AFFORDABLE METHOD FOR WATER CONTACT ANGLE MEASUREMENT

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ABSTRACT

The research on hydrophobic and superhydrophobic surface has been extensively studied by many groups around the world. The parameter determined the wetting ability of a surface is value of water contact angle. Measuring contact angle become extremely important for both academic and industrial field. In this study, we propose a simple and affordable methodology to calculate contact angle. This approach used portable microscope of Koolertron for droplet images capturing and free software of ImageJ for contact angle fitting and calculation. The contact angles of bare and Octadecyl trichlorosilane (OTS) modified glass slide are approximately 27° and 107°, respectively. The results were compared and confirmed with the published literatures. In addition, the superhydrophobic state was achieved by applying OTS on a glass microfiber filter. We have proven that the proposed method could be applied in a wide range of surface from hydrophilicity to superhydrophobicity.

Keywords: ImageJ, contact angle, hydrophobic, hydrophilic, portable microscope.

1. INTRODUCTION

Contact angle value is a useful parameter to evaluate the surface tension and wetting property of a surface [1, 2]. A drop of water placed on a solid surface in ambient atmosphere induces competitive forces which decides the shape of the formed droplet. The first one is the internal adhesive force of molecules inside of the liquid itself. This force could make the liquid maintain a sphere shape in the space where the gravity has no effect. The second one is the interaction force between the molecules of the liquid and molecules of the solid surface. If the interaction force is stronger than the internal force, the water would be spread on the surface. The ground shape droplet could be formed if there is little interaction between water and solid surface. The balance of these forces was described in a relationship to contact angle θ by Young equation [3].

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} cos\theta$$

Where:

γ^{sv} is the solid surface free engergy.

γ^{lv} is liquid surface free engergy.

γ^{sl} is the solid/liquid interfacial free engergy.

If the contact angle is equal 0°, the surface could be considered as absolute wetting while the surface is no wetting for the contact angle values of 180° [4]. Based on the value range of water contact angle, the water wetting of a surface could be divided into three categories: hydrophilicity (0° < θ < 90°), hydrophobicity (90° < θ < 150°) and superhydrophobicity (150° < θ) [5, 6]. Superhydrophobic surface has been received great attention owing to its potential applications such as drag reduction, anti-icing, water-resistance coating [6, 7]. As the water contact angle reaches more than 150°, the surface possesses the self-cleaning property [4] which could be applied in automobile industry [8]. Another application is oil/water filtration by utilizing a mesh which has both superhydrophobicity and superoleophilicity [9, 10].

The most popular method to measure the contact angle is sessile drop technique using a goniometer [11]. In general, a constant amount of water shall be dropped on the surface. The droplet profile shall be captured by a camera through a magnify lens. The water contact angle in this case is defined as the angle made by two lines: liquid/solid baseline and liquid/air interface line. After capturing the images, the water contact angle could be calculated manually or using software processing. Nowadays, the precision of the measuring contact angle is increasing as many goniometers have been developed by the companies. However, most of the commercially available equipment are out of reach of the most Vietnamese research groups due to expensive price and limited funding. A simple method which is affordable, reliable and consistent in measuring contact angle would be extremely useful.

In this study, a simple portable microscope and a free image software was applied to measure water contact angle. The microscope could be easily acquired and replaced with similar tool through many available shops. The software of ImageJ with the contact angle plugin could be freely downloaded from the internet. In addition, we have also modified the glass slide with a hydrophobic layer and tested the water contact angle range that the method can be applied.

2. EXPERIMENTAL SECTION

2.1. Materials

The solvents used in this study are pure grade from Xilong Company. The microscope slide was chosen as a targeted substrate for measuring contact angle. The glass slide was obtained from Sail Brand (China). Another surface was the glass microfiber filters (grade GF/A with diameter of 47 mm produced by GE Healthcare Whatman company, United Kingdom). The glass slide and filter surface were modified with trimethylchlorosilane (TMCS) (Shanghai Aladdin Bio-Chem Technology Co. LTD, China) or Octadecyl trichlorosilane (OTS) (Richest group, Shanghai, China).

2.2. Contact angle measurement

A constant amount of water shall be used to ensure the consistency of the method. 5 μL of double distilled water was gently dropped on the sample surface using a micro-pipette. The images of water droplet formed on the sample surface were captured by the portable microscope (4.3" LCD Digital type, Koolertron, China). The image files were transferred to a computer and processed using the software of ImageJ with the contact angle plugin.

2.3. Surface modification

The glass slides or glass filters were carefully cleaned with acetone and *n*-hexane. The cleaned samples were immersed into 5% solution of TMCS or OTS in *n*-hexane. The sample was coated with TMCS in 5 min while the reaction time for OTS solution was 15 min. The glass samples after reaction were put into oven (60 °C) in 2 hours to remove the solvent. Measurement of water contact angle was performed before and after reaction for comparison.

3. RESULTS AND DISCUSSION

The portable microscope used in this study possesses the function of capturing images with high quality. The water droplet on the surface of the glass slide modified with OTS was shown in Figure 1.

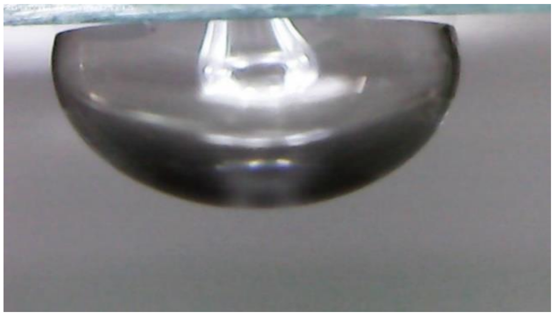

Figure 1. Water droplet image on OTS-treated glass slide captured using picture function of Koolertron microscope.

The image was in the upside down state which is a normal result for the magnify lens system in the microscope. As can be seen, the image was stretched due to the auto resize function of the used microscope. The microscope has widescreen 4.3" LCD display and the final images might have been automatically changed to fit the screen. Based on our preliminary studies, the capturing picture function for this Koolertron microscope must be very carefully used as an input for contact angle measurement. The acquired droplet images might not represent the true wetting properties. Therefore, in this study, we proposed a slightly different method to obtain the water droplet image for ImageJ input data. Instead of capturing images, the microscope and the droplet were kept in a steady state and the function of recording videos with high resolution was applied. After obtaining a video file, there are two possible ways to process the data. The first method is extracting the image using Windows Media Player Classic (Figure 2a). The second method is dragging and dropping the video file directly to the ImageJ software (Figure 2b).

a)

b)

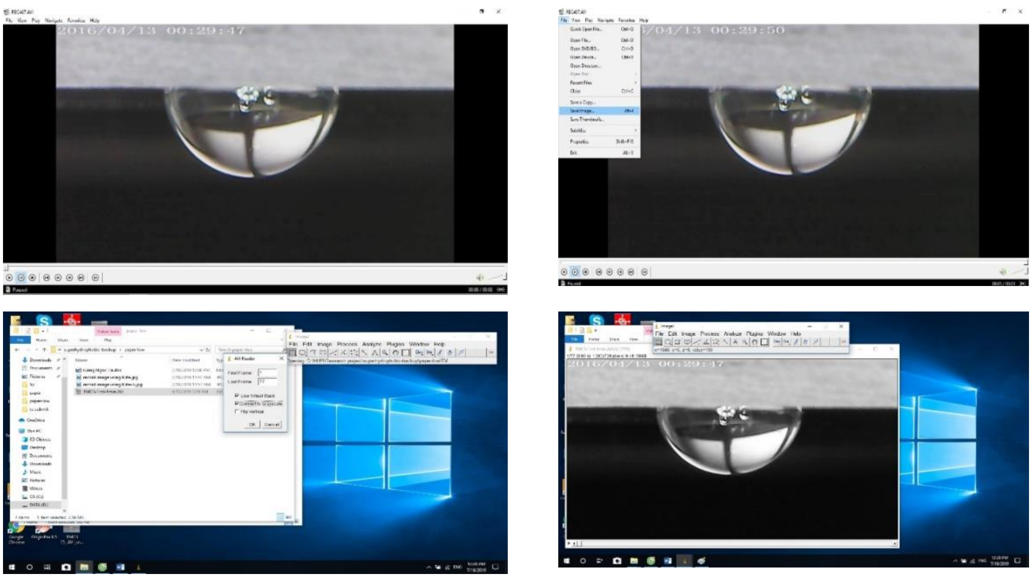

Figure 2. Capturing droplet images from a video file using (a) Windows Media Player Classic; (b) imageJ.

As can be seen, good quality image from high resolution video could be obtained. In the next step, the images would be used as an input for calculating contact angle with ImageJ and contact angle plugin. The plugin requires picking manually of at least 5 points on the droplet edges (Figure 3). The first two points will define the base line which could be considered as the interface between water and the substrate.

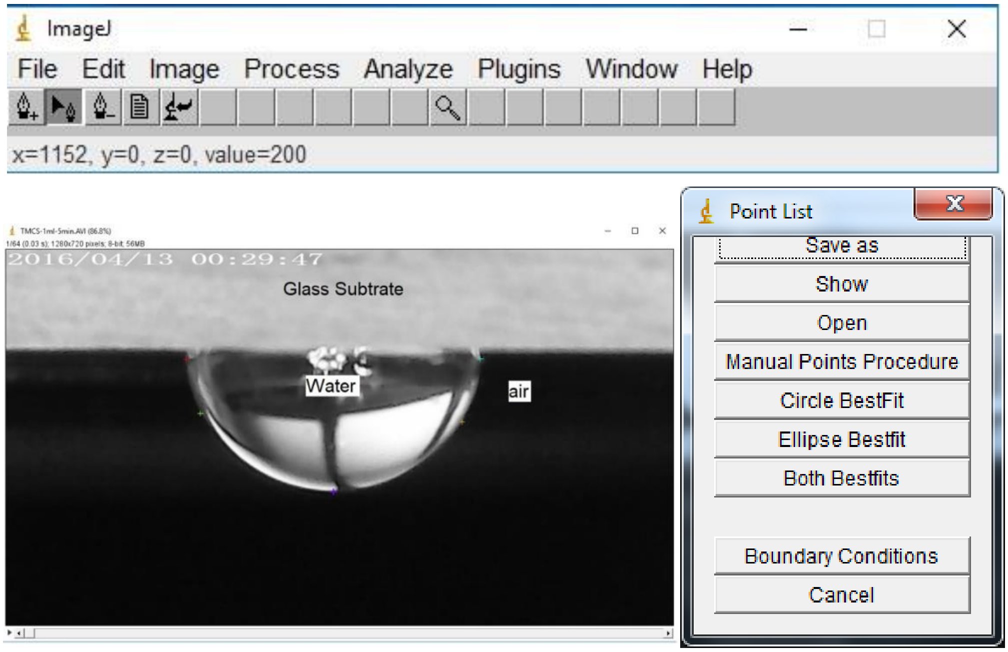

Figure 3. Points picking on water droplet

The other three points are to fit the droplet curves. By clicking on the symbol, there are four methods for fitting the curve including: Circle, Ellipse, Both Bestfit and Manual Points Procedure. Figure 4 showed the fitting curve by using the methods of circle, ellipse and both bestfit and manual procedure. The program then calculated the contact angle based on sphere or ellipse approximation [12].

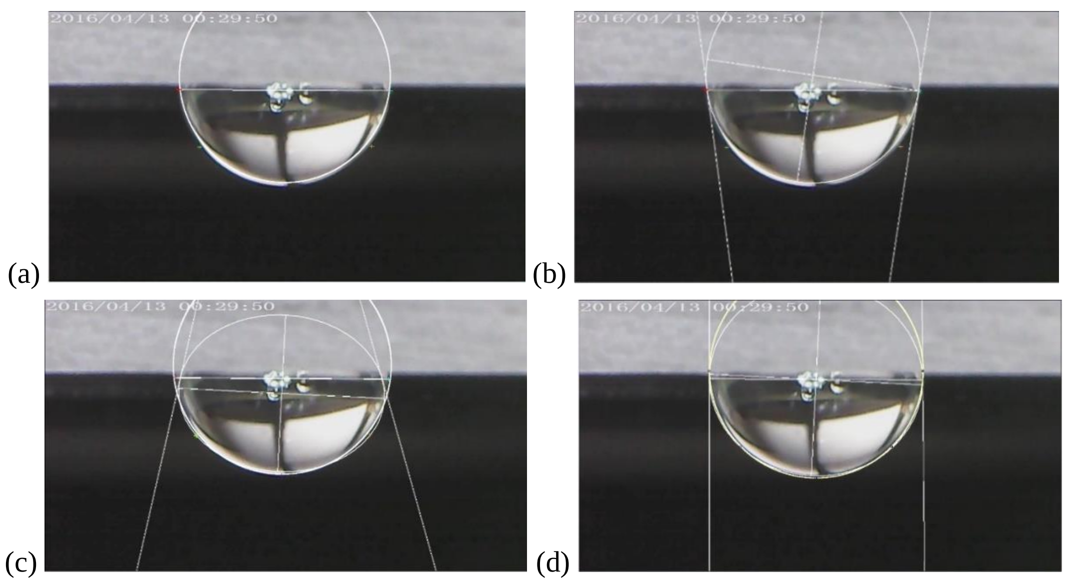

Figure 4. Fitting droplet curve using ImageJ with (a) circle best-fit; (b) ellipse best-fit; (c) both best-fit; (d) manual point procedure.

The initial picking points were kept constant before applying four types of fitting for a good comparison. The contact angle values in these cases were shown as theta and the result was summarized in Table 1. The values of circle and ellipse fitting were comparable. However, as can be seen in Figure 4a-c, the fitting curve could not follow the actual droplet edge while the best fitting was observed by using manual points procedure (Figure 4d) with the same initial points. When the circle, ellipse fitting or both Bestfit procedure was applied, the edge detection algorithm was included in ImageJ. The drop profile could be automatically detected to define the circle or ellipse [13]. This is a very powerful tool to reduce the man-made mistake due to choosing the wrong point. However, to apply the algorithm, the high contrast between the droplet and the atmosphere background is required. This condition only can be achieved with other devices setup and additional tools and equipment [12, 13]. The result of contact angle by using manual point procedure and both bestfit function included theta C (for circle fitting) and theta E (for ellipse fitting). The circle fitting function was designed with an assumption that the droplet had the sphere shape. However, the perfect sphere shape is difficult to achieve in reality. Although a small amount of water (5 µL) was used, the droplet shape is still slightly affected by the gravity. Therefore, the ellipse curve generated by the program (the white curve Figure 4d) showed a better fitting with the drop profile and the theta E could represent a better contact angle result.

Table 1. Result of water contact angle after fitting

Function	Theta (°)	Theta C (°)	Theta E (°)
Circle bestfit	82.6	-	-
Ellipse bestfit	82.0	-	-
Both bestfit	-	82.8	104.2
Manual point procedure	-	85.5	90.2

In the next experiment, the glass slide and glass filter were modified with TMCS and OTS. For each sample, water was dropped on 6 different positions on the surface. As a result, 6 droplet images were obtained and the water contact angle was analyzed using the above method with manual points procedure. The average values calculated from theta E for 6 positions were summarized in Table 2. The data was also presented graphically in Figure 5. Each data for the sample type was accompanied with a represented water droplet image. The upside down images were used to calculate contact angle while the rotated images was presented in Figure 5 to have an easier comparison.

Table 2. Contact angle values of various sample

Sample	Contact angle (theta E) (°)	Standard deviation
Untreated glass slide	27.93	4.05
Glass slide with TMCS	85.18	3.63
Glass slide with OTS	107	2.76
Glass filter with OTS	151.72	0.51

The water contact angle of original glass measured by the present method is approximately 27.9 ± 4°. This result is comparable to the previous reports [14, 15]. These results have provided a strong evidence that the propose procedure can yield a good water contact angle measurement with the affordable and simple tools. This work can be used as a model for other research groups in Vietnam who are interested in the contact angle detecting with limited funding. However, the method firstly has to prove the ability to apply to a wide range of contact angle. The research team moved to a next step by applying a hydrophobic layer to the glass slide to increase the contact angle. The sample B is the glass slide which was modified using TMCS. As can be seen, the water contact angle in this case was significantly improved to 85.2 ± 3.6°. However, the surface could not be assigned as hydrophobic as the value is limited of less than 90° [16]. In another experiment, the glass slide after carefully cleaning was immersed into 5% OTS solution in *n*-hexane in 10 min. The outcome was very promising as the detected water contact angle could reach 107.0 ± 2.8° while the result of OTS treated-glass slide reported by Lamour *et al*. was 110° [12]. The surface has been successfully transformed from a hydrophilic to hydrophobic state. In sample D, instead of glass slide, the glass microfiber filter was used. The filter surface was modified with OTS and the superhydrophobic state was achieved as the water contact angle exceeded 150° (Figure 5 and Table 2).

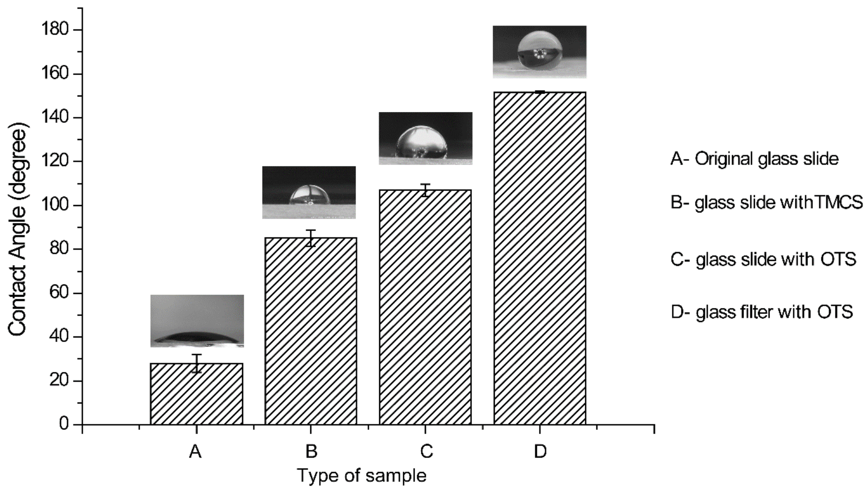

Figure 5. Change of contact angle values by chemical treatment.

The wettability of a surface which represented by the value of water contact angle is mainly depended on two factors: surface's chemical composition and surface roughness [17, 18]. In the case of modifying glass slide with OTS or TMCS, the surface composition has changed from the hydrophilic groups (–OH) to hydrophobic alkyl chains. As a result, it leaded to the significant increase of contact angle. The OTS with longer alkyl chain compairing to TMCS has higher ability to improve the water contact angle. However, our result is in good agreement with the conclusion from the previous study [19]: if only chemical modification was applied, the water contact angle was limited less than 120°. To achieve the superhydrophobic and high water contact angle, many sophisticated methods to fabricate the sub-micron roughness have been proposed [6, 14, 16, 20, 21]. Comparing to glass slide samples, the glass filter formed by various micro-size of the fibers provided a rough surface which might be the main cause for large water contact angle and the good water-repellence. To the best of our knowledge, this is the first report that the superhydrophobic surface could be obtained with a simple chemical treatment and without using any nano materials. The result also clearly indicated that the present contact angle could be applied for a wide range of surface from hydrophilicity to hydrophobicity or even superhydrophobicity.

4. CONCLUSIONS

The proposed method has been performed successfully in measuring water contact angle. Because of the resizing mode included automatically in the microscope software, the obtained images do not represent the actual situation. Based on our investigation, the video mode of Koolertron microscope should be applied instead of directly using picture capturing function. By using the popular software of ImageJ, the water contact angle could be calculated and the manual points procedures gave the best fitting. The water contact angle results of both hydrophilic and hydrophobic glass surface were comparable to the published articles. The superhydrophobic state with contact angle values of 151.7 ± 0.5° was obtained by simple chemical treatment. The proposed method showed the applicability to a wide range of surface.

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REFERENCES

1. Kabza K.G., Gestwicki J.E., McGrath J.L. - Contact angle goniometry as a tool for surface tension measurements of solids, using zisman plot method. A physical chemistry experiment, Journal of Chemical Education **77** (2000) 63.
2. de Gennes P.G. - Wetting: statics and dynamics, Reviews of Modern Physics **57** (1985) 827-863.
3. Young T. - An essay on the cohesion of fluids, Philosophical Transactions of the Royal Society of London **95** (1805) 65-87.
4. Simpson J.T., Hunter S.R., Aytug T. - Superhydrophobic materials and coatings: a review, Reports on Progress in Physics **78** (2015) 086501.
5. Marmur A. - Hydro- hygro- oleo- omni-phobic? Terminology of wettability classification, Soft Matter **8** (2012) 6867-6870.
6. Jeevahan J., Chandrasekaran M., Britto Joseph G., Durairaj R.B., Mageshwaran G. - Superhydrophobic surfaces: a review on fundamentals, applications, and challenges, Journal of Coatings Technology and Research **15** (2018) 231-250.
7. Latthe S.S., Gurav A.B., Maruti C.S., Vhatkar R.S. - Recent progress in preparation of superhydrophobic surfaces: A review, Journal of Surface Engineered Materials and Advanced Technology **2** (2012) 76-94.
8. Aegerter M.A., Almeida R., Soutar A., Tadanaga K., Yang H., Watanabe T. - Coatings made by sol–gel and chemical nanotechnology, Journal of Sol-Gel Science and Technology **47** (2) (2008) 203-236.
9. Zhang Z.H., Wang H.J., Liang Y.H., Li X.J., Ren L.Q., Cui Z.Q., Luo C. - One-step fabrication of robust superhydrophobic and superoleophilic surfaces with self-cleaning and oil/water separation function, Scientific Reports **8** (1) (2018) 3869.
10. Singh V., Sheng Y.-J., Tsao H.-K., Facile fabrication of superhydrophobic copper mesh for oil/water separation and theoretical principle for separation design, Journal of the Taiwan Institute of Chemical Engineers **87** (2018) 150-157.
11. Chau T.T. - A review of techniques for measurement of contact angles and their applicability on mineral surfaces, Minerals Engineering **22** (2009) 213-219.
12. Lamour G., Hamraoui A., Buvailo A., Xing Y., Keuleyan S., Prakash V., Eftekhari-Bafrooei A., Borguet E. - Contact angle measurements using a simplified experimental setup, Journal of Chemical Education **87** (2010) 1403-1407.
13. Williams D.L., Kuhn A.T., Amann M.A., Hausinger M.B., Konarik M.M., Nesselrode E.I. - Computerized measurement of contact angles, Galvanotechnik **101** (11) (2010) 2502-2512.

14. Thirumalai K., Shanthi M., Swaminathan M. - Hydrothermal fabrication of natural sun light active Dy_2WO_6 doped ZnO and its enhanced photo-electrocatalytic activity and self-cleaning properties, RSC Advances **7** (2017) 7509-7518.
15. Winandy L., Hilpert F., Schlebusch O., Fischer R. - Comparative analysis of surface coating properties of five hydrophobins from *Aspergillus nidulans* and *Trichoderma reseei*, Scientific Reports **8** (2018) 12033.
16. Das S., Kumar S., Samal S.K., Mohanty S., Nayak S.K. - A review on superhydrophobic polymer nanocoatings: Recent development and applications, Industrial & Engineering Chemistry Research **57** (2018) 2727-2745.
17. Barthlott W., Neinhuis C. - Purity of the sacred lotus, or escape from contamination in biological surfaces, Planta **202** (1997) 1-8.
18. Feng L., Li S., Li Y., Li H., Zhang L., Zhai J., Song Y., Liu B., Jiang L., Zhu D. - Super-hydrophobic surfaces: From natural to artificial, Advanced Materials **14** (2002) 1857-1860.
19. Blossey R. - Self-cleaning surfaces - virtual realities, Nature Materials **2** (2003) 301-306.
20. Khan S.A., Zulfiqar U., Hussain S.Z., Zaheer U., Hussain I., Husain S.W., Subhani T. - Fabrication of superhydrophobic filter paper and foam for oil-water separation based on silica nanoparticles from sodium silicate, Journal of Sol-Gel Science and Technology **81** (2017) 912-920.
21. Yu S., Guo Z., Liu W. - Biomimetic transparent and superhydrophobic coatings: from nature and beyond nature, Chemical Communications **51** (2015) 1775-1794.

TÓM TẮT

PHƯƠNG PHÁP ĐƠN GIẢN CHO QUÁ TRÌNH XÁC ĐỊNH GÓC TIẾP XÚC

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Bề mặt kỵ nước và siêu kỵ nước đã được nghiên cứu rộng rãi bởi nhiều nhóm tác giả trên thế giới. Thông số xác định khả năng thấm ướt của bề mặt là giá trị góc tiếp xúc của bề mặt với nước. Đo góc tiếp xúc trở nên cực kỳ quan trọng đối với cả lĩnh vực học thuật và công nghiệp. Trong nghiên cứu này, nhóm tác giả đề xuất một phương pháp đơn giản và giá cả phải chăng để tính toán góc tiếp xúc. Cách tiếp cận này sử dụng kính hiển vi cầm tay của Koolertron để chụp ảnh giọt nước và phần mềm miễn phí ImageJ để tính toán góc tiếp xúc. Góc tiếp xúc của lam kính nguyên gốc và lam kính được biến đổi hóa học với octadecyl trichlorosilane (OTS) lần lượt là khoảng 27° và 107°. Các kết quả được so sánh và xác nhận với các tài liệu đã công bố. Ngoài ra, trạng thái siêu thấm nước đã đạt được bằng cách áp dụng OTS trên giấy lọc vi sợi thủy tinh. Nhóm tác giả đã chứng minh rằng phương pháp này có thể được áp dụng trong một phạm vi bề mặt rộng từ tính ưa nước đến siêu kỵ nước.

Từ khóa: ImageJ, góc tiếp xúc, kỵ nước, ưa nước, kính hiển vi cầm tay.