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The variation of surface free energy of Al during superhydrophobicity processing

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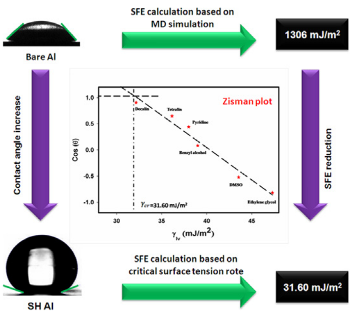
HIGHLIGHTS

- Surface free energy variation after superhydrophobicity creation of Al surface is examined.
- Molecular dynamics simulation is employed for surface free energy calculation of bare Al.
- For superhydrophobic Al, critical surface tension approach was used to measure surface free energy.
- Both experimental and theoretical approaches verify surface free energy reduction after superhydrophobicity creation.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface free energy (SFE) of solids is a main property. This parameter can be affected by various phenomena such as superhydrophobicity creation. Two circumstances are necessary to achieve superhydrophobicity characteristics. These requirements are roughness improvement as well as surface energy reduction. The ZnO nanoparticle deposition is a suitable method for obtaining desirable roughness and consequently decreased SFE with stearic acid (STA) ethanol solution. The SFE of bare Al at room temperature was investigated using molecular dynamics (MD) simulation. After fabrication of superhydrophobicity property on Al surface, its SFE was calculated by applying equation of state and critical surface tension methods. The comparison between results based on two considered methods led to the fact that SFE significantly reduces after superhydrophobicity processing and reaches to STA, applied as a modifier, surface tension value. In addition to the theoretical results, water contact angle (CA) measurements confirm the SFE reduction due to superhydrophobic processing. Furthermore, the presence of STA on the superhydrophobic surface can be verified experimentally with Fourier transform infrared in conjunction with attenuated total reflection (FTIR-ATR) analysis. Therefore, both computational and experimental results approve the existence of STA on superhydrophobic Al surface and its grafting may lead to SFE reduction.

1. Introduction

It is believed that solid surface free energy (SFE) is a major property, which can control various phenomena, such as, the rate of sintering and the stress for brittle fracture [1]. One of the well-known

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phenomena for changing SFE of solid surface is fabrication of superhydrophobic (SH) surfaces. SH surfaces possess water contact angle (CA) higher than 150° and can be classified into two categories based on sliding angle (SA) values which are low adhesive (with SA lower than 10°) and high adhesive (with very high SA) SH surfaces [2]. In other words, for rough surfaces, the Wenzel [3] and Cassie-Baxter [4] models can be applied to describe wetting state. In Wenzel model, a water droplet is able to enter to the asperities and totally fill any surface groove. The factor of roughness in Wenzel equation can improve the innate state of the material and gives a lower CA to hydrophilic surfaces and a larger CA to hydrophobic ones. The Cassie-Baxter model establishes another novel wetting state, in which air molecules may be trapped in the asperities and the air-water interface allows free movement of droplet which induces low SA. Though both of these wetting models (Cassie-Baxter and Wenzel) cause high CA, just only the Cassie-Baxter state results in very low SA. Therefore, a true low adhesive SH surface considerably matches to the Cassie-Baxter state [5]. As a result, CA measurement on the surfaces is not sufficient for surface wettability description and it is essential to report SA accompanied with CA.

To create SH surfaces, it is essential to perform roughness improvement as a first step and SFE reduction as the second one [6–10]. In other words, as well the chemicals with low surface energy, the formation of multiple scales structures on material surfaces is a crucial necessity for superhydrophobicity [11].

A variety of techniques has been developed for roughness production. For example, sol-gel method, phase separation, solution immersion method, plasma etching, lithographic, and electrochemical deposition are practical ways for this purpose [12–20]. Furthermore, costly silanes or fluorides were applied for SFE reduction in the final step of SH surface processing. It is well identified that treatment with fluoride can efficiently diminish the SFE. However, flour derivatives are not essential materials to generate SH surfaces and there are alternatives for these materials [21].

In comparison with conventional surfactants, stearic acid (STA) is a good choice in superhydrophobicity field due to its low cost, biocompatibility, and low toxicity [22,23]. STA has low surface energy and its grafting on rough surface results in superhydrophobicity property. There are many works relating to SH surfaces. In these works, the SFE reduction after superhydrophobicity creation has been assessed qualitatively [24–26]. In the current study, our goal is to present a quantitative estimation of SFE reduction after superhydrophobicity. Therefore, it is necessary to compute SFE of Al metal at room temperature and then SFE calculation of SH Al to conclude that how much SFE changes.

SH Al surface possesses a low SFE value; as a result, equation of state and critical surface tension approaches are applicable to achieve SFE value for this surface. These methods (equation of state and critical surface tension) as appealing findings have been introduced for surfaces with insignificant SFE values (such as polymers [27]).

From the other side of view, Al enjoys a high SFE, i.e. equation of state and critical surface tension methods are not applicable for this condition. Therefore, it is necessary to employ another method to examine SFE. One accurate method is liquid surface tension measurement, which is carried out precisely [1]. Interestingly, the surface tension of molten metal can be determined experimentally and computed theoretically. The experimental routes are drop weight (DW), sessile drop (SD), etc. that are accomplished in the gaseous environment [28]. The inconsiderable amount of impurities in the gas plays a key role in the accuracy of measurement. Consequently, reports on the surface tension values witness the diversity of quantities as Keene claims [29]. In other words, because of melt contamination and high reactivity, exact values of surface tension are difficult to be acquired via straight experimental techniques. In these conditions, computational and theoretical methods are present as practical means to evaluate the surface tension accurately [28]. One of the computation methods to evaluate surface tension of liquid metals is computer simulation [30,31] in addition to the various theories in statistical mechanics [32–35] and density functional theory [36]. If the liquid metal surface tension is computed accurately, it is possible to correlate it with SFE of solid metal at the melting point. For instance, Tyson and Miller [1] have introduced a correlation between SFE of solid metal at the melting point with this property at different temperatures. By applying SFE of solid metal at the melting point, it is possible to compute SFE values of solid metal at ambient temperature according to Eq. (1).

$$\gamma_{sv} - \gamma_{sv}(T_m) = \int_T^{T_m} \frac{S_{sv}}{A} dT \tag{1}$$

where γ_{sv} and $\gamma_{sv}(T_m)$ are SFE of solid Al at T and T_m, respectively, S_{sv} is surface entropy, and A is introduced as surface area per mole of surface atoms.

Recently, Rezayi and Entezari [37] have synthesized SH Al surface using ultrasound as a novel technique. In the present study, one goal is to examine SFE value change due to superhydrophobicity creation. In spite of several papers about surface tension calculation of liquid metals and SFE measurement of various solids [38–41], the number of publications on SFE comparison before and after superhydrophobicity processing is scarce. Therefore, the main novelty of current investigation is the mentioned issue. Based on experimental results (water CA measurement and ATR-FTIR analysis) [37], SFE of Al decreases considerably after SH creation which is in acceptable agreement with the current results. Another purpose is to verify this observation theoretically. In the present study, surface tension of liquid Al at melting point is computed by MD simulation. Afterward, SFE of solid Al at melting point was obtained using their correlation. To obtain SFE of Al at ambient temperature, a suitable equation was taken into consideration (Eq. (1)). Eventually, for SH Al, equation of state and critical surface tension approaches were used to measure SFE. The comparison between SFE results before and after superhydrophobicity process demonstrated the SFE reduction quantitatively. For SH Al, SFE is nearly equal to STA surface tension. Besides, experimental data confirm the presence of STA after modification that computational results are in excellent agreement with experiment.

2. Methods: theory and experiment

2.1. SFE calculation

Based on EDX results [37], Al plate is actually an alloy containing 96% Al and 4% Mg; consequently, considering Mg atoms in Al structure is an essential part of the study. In the present MD simulation study, NVT ensemble containing 256 atoms (241 Al atoms and 15 Mg atoms) in an orthorhombic cell with dimensions of $16.16 \times 16.16 \times 40.80$ Å^3 was applied. Berendsen thermostat has been utilized in order to control the temperature with a relaxation time of 1.00 ps. Furthermore, Gupta potential was selected for the interatomic interaction of Al-Al, Mg-Mg, and Al-Mg particles in the system [42,43]. The simulations were carried out at a temperature range from T = 900 K to T = 1100 K at ambient pressure. The time step was 1.00 fs and all simulations were continued up to 5 ns, performed by DL_POLY_2.17 [44,45]. Solid Al SFE at desirable temperatures is followed by Eq. (1) [1] where S_{sv} can be written as the sum of configurational and vibrational contributions:

$$S = S_{sv}^{conf} + S_{sv}^{vib} \tag{2}$$