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Grafting of PMMA brushes layer on Cu surface to create a stable superhydrophobic surface

Junhong Zhang, Junyan Cai, Ming Li*

State Key Laboratory of Metal Matrix Composites, School of Material Science and Engineering, Shanghai Jiao Tong University, No. 800 Dongchuan Rd., Shanghai 200240, China

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A B S T R A C T

In this paper, poly(methyl methacrylate) (PMMA) brushes were grafted on Cu micro-cone structured substrate by a simple one-step cathodic electro-initiated polymerization method which was carried out in aqueous solution at room temperature in the open air. The PMMA brushes were continuous, uniform and thickness-controllable, and it covalently bonded to the Cu surface. In the brushes, nitrophenyl moieties acted as cross-linker between PMMA chains. After removed from the solution followed by treated with water, the PMMA brushes (basically a hydrophilic material)/micro-cone structured Cu surface was hydrophilic with water contact angle (CA) of 74.4°. However, it exhibited superhydrophobicity by treating it in the acetone. The conversion from hydrophilic surface to superhydrophobic one may due to rearrangement of nitrophenyl moieties and PMMA chains at the topmost of the brushes. In addition, its water CA increased with grafting time of the brushes from 145° to about 166°, because there was no available space in thinner film for group reorientation. The surface was conversed to hydrophilic again after treated with hot water, but it was still superhydrophobic after treated in water at room temperature. This revealed that the group reorientation also easily occurred in hot water like in the acetone. More importantly, the surface retained good superhydrophobic stability in acidic environment and in long-time storage. Furthermore, the superhydrophobic surface had excellent resistance that can provide effective protection for the bare Cu substrate.

1. Introduction

Copper (Cu) is one of the most important materials in industry due to its high electrical and thermal conductive, mechanical workability and relatively noble properties. However, corrosion is the major problem in its applications. A superhydrophobic surface is commonly fabricated to improve its corrosion resistance in recent years' reports [1,2]. The superhydrophobic surfaces with a contact angle (CA) higher than 150° have many excellent properties, such as self-cleaning [3–5], corrosive resistance [6,7] and contamination inhibiting [8]. So far, inspired by naturally occurring superhydrophobic surfaces (i.e., the lotus leaf), numerous methods for preparing the superhydrophobic have been developed. They are mostly based on two main routes: creating the rough structure on a hydrophobic surface [9–12] and modifying a rough surface by materials with low surface free energy [13–18]. However, up to now, for organic superhydrophobic surface on Cu with special micro-nanostructures, only one self-assembled monolayer can be created [3], which is definitely too thin for long time storage.

Recently, the surface electroinitiated emulsion polymerization method (SEEP) [19–21], which can provide covalently grafted polymer films on any conducting substrate, has attracted attention. This cathodic electroinitiated polymerization is a one-step process that works in aqueous dispersed media from available reagents with short reaction time, which makes it perfectly acceptable for industrial applications. More importantly, the thickness of organic polymer film is controllable from several nanometers to hundreds of nanometers. Based on this simple one-step electro-initiated polymerization process, we will show in this paper that PMMA films are able to covalently bond to the Cu substrate in the presence of an externally applied potential. In addition, the synthesis of polymer film also offers opportunities to design hydrophobic surface from hydrophilic materials by changing the surface conformation or end groups [22–26]. Up to now, the effects of the surface composition adjustment can be observed for porous poly(methyl methacrylate) (PMMA) [27], poly(vinyl alcohol) (PVA) nanofibers [28], micro-nano binary structured fluorine-end-capped polyurethane

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* Corresponding author.
E-mail address: mingli90@sjtu.edu.cn (M. Li).

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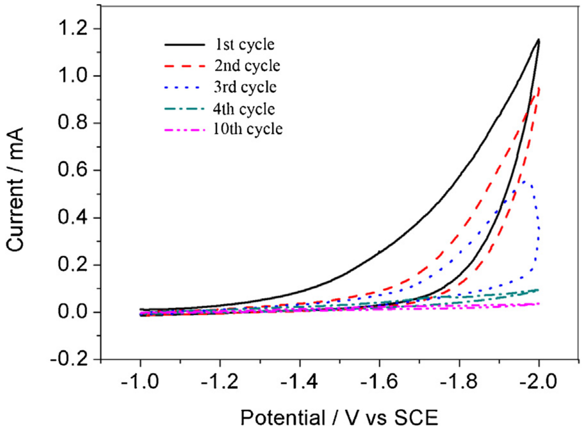
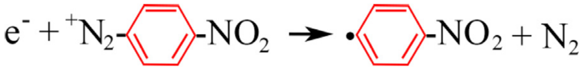


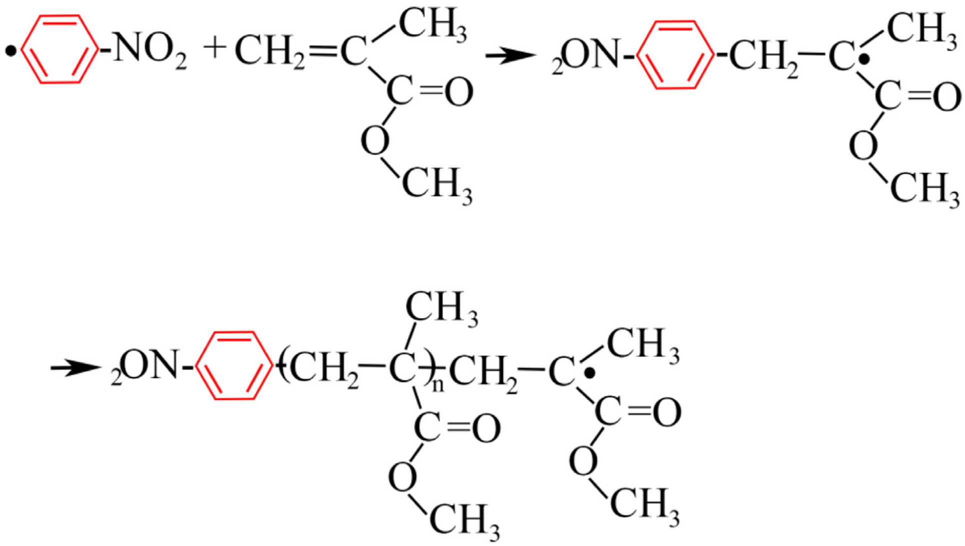
Fig. 1. Cycle voltammetry (ten cycles) registered on microstructured Cu electrode with an aqueous solution containing 0.72 M MMA and 2.3 mM NBD at scan rate 10 mV/s.



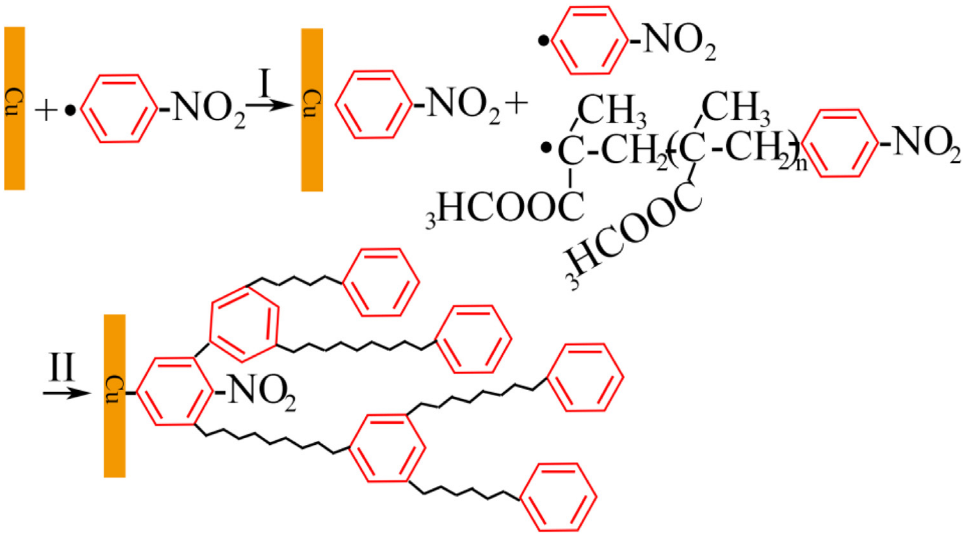
Scheme 1. The reductive reaction of aryl diazonium salt.

(FPU)/PMMA mixtures [29]. Nevertheless, reports about fabrication of super-hydrophobic surfaces from hydrophilic polymers, especially ultrathin polymer, are still limited.

The present paper reports the electro-initiated redox activation of aryl diazonium salts on Cu substrate in presence of MMA monomers in aqueous solution can form very homogeneous polymer film strongly grafted on Cu cones surface. This method also offered the possibility of controlling the thickness of the organic films and the orientation of the PMMA brushes. It is a facile, low cost and water-based method for grafting hydrophilic PMMA on microstructured Cu to provide a stable superhydrophobic surface without surface modification of low-surface-energy materials such as fluorides. Therefore, it may be extended to prepare superhydrophobic surfaces using broad hydrophilic polymers.



Scheme 2. The polymerization of MMA monomers initiated by aryl radicals.



Scheme 3. The formation of final PMMA film through chemical interaction between PMMA chains and previously grafted polynitrophenyl-like layer.