



Optimal condition for fabricating superhydrophobic copper surfaces with controlled oxidation and modification processes



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ABSTRACT

In this paper, superhydrophobic (SH) copper surfaces were prepared by an oxidation process with NaClO₂, NaOH and Na₃PO₄·12H₂O and modification with 1-Octadecanethiol as a modifier. Effects of oxidation time, modifier concentration, and modification time were examined. Results showed that the oxidation time 30 min, modifier concentration 2.5 mM, and modification time 5 h gave the optimal condition where contact angle (CA) and sliding angle were 161.1°, and 2.2° respectively. As well as, surface durability was examined by immersing acquired surfaces in de-ionized water and subjecting to open air for several days. Results showed the CA reduced to 119° for immersing in water after one week while it did not degrade in the air even after 45 days.

1. Introduction

Hydrophobicity is one of the most important features of solid surface. Analysis of natural superhydrophobic (SH) surfaces which have contact angle (CA) greater than 90° such as lotus leaves reveals that macro-nano structures and low surface energy are two main characteristics of these surface [1]. Surveying literature reveals that various methods such as etching [2], oxidation [3], and electrodeposition [4] have been used to create micro/nano structures, and some techniques including ion implantation [5], self-assembled monolayer (SAM) [6,7], and paraffin wax coating [8] have been used to fabricate SH surfaces. Among them some methods such as oxidation, which are applicable for complex surfaces and are inexpensive for mass production, have been in centre of attention. There are also some investigations which well explain formation of copper oxides nanoparticle [9,10]. Many researchers have adopted SAMs because of their simplicity, small thickness, and low thermal resistance, which are proper for heat exchanger (HE) design. In addition, various materials have been used as substrates among them, copper as an important engineering material, have received much attention in many industries such as heat transfer engineering and HE design. For example, published studies have shown that dropwise condensation occurring on SH surfaces have one order of magnitude greater heat transfer coefficient than filmwise condensation occurring on usual surfaces [11]. Hence using SH copper surfaces in design of HEs with condensation can significantly improve heat transfer process and reduce raw material consumption or save energy.

In this paper the pure copper plates are oxidized in an alkaline

solution for different times, and then modified with ethanol solution of 1-Octadecanethiol (ODT), which forms a SAM on those the surfaces, with different concentrations and modification times. The effects of oxidation time, concentration of modifier and modification time are investigated systemically. Consequently, an optimum condition is fined which helps to fabricate SH copper surfaces with minimum trials and costs. The distinct features of this work with respect to Refs. [3,8] is 1- they used another reagents for oxidation and 2- Ref. [3] used lauric acid to reduce surface energy; Lauric acid is a member of carboxylic acids which are unstable than ODT exposing to saturated vapour [6]; Ref. [8] used paraffin wax coating after oxidation, which its low melting point hinders the practical application of the resulting surfaces [11] especially in high temperature applications such as HEs. With respect to Ref. [2] the current work is simpler and can easily be used for mass production.

2. Experiments

2.1. Materials

Copper with purity of 99.996% was purchased from the National Iranian Copper Industries Corporation. All reagents were of analytical grade, including deionized water (DIW), NaOH, ethanol (99.9%), Na₃PO₄·12H₂O, NaClO₂, nitric acid (65%), ODT, and acetone (99.9%) were purchased from Merck Chemicals and used without further purification.

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2.2. Preparation of samples and fabrication of SH structure

Samples with a size of 20×20×2 mm were cleaned ultrasonically with acetone for 10 min and then cleaned with ethanol and DIW respectively. Subsequently, they were ultrasonically treated with nitric acid (65 wt%) for 15 min to get rid of native oxides and remove impurities. Then, the substrates were washed with DIW and dried at room temperature. The cleaned surfaces were oxidized by immersing in an alkaline solution composed of NaOH, Na₃PO₄·12H₂O, NaClO₂ and DIW (3.75: 5: 10: 100 wt%) in 96 ± 3 °C [12]. The oxidation times were 2, 5, 10, 15, 20, and 30 min respectively. After oxidation, samples were rinsed ultrasonically with DIW and dried in room temperature. Ethanol solution of ODT with different times (3, 5, 7, 12, and 24 h) and concentrations (1, 1.5, 2, 2.5, 3, and 5 mM) were used to modify oxidized surfaces.

2.3. Characterization

Surface morphology of as-prepared surfaces was observed on a scanning electron microscopy (SEM, Leo-1530 Field Emission, LEO Co., Germany) at 5.00 kV. The CA of samples was measured by a CA meter (Contact AngleSystemOCA20, Dataphysics Co., Germany). The X-ray diffraction (XRD) analyses of the samples were carried out using a Rigaku X-ray diffractometer. The sliding angle (SA) defined as the angle at which a water droplet begins to slip from the gradually inclined

surface. Both CA and SA were measured at 23 °C under relative humidity of 30%. The CA and SA values are reported based on the average of 30 different measurements on sample at room temperature with 5 μL probe liquid of water. The standard deviations of all CA measurements are within ± 2.1°.

3. Results and discussion

3.1. The effect of modifier concentration

Different modifier concentrations were examined with constant oxidation and modification times. As shown in Fig. 1a it can be seen that the concentration of 2.5 mM of the modifier is the optimal condition with CA of 156.1°. In this condition, drops easily slide off the inclined surface which is same as lotus plant leaves behavior against water. Oxidation and modification of copper surfaces with ODT leads to appearing of low surface energy micro-nano structures, where trapped air beneath a droplet and between micro-nano structures reduces solid-liquid contacts and SA; hence the droplet can easily slide. Further details on the role of micro-nano structures and hydrophobic promoter on the appearance of superhydrophobicity can be found in Ref. [2].

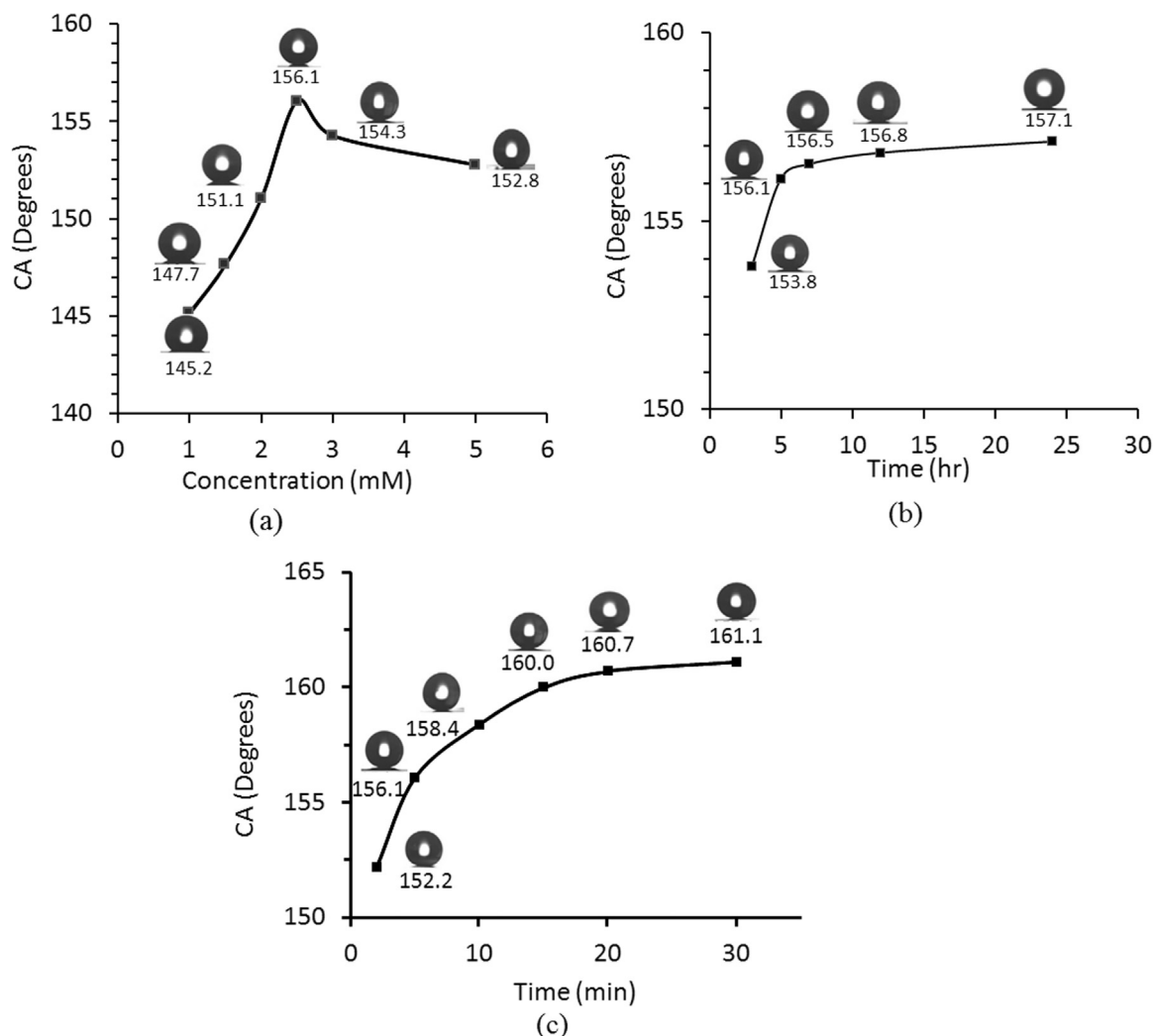


Fig. 1. Variation of CA with respect to (a) modifier concentration for a constant modification time 5 h and oxidation time 5 min, (b) modification time with constant modifier concentrations 2.5 mM and oxidation time 5 min and (c) oxidation time with constant modifier concentration 2.5 mM and modification time 5 h.

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