated and the Au-NPs attached PET substrates were then soaked in 1 mM 1-octadecanethiol for 0.5 h and washed with ethanol carefully.

3. Results and discussion

Aminolysis was used to introduce primary amine groups onto the PET films. During aminolysis amines attack the electron deficient carbonyl carbon where chain scission and amide formation occur, which results in a reduction of the molecular weight of the sample. It was assumed that the ordered or crystalline regions are insoluble while the amines predominantly react with the noncrystalline regions. This surface etching techniques has been used in several studies and is used in this study to prepare regular pattern on PET films [26–28]. Then, Au nanoparticles were covalently bonded onto the PET surfaces via the binding between the gold nanoparticles and the primary amine groups. Micro- and nano scale hierarchical structures were then tailored by using the enzyme-generated H_2O_2 as reducing agent for the reduction of $AuCl_4^-$ at the attached Au nanoparticle seeds on the PET
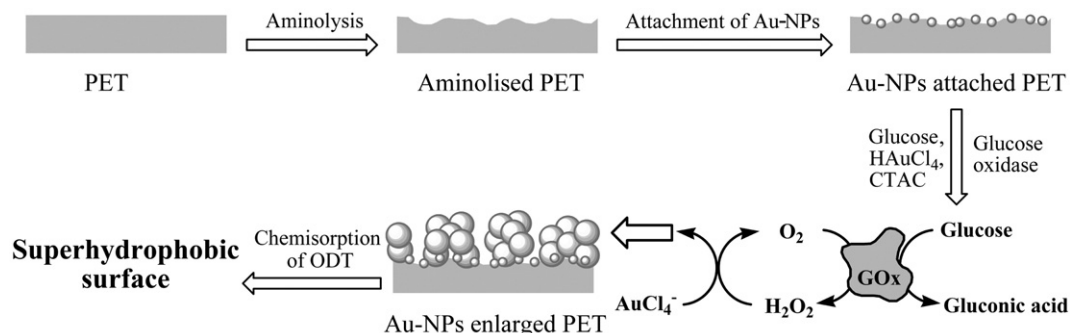
Scheme 1. Schematic representation of construction of the superhydrophobic surfaces on microstructured PET films via biocatalyst route.