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Validation of surface wettability theories via electrochemical analysis

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ABSTRACT

We have developed an experimental method to quantify the parameters defining the shape of a droplet placed on a rough surface. The parameters include the solid–liquid interfacial area under a sessile drop (measured via cyclic voltammetry) along with the optically measurable properties such as the contact angle and projected geometrical area. Using these parameters, it is possible to quantitatively validate many theoretical models proposed for predicting the wetting behaviour on rough surfaces. Carbon substrates with nanostructured surface features were prepared using plasma treatment to test the predictions from the Cassie-Baxter and Wenzel models. These predictions are compared with our experimental results.

1. Introduction

Recent advances in the field of wettability are strongly influenced by the fact that changing the surface roughness can alter the surface wettability. Conventionally, the contact angle is used as a direct metric to quantify the surface wettability. To predict the roughness induced change in the contact angle, various theoretical formulations have been developed where the objective is to predict the apparent contact angle (θ^*) for a rough surface as a function of the Young's contact angle (θ_Y). The vast majority of these models involve a direct or an indirect correlation between three important parameters: θ^*, θ_Y and the solid–liquid (S–L) interfacial area under the droplet. While the optical evaluation procedure for the contact angle is well established, estimating the wetted interfacial area poses problems primarily due to the limited optical accessibility.

Even though the Cassie-Baxter [1] and the Wenzel models [2] have been widely used in the literature, there has been a long standing debate regarding the validity of the models and their range of applicability [3,4]. The influence of droplet volume during the measurement of wettability parameters has also shown some contradictory results [5]. A quantitative evaluation of the wetted area can provide additional insights into addressing these issues. Also, based on the optically measurable θ^* and θ_Y values, identifying a model which can represent the wetting behaviour can be challenging. For example, when the substrate is intrinsically hydrophobic, both the Cassie-Baxter model and the Wenzel model predict an increase in the contact angle with roughness [6,7]. Understanding the dynamic behaviour of the droplet on hydrophobic surfaces is also an important field that can benefit from the accurate measurement of solid–liquid interfacial area [8,9].

Model systems with patterned roughness of known dimensions for approximating the S–L interfacial area have been used to circumvent these problems [4,10,11]. However, even for the patterned roughness, the liquid meniscus under the droplet can behave differently depending on the geometry, leading to inaccuracies in the predicted values [11–13]. Additionally, the approximations based on a pattern cannot be extended for the surface with irregular roughness features due to the stochastic nature of the surface topologies [14].

We have developed an experimental approach to overcome the limitations in optical measurements. The method evaluates the parameters, θ^*, θ_Y and S–L interfacial area, using a combination of optical and electrochemical measurements. Experimental evaluation has been shown for a hydrophobic surface, for which introducing surface roughness results in a contact angle increase. Using a quantitative comparison of the model predictions with the experimental results we identified the model which can best describe the wetting behaviour. The approach can be adopted for a wide range of roughness and surface structures, therefore, is a potential tool to characterize and enhance our understanding of wetting phenomena.

2. Materials and methods

Glassy carbon (GC) discs from Hochtemperatur-Werkstoffe GmbH (10 mm dia.) were plasma etched in two stages to generate homogenously distributed nanostructured roughness. The roughness variation was achieved by controlling the etching condition and the time. A Sentech Etchlab 200 reactive ion etcher instrument was used for this purpose. The samples were dried overnight and pre-evacuated in the pressure range of 10^{-6} Torr. Etching process was performed

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under 300 mTorr of O_2 gas and 300 W of RF power to create nanostructures on the surface [15,16]. To generate different roughness scales, different duration of etching (2 min, 5 min and 10 min referred to as Sample 2, Sample 3 and Sample 4) were utilized. The O_2-etched samples were hydrophobized under 300 mTorr of CF_4 and 100 W RF power for the duration of 1 min as described in the literature [17]. A smooth mirror-polished sample was cleaned using a short (20 s) O_2 plasma step followed by the same hydrophobic treatment to serve as the smooth surface (Sample 1) for this study. Similar surface treatment (O_2 treatment followed by CF_4 treatment) leads to similar surface properties and therefore similar electrochemical behaviour is expected. A FEI Helios NanoLab scanning electron microscope (SEM) was used to image the roughness features on the substrate.

A modified sessile drop contact angle setup with the electrochemical measurement capabilities was used. Apart from the optical measurements, the setup evaluates the electrochemical double layer capacitance proportional to the solid–liquid interface under the droplet [18]. Using this proportionality, the S–L interfacial area is quantified and used as a wettability parameter along with the optically measured contact angle and the geometrically projected area. The experimental procedure involves, placing a droplet of 10 μL on the substrate (working electrode) followed by lowering the two platinum wires (fisher scientific) into the droplet bulk which acts as the counter and the pseudo-reference electrode, respectively. The thickness of the platinum wires is 25 μm, which ensures minimum distortion of the droplet shape with <1° change in the contact angle. A 0.1 M sodium sulphate (Na_2SO_4, fisher scientific) solution was used as the liquid phase to provide the necessary conductivity and to facilitate the electric double layer formation. The capacitance was quantified based on the total charge enclosed by the cyclic voltammetry (CV) curve. For the present study a potential window of 0.2V (−0.1 to 0.1 V) was used at a scan rate of 100 mV/s. The average values of three measurements for each sample are reported along with the standard deviation. The side view image of the droplet was captured using a Canon camera (T6i) and the contact angle and the droplet base diameter were measured using open access software ImageJ. The electrochemical measurements were performed using a Solartron 1470E Cell Test System along with a Solartron SI 1260 Impedance/Gain-Phase analyser.

3. Results and discussions

SEM images (Fig. 1) show the surface morphology of the four samples used in this study. Sample 1 consists of minimal amount of surface features as shown in Fig. 1(a) and has been considered as the smooth surface in this study. Size distribution of conical features from the SEM image was obtained using image analysis reported elsewhere [19,20]. The width at half maximum height for 200 features, or more, was used to compare roughness dimensions between Samples 2–4. The average (μ) and standard deviation (σ) feature size are reported in the inset of Fig.1(b)–(d). The average feature size was found to increase from Samples 2 to 4. Fig. 2(a–d) shows the droplet shape, projected geometric area (A_{geo}) and the corresponding contact angle obtained using the image analysis. All the samples demonstrated a hydrophobic behaviour with contact angle >90°. The contact angle increased with the roughness and for Samples 1, 2, 3 and 4. It was evaluated as 100°, 127°, 128° and 137°, respectively. Following the optical imaging, the capacitance corresponding to the solid–liquid interfacial area under the droplet was electrochemically evaluated using cyclic voltammetry (Fig. 2(e)).

When a droplet is placed on a rough surface, depending on the energy dynamics, there can either be a heterogeneous (mixture of solid–liquid (S–L) and liquid–gas (L–G)) or a homogenous (only S–L) interface under the droplet. The most widely used models for describing these two situations, i.e. the presence of homogenous and heterogeneous interface under the droplet are the Wenzel and the Cassie-Baxter model, respectively. These two models correlate the apparent contact angle (θ^*) and the intrinsic contact angle (θ_Y) based on the interfacial behaviour under the droplet. The Wenzel model is

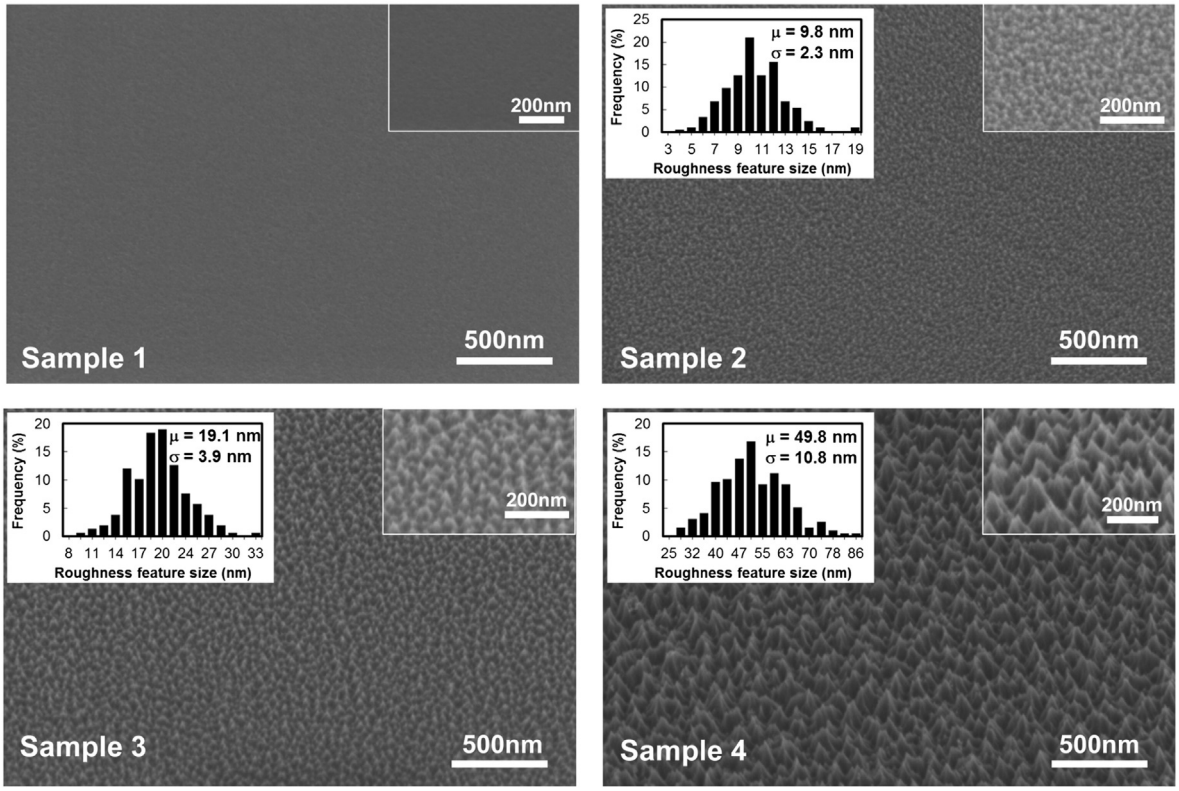

Fig. 1. The SEM micrographs of the 4 samples in this study. The histograms (inset) show the width at half maximum height of features, the average (μ) and standard deviation (σ).