Improved Hydrophobicity of Polydimethylsiloxane (PDMS) Coating with ZnO Nanostructures

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Abstract. In this present work, an environmentally safe hydrophobic cotton surface comprising of PDMS and different morphology of Zinc oxide (ZnO) nanostructures via simple dip coating method was developed. ZnO nanosphere and ZnO nanoflakes were synthesized via sol gel method while ZnO nanorods were synthesized via solution precipitation method. The precursors used to prepared ZnO nanospheres, nanoflakes and nanorods are zinc acetate dehydrate, zinc chloride and zinc nitrate tetrahydrate respectively. ZnO nanostructures were analysed using FESEM and XRD. The hydrophobic cotton surface was characterized via FT-IR and WCA analysis. A WCA of 144.15° was achieved when coating the cotton with ZnO nanoflakes (ZnO-NF:PDMS).

1. Introduction

Hydrophobicity is the physical property that provides water repellence and non-wettability of a solid surface. The hydrophobic coating has been achieved in many ways with different kinds of materials by mimicking the surface roughness of lotus leaves and low surface energy. The surface structure of the leaves enables entrapment of air between water droplets and the surface [1]. Meanwhile, low surface energy attained from non-polar molecules. This contributes to less wetting and adherence between the water droplets and the surface, thus creating a highly water repellent surface.

The attractive features of hydrophobicity behaviour on solid surface clearly is very important and can be exploited in a variety of applications including in electronic, medical, paint coating, textiles and many other industries. Self cleaning glass, anti-corrosion coatings and waterproof textiles are some of the potential areas for its application[2]. Typically, fabricating hydrophobic textiles involve the treatment of the textile with selected low surface energy material purposely to prevent properties changes of the textiles[3].

Various research has been directed in several decades towards the creation of textiles which are water repellent, dust resistant and anti-bacterial. However, its application as a hydrophobic barrier to replace paraffin wax in batik making has not been explored yet. Research in substituting paraffin wax is essential to reduce large volume of solid suspended discharge from paraffin wax that cause clogging issue on batik waste water treatment system. Therefore, in this present work we attempt to study the effect of ZnO with different morphology to promote the bonding interactions. The solvated zinc acetate acts as a “bridge” between the textile substrate and PDMS by forming hydrogen bonds.
2. Experimental study

2.1 Materials

Zinc acetate dihydrate (183.48 g/mol, 99.8%), Zinc nitrate tetrahydrate (261.44 g/mol, 99.8%), Zinc chloride (136.315 g/mol, 99.8%), hydroxy terminated poly(dimethylsiloxane) (PDMS), Hexamethylenetetramine (HMT), Polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich. Ethanol, Potassium hydroxide (KOH) and n-hexane were purchased from Merck Millipore. All the chemicals used were of AR grade and used as received without further purification. Textile/cloth was purchased from Ayu Fashion Sdn. Bhd.

2.2 Synthesis of ZnO spherical particles

In this experiment, 5.2 g of zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O (99.5%)] was dissolved in 200 ml deionized water (DI) and heated at 65 °C under constant stirring. Simultaneously, 2.96 g of potassium hydroxide (KOH) solution was prepared in 100 ml deionized water. Then, appropriate amount of potassium hydroxide solution was added drop wise with this zinc acetate dihydrate solution under vigorous stirring at 1200 rpm at 65 °C. This mixtures solution was stirred continuously at 65°C for 1 h to achieve the white colour milky suspension. Now the product was centrifuged several times in ethanol for filtration and dried at 100 °C for 2 hours in normal oven for characterization.

2.3 Synthesis of ZnO rod particles

ZnO rods were synthesized via solution precipitation method using zinc nitrate tetrahydrate (Zn(NO₃)₂·4H₂O, Merck), hexamethylenetetramine (HMT, (CH₂)₆N₄, Merck) and polyvinylpyrrolidone (PVP). In a typical synthesis, 3.14 g of Zn(NO₃)₂·4H₂O in 100 ml of deionized water (solution I), 0.56 g of HMT in 100 ml of de-ionized water (solution II) and 1 g of PVP in 100 ml of de-ionized water (solution III) were prepared separately. The solution was stirred for 30 min at 90 °C. Subsequently, solution I and solution II were added into the solution III under constant stirring rate at 90 °C. The mixture of solution was heated to 90 °C in a water bath. White precipitate was found in the solution. Centrifugation was carried out at 3000 rpm for 20 min in order to separate the precipitate from the solution. The precipitate was washed by de-ionized water for several times. The precipitate was dried in the oven for overnight at 100 °C.

2.4 Synthesis of ZnO flake particles

In this experiment, 5.45 g of zinc chloride (Zn(Cl₂)·4H₂O) was dissolved in 100 ml of ethanol and kept under constant stirring using magnetic for one hour. 4.49 g of Potassium hydroxide (KOH) was also prepared in 100ml with stirring of one hour. After complete dissolution of zinc chloride, KOH aqueous solutions were added under high speed constant stirring drop by drop for 45 min. The beaker was sealed at this condition and the solution was allowed to settle for overnight. Further, the supernatant solution was separated carefully. The remaining solution was centrifuged for 20 min and the precipitate was removed. Precipitated ZnO particles were cleaned three times with de-ionized water and ethanol then dried in oven for 8 hours at 60°C.

2.5 Preparation of hydrophobic coating

PDMS and hexane were used as the raw materials. The volume required of PDMS and hexane was measured. PDMS was dissolve in hexane that act as solvent. The PDMS-hexane dissolved with ratio of 1:3 (ml) using a magnetic stirrer for 30 minutes. Different amount of ZnO particles (0.02g, 0.05g, 0.1g, 0.30g, 0.50 g) was added in the PDMS solution and ultrasonicated separately for 10 minutes. Optimum amount of ZnO particles were varies with different morphology of spherical, rod and flake particles. Homogeneous solution typically occurred within 8 hours after stirred at heating temperature 60 °C.
Before the coating, cloth of 3 cm x 3 cm was cleaned with ethanol and deionizes water. The pre-cleaning process is compulsory to remove possible impurities before drying for further processing. The cleaned cloth was then dip-coated into the hydrophobic solution at a controlled rate of 5 mm/s. The coatings were allowed to cure at room temperature for 1 hour and then dried in oven at 100 ºC for 48 h.

2.6 Characterization

Fourier Transform Infrared (FTIR, Perkin Elmer) spectroscopy was used to investigate the functional groups of super-hydrophobic coating. The morphology was examined with a help of field emission scanning electron microscopy (FESEM-EDX, Zeiss, Supra 35VP). The crystalline phases of ZnO were identified using a Philips PW1729 powder X-ray diffractometer (XRD). The water contact angle (WCA) was measured by the sessile drop method with a droplet volume of 5 μL using a goniometer (Rame hart Instrument. Co, USA) on one side of the sample. Briefly, the samples were placed in a Contact Angle Goniometer, attached to an Image analyzer. Each sample was subjected to 10 measurements in each 4-angle position: vertical left, vertical right, horizontal left, horizontal right. DROPimage Advanced software was used to obtain the WCA.

3. Results and discussion

The surface morphologies of ZnO particles were investigated by FESEM. The ZnO particles which synthesized by using sol-gel method via zinc acetate dehydrate and potassium hydroxide, exhibited quasi-sphere structure as shows in Figure a. It is found that the particles are well dispersed and have a regular quasi-spherical with average diameters of 60.66 nm. Figure 1b show the SEM image of the synthesized ZnO flake particles by using zinc chloride as Zn⁺² and potassium hydroxide as OH⁻ to growth the ZnO. The edge length of the nanoflakes are vary from 370 nm to 840 nm, with the average thickness of 61.91 nm. Meanwhile, Figure 1c shows the representative FESEM image of ZnO rod particles which synthesized by precipitation method using zinc nitrate tetrahydrate. The sample composed of rod-like structure with diameter ranging from 140 nm to 340 nm and average length of 2.51µm.

![Figure 1](image)

**Figure 1.** FESEM images of the as-synthesized samples in different morphology (a) ZnO spherical particles, (b) ZnO flake particles and (c) ZnO rod particles: inset showing the stacking rod

The crystal structure of various ZnO was characterized by XRD in order to determine the crystallinity of the as-synthesized ZnO particles. The diffraction peaks at 31.79°, 34.43°, 36.26°, 47.56°, 56.62°, 62.85°, 66.38°, 67.96°, 69.08°, 72.55°, and 76.95° are corresponded to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) crystal planes of hexagonal wurzite structure. No other diffraction peak from ZnO could be found, indicating high purity of ZnO formation. Although the obtained ZnO shows similar crystal structure of hexagonal ZnO, there are some differences with the lattice constant. For ZnO spherical, the wurzite structure match ICDS of 01-075-0576 with lattice constant of a = 3.2477 Å and c = 5.1948 Å, for ZnO flake particles match with ICDS of 01-079-0205 with lattice constant of a = 3.2499 Å and c = 5.2066 Å while for ZnO
rod particles match with ICDS of 01-079-0205 with lattice constant of \( a = 3.2417 \text{ Å} \) and \( c = 5.1800 \text{ Å} \).

**Figure 2:** XRD patterns of the as-synthesized samples in different morphology (a) ZnO rod, (b) ZnO flakes and (c) ZnO spherical

As seen in Figure 2a, the peak intensity of rod structure is higher than the rest of the sample, indicating better degree of crystallinity. The (002) and (100) planes for rod appear to be stronger than the other sample, indicating rods grows along the direction of polar (002) that surrounded by six (100) planes[4], preferentially. This is in agreement with the FESEM image which shows the growth of the rod along \( c \)-axis. Besides (002) and (100) plane, (101) appear to be intense for rod probably due to non-uniform alignment of the rods perpendicular to the substrate (XRD sample holder). As demonstrated in Figure 2b, the interfaces are found mainly in the middle of the ZnO particles, indicating that each particles at least consists of two rods that stacked in their (002) polar surface. This result is in agreement with the work reported by Thuya and Pung, 2015[4], which demonstrated the role of Zinc nitrate tetrahydrate as zinc precursor as charged positively (Zn\(^{2+}\) terminated) and HMT which provides hydroxide ion (OH-) as charged negatively (O\(^{2-}\) terminated)[4]. In zinc-HMT growth process, these ions are tends to stacked together on another polar surface (002) plane in order to minimize the total surface energy. Such a process is repeated over time, leading to a fast growth of ZnO nuclei along the \( \pm[0001] \) directions. As a result, ZnO rods will be continue synthesized if no complexing agent is added to alter the preferential growth direction of ZnO in [0001][5]. In order, to overcome the fast growth of ZnO, the PVP was adding into the solution as capping agent or stabilizer to minimize the issues of agglomeration and secondary nucleation on the surface of ZnO micronrods. As shown in Figure 2c, the peak intensities of (002) and (100) plane for spherical particles are similar while (101) plane are more intense, indicating preferential orientation of hexagonal ZnO[5].

Hydrophobic solution were analysed by FTIR to determine functional group of ZnO particles and ZnO/PDMS hydrophobic solution. Figure 3a, 3b, and 3c show the FTIR spectra of ZnO, PDMS and ZnO/PDMS hydrophobic solution in the range of 4000-400 cm\(^{-1}\) respectively.
Figure 3: FTIR spectra of (a) ZnO particles, (b) PDMS solution and (c) PDMS/ZnO hydrophobic solution

From the FTIR spectrum, it was observed that ZnO particles peak at 3815 cm\(^{-1}\) is attributed to O-H stretching band vibration, assigned to small amount of adsorbed water on the ZnO surface\([6]\). A strong peak at 523 cm\(^{-1}\) is ascribed to Zn-O stretching vibration. For PDMS hydrophobic solution, strong peaks at 3468 cm\(^{-1}\) and 3513 cm\(^{-1}\) correspond to the intense anti-symmetric and symmetric –CH\(_3\) group stretching confirming the presence of Si-(CH\(_3\))\(_3\) and Si-O-CH\(_3\) groups. A series of absorption peaks from 1000 to 2000 cm\(^{-1}\) are found corresponding to vibration of various functional group of the silane compound such as Si-O in Si-O-Si back bone and Si-CH\(_3\) vibration present on the PDMS surface. The absorbance peaks between 953 cm\(^{-1}\) to 792 cm\(^{-1}\) represent the vibration of the CH\(_3\) at Si(CH\(_3\))\(_2\).

Meanwhile, PDMS/ZnO spectrum was observed peak at 2963 cm\(^{-1}\) is attributed to O-H stretching band vibration, assigned to small amount of adsorbed water on the ZnO surface. A series of absorption peaks from 1000 to 2000 cm\(^{-1}\) are found corresponding to vibration of various functional group of the silane compound such as Si-O in Si-O-Si back bone and Si-CH\(_3\) vibration present on the PDMS surface. A strong peak at 485 cm\(^{-1}\) is ascribed to Zn-O stretching vibration. Other than that, a weak peak at 889 cm\(^{-1}\) was observed in PDMS-ZnO spectra, which could be originated from Zn-O-Si. This observation gives an idea that ZnO particles reacts also with some of the residual silanol (Si–OH) groups. The super-hydrophobic properties of a coating are greatly affected by the existence of these methyl group. From this spectra, it can be inferred that the PDMS/ZnO contain methyl group, thus improvement of hydrophobicity behaviour is observed.

Figure 4 shows the overall result of WCA with ZnO different morphologies. PDMS/ZnO-flake particles, PDMS/ZnO-rod particles and PDMS/ZnO-spherical particles coated on cotton cloth is more hydrophobic as the water contact angle increased to 144.15º, 139.65º and 141.15º respectively as compared to without ZnO particles. It has proved that ZnO morphology studied which are spherical, rods and flakes has influences wettability properties ZnO/PDMS coating. The differences in water contact angle of these coatings can be attributed to different topography induced by the different morphology of the ZnO particles. Morphology of ZnO particles has improved the wettability by following Wenzel state where the hydrophobicity was improved by increasing in surface roughness. However, due to non-perpendicular alignment of ZnO rod particles, the wettability has decrease followed the stable Wenzel state where the liquid fills between the rough structures. Remarkable WCA can be observed from results which show the incorporation of ZnO particles with flake shape produced better roughness surface, supporting Wenzel model, thus lead to an increase in static contact angle, 144.15º compared to other structures.
Figure 4: Overall WCA result with different morphology

4. Conclusion

In this project, ZnO particles with different morphology have been successfully synthesized using different precursor by sol-gel and solution-precipitation method. XRD and FESEM characterization shows that ZnO particles has good crystallinity and morphology structure of quasi-sphericals, rods and flakes. WCA of ZnO-NF:PDMS shows the highest WCA $144.15^\circ$ due to rough surface morphology which followed Wenzel theory.

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