Research Article

Improved Adhesion of Nonfluorinated ZnO Nanotriangle Superhydrophobic Layer on Glass Surface by Spray-Coating Method

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In this present work, a superhydrophobic glass surface comprising zinc oxide nanotriangles (ZnO-nt) and nontoxic silylating agent was developed via a cost-effective spray-coating technology. ZnO-nt was synthesized by a hydrothermal method. Poly(dimethylsiloxane) (PDMS) and dimethyldiethoxysilane (DMDEOS) were used as nontoxic (nonfluoro) silylating agents. The morphology and crystallinity of ZnO-nt were studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. ZnO-nt with polymeric silane (PDMS) exhibited maximum wettability as compared to nonpolymeric silane (DMDEOS). The water contact angle (WCA), sliding angle (SA), and surface roughness of ZnO-nt/PDMS-coated glass substrate under UV treatment were $165 \pm 1^\circ$, $3 \pm 1^\circ$, and 791 nm, respectively. The WCA of ZnO-nt/PDMS was higher (165°) than that of commercial ZnO/PDMS (ZnO-C/PDMS). ZnO-nt/PDMS was strongly attached to the glass substrate with good stability and adhesion. The reasons for improved hydrophobicity, adhesion, and mechanism of hierarchical microstructure formation on the glass substrate were explained in detail. PDMS was attached to the glass substrate via hydrogen bonds from solvated zinc acetate.

1. Introduction

In recent years, there is tremendous interest for surfaces that are extremely repellent to water droplets. The minimal contact of water on such surfaces makes them appealing for a variety of applications such as self-cleaning [1], anti-icing [2], anticorrosion [3], water harvesting [4], and antibacterial coating [5]. These surfaces are called as superhydrophobic with a water contact angle (WCA) higher than 150° and a sliding angle (SA) lower than 10° [6]. The following conditions are necessary to fabricate a superhydrophobic surface: (i) creation of hierarchical rough surface [7] and (ii) chemical modification of rough surface with low surface energy materials [8]. The most popular methods to create superhydrophobic surfaces are plasma etching [9], sol-gel [10], electrospinning [11], layer by layer assembly [12], phase

separation [13], and solution immersion [14]. However, the feasibility of these methods for real applications is limited by the following factors: time-consuming, sophisticated instruments, and using of expensive and toxic fluorosilanes. Therefore, the recent research works have been focused on the fabrication of superhydrophobic surfaces using inexpensive raw materials, nontoxic surface modifiers, and convenient spray-coating technique. Moreover, spray coating is a convenient technique for ready-made applications such as construction and building applications.

Table 1 summarizes the results of various superhydrophobic coatings produced by spray-coating technique, nanoparticles (ZnO, SiO₂, TiO₂, and colloidal zinc hydroxide) [15–21], and nonfluorinated silylating agents. Among the various metal oxide nanoparticles, ZnO is widely used to fabricate a rough surface [22–24]. The synthesis of ZnO

TABLE 1: A summary of various nanoparticles used for superhydrophobic glass coating.

Nanoparticle (shape, diameter)	Binder	Hydrophobic agent	Method	WCA (°)	SA (°)	Adhesion	Stability	Ref
SiO ₂ (nanosphere, 16–20 nm)	N/A	TEOS, PDMS	Spray coating, and calcined at 300°C	153	2	N/A	N/A	[16]
TiO ₂ (nanosphere, 30 nm)	N/A	TEOS	Spray coating	155	3	N/A	N/A	[17]
ZnO (Hexagonal, 100–150 nm)	N/A	PDMS	Spray coating	155	<5	N/A	N/A	[31]
ZnO (hexagonal, 50–200 nm)	N/A	Stearic acid	CVD ZnO, calcined at 120°C	162	<2	N/A	N/A	[34]
ZnO (hexagonal, 100–150 nm)	N/A	Stearic acid	Spray coating	152	<5	N/A	N/A	[19]
SiO ₂ (nanosphere, 10 nm)	Ethyl alpha-cyanoacrylate	HMDS	Spray coating	157	N/A	Abrasion test, WCA decreased to 150°	N/A	[47]
ZnO (NA)	Epoxy resin	PMMA	Spray coating	158	<5	N/A	WCA is decreased to 155° after 90 days at ambient condition	[48]
Colloidal Zinc hydroxide (rod, 250–500 nm)	Matrix of TEOS and methyltriethoxysilane (MTEOS)	Stearic acid	Spray coating and heat treatment at 400°C	165	<5	Tape peeling test, the contact angle decreased to 159°	N/A	[20]
SiO ₂ (nanosphere, 5–30 nm)	Epoxy resin	PDMS	Spray coating	156	N/A	Tape peeling test, no changes in contact angle	N/A	[15]

in various dimensions (0D, 1D, 2D, and 3D) via precipitation, sol-gel, hydrothermal, solvothermal, and microwave irradiation methods has also triggered considerable interest to investigate the effect of morphology on superhydrophobicity [25–28]. Nevertheless, the superhydrophobicity of ZnO with nanotriangle morphology (ZnO-nt) has not been reported. Furthermore, ZnO is generally regarded as a safe material to human beings and animals [29]. It also has numerous applications in industries, cosmetics, and medical devices [5, 30].

Eco-friendly hydrophobic coatings with high WCA were also attained by non-fluoromaterials with low surface energy such as stearic acid, dimethyldiethoxysilane (DMDEOS), methyltriethoxysilane (MTEOS), hexamethyldisilazane (HMDS), poly(methyl methacrylate) (PMMA), and poly(dimethylsiloxane) (PDMS). Among these surface modifiers, polymeric silylating agents (such as PDMS) have extra advantages such as chemical stability, mechanical elasticity, long endurance, and attractive transparency for outdoor applications [20, 31, 32]. Furthermore, PDMS has the capability to reduce the surface free energy of the coating within a short period [31].

Several groups have developed superhydrophobic coatings using ZnO and PDMS but only few of them tried to solve the poor adhesion of these materials on the glass surface [31, 33]. The main reason for the poor adhesion and mechanical strength is the lack of necessary hydrogen-bonding interactions between the glass surface and the hydrophobic mixture (silylating agent/ZnO). Few reports are available on the use of complex techniques, binder, epoxy, or additional heat treatment to form a strong bond between the coating and the substrate. For example, Li et al. reported the superhydrophobicity of ZnO with stearic acid. The surface was fabricated by spray coating followed by chemical vapour deposition technique. The coating fabricated via this method possessed an excellent superhydrophobicity, nevertheless the process involved multiple steps. Besides, the stability and adhesion of the coating were not reported [34]. Chakradhar et al. [31] studied the superhydrophobicity of ZnO-PDMS through a facile spray-coating method. The usage of primes (epoxy) as a binder was a prerequisite to improve the adhesion of the coating. Das et al. [8] examined the fabrication of robust superhydrophobic surface on glass using ZnO at high temperature curing (400°C). Simovich et al. [35] fabricated a robust superhydrophobic surface by the combination of epoxy resin, hexamethylenediamine, and silica nanoparticles. Nevertheless, the hydrophobic solution was maintained at a temperature in the range of 70–80°C, the substrate was heated to 150°C prior to spraying process, and then it was cured at 130°C for 24 h. All these techniques with high temperature curing and multiple steps are not favorable for industrial applications.

Therefore, in this present work, the superhydrophobicity of ZnO-nt with nonfluorinated silanes such as hydroxy-terminated PDMS (long-chain polymeric silylating agent) and DMDEOS (short-chain nonpolymeric silylating agent) was studied by spray-coating technique. The existence of solvated Zn acetate as a minor impurity could promote the bonding interactions between the glass substrate and

FIGURE 1: XRD patterns of (a) ZnO-C and (b) ZnO-nt.

hydrophobic mixture The superhydrophobicity of commercial ZnO (ZnO-C) was also studied for reference.

2. Experimental

2.1. Materials. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.8%), dimethyldiethoxysilane (DMDEOS, 98%), hydroxy-terminated poly(dimethylsiloxane) (PDMS), commercial zinc oxide (ZnO-C, 99.0%), acetic acid (98%), and sulphuric acid (97%) were purchased from Sigma-Aldrich. Ethanol (99%), isopropanol (98%), and n-hexane (98%) were purchased from Merck Millipore. All the chemicals used were of AR grade and used as received without further purification. The plain microscopy glass slides were supplied by Fisher Scientific.

2.2. Synthesis of ZnO Nanotriangle (ZnO-nt). ZnO-nt was synthesized using a hydrothermal method [36]: 0.1 M of zinc acetate dihydrate solution was prepared using ethanol. Then, the pH was adjusted to 3 using acetic acid and the solution was stirred for 3 h at room temperature. The final mixture was transferred into a Teflon-coated stainless steel autoclave and was heated at 120°C for 5 h. The product was centrifuged and washed one time with deionized water. To preserve the content of unreacted zinc acetate, further washing procedures with water or alcohol were not performed. The final product was dried at 100°C for 24 h in an air oven.

2.3. Synthesis of Hydrophobic Mixture

2.3.1. ZnO-nt/DMDEOS. 50 ml of isopropanol, 3.5 ml of 1 M H_2SO_4 , 1 ml of deionized water, and 15 ml of DMDEOS were vigorously stirred for 30 min. This mixture was labelled as sol A. Simultaneously, 7 wt% of ZnO-nt was dispersed in a mixture of isopropanol (50 ml), 1 M H_2SO_4 (3.5 ml), and deionized water (1 ml). This mixture was labelled as sol B. The superhydrophobic solution was prepared by adding sol B into the sol A drop wisely under constant stirring.

FIGURE 2: TEM images of (a) ZnO-nt and (b) ZnO-C.

2.3.2. ZnO-nt/PDMS. 2.52 g of PDMS was dissolved in 50 ml of n-hexane and stirred vigorously for 30 min. 7 wt% of ZnO-nt was dispersed in PDMS solution and further stirred magnetically for 30 min. For comparison, PDMS with ZnO-C was also prepared.

2.4. Fabrication of ZnO-nt/DMDEOS and ZnO-nt/PDMS Coatings. The glass substrate was ultrasonically cleaned in acetone for 10 min followed by rinsing with deionized water for 5 min. Then, the coating mixture was applied on the glass substrate using an airbrush (IWATA) with a 1.5 mm-diameter nozzle. The atomizing air pressure was maintained at 40 psi. The distance between the airbrush and the substrate was kept at 10 cm. The airbrush was moved laterally back and forth to make a uniform coating on the glass substrate. The coated glass substrate was dried at 80°C for 5 min in an oven. This procedure was repeated for 5 times with a time interval of 5 min. The glass substrate was allowed to cure at 80°C for 12 h. Finally, the dried glass substrates were exposed to UV irradiation (254 nm, 36 W germicidal lamp) for 48 h. Based on our preliminary work, UV exposure is beneficial to create a tightly packed structure due to the photooxidation of organic compounds [21].

2.5. Stability Test. Acid-base resistance is one of the important factors that would increase the widespread practical applications of hydrophobic coatings. To evaluate the acid-base resistance, an experiment was conducted by immersing the hydrophobic coated glass substrate in solutions with different pH (4, 7, and 10) for 100 days. The pH values were selected by considering the pH of washing solution (9–11) [37], tap water/deionized water (6–7), and acid rain (4) [38]. WCA was measured after an immersion period of 100 days in the desired pH [39].

FIGURE 3: FTIR spectrum of (a) ZnO-nt, (b) DMDEOS, (c) PDMS, and (d) ZnO-nt/PDMS.

2.6. Adhesion Test. Peel-off tape test was used to determine the adherence of hydrophobic coating. As reported, at the expense of adherence functionalization and micro-/nanosurface roughness, the primary function of ZnO-nt is to deliver the hydrophobicity through its functionalization with PDMS [31]. The peel-off adhesion test was carried out using a cellophane tape. The tape was laid across the coated surface and rubbed vigorously to ensure a good contact with the coating, then slowly pulled away from the sample at about 45° to the surface, and this process was repeated for 10 times at the same place using a new tape [40].

FIGURE 4: 2D AFM images of (a) bare glass, (b) DMDEOS, (c) PDMS, (d) ZnO-nt/PDMS, and (e) ZnO-C/PDMS coated-glass. (a^a, b^a, c^a, d^a, and e^a) The FE-SEM images of corresponding samples; (a^b, b^b, c^b, d^b, and e^b) the AFM line profile; the red arrow shows the narrow scan of AFM line profile of ZnO-nt/PDMS.

2.7. Characterization. The functional groups of glass substrates were confirmed by a Fourier-transform infrared spectrometer (FTIR, Tensor27, Bruker, Germany). The crystalline properties were characterized using an X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 0.1542$ nm) operated at 40 kV and 40 mA. The morphology of ZnO-nt was studied with the help of a transmission electron microscopy (TEM, TEM; H-7600, Hitachi) and a field emission scanning electron microscopy (FESEM-EDX, Zeiss, Supra 35VP). The surface topology was characterized using an atomic force microscopy (AFM, NanoNavi, SPA400) operated in contact mode. The root mean square (RMS) of the hydrophobic coating was calculated according to the following equation:

$$\text{RMS} = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{av})^2}{N}}, \quad (1)$$

where Z_{av} is the average height for the entire region, Z_i is the height of individual point i , and N is the number of points measured within the given area. The water contact angle (WCA), surface energy, and sliding angle were measured with a droplet volume of 5 μ L using a goniometer (Rame-Hart Instrument. Co, USA) on one side of the sample (sessile drop method). DROPimage Advanced software was used to analyze the data. Briefly, the glass substrates were placed in a contact angle goniometer, attached to an image analyzer. Each sample was subjected to 10 measurements in 4-angle positions: vertical left, vertical right, horizontal left, and horizontal right.

3. Results and Discussion

3.1. XRD. The crystalline phases of ZnO-C and ZnO-nt are shown in Figure 1. The major diffraction peaks of ZnO-C and ZnO-nt are perfectly matched with the standard JCPDS pattern (36-1451) [36]. For ZnO-nt, some additional peaks are detected at 2θ of 13.21°, 33.11°, and 59.26°. This is ascribed to the existence of unreacted zinc acetate dihydrate (JCPDS no. 01-0089) in low concentration, based on The Rietveld refinement of the compound has confirmed that, ZnO-nt contained 73% of ZnO and 27% of Zinc acetate. This is beneficial to induce hydrogen bonding and promotes the interaction between glass substrate and hydrophobic mixture. The average crystallite sizes were determined using the Debye-Scherrer equation. The average crystallite sizes were found to be 51 nm and 34 nm for ZnO-C and ZnO-nt, respectively.

3.2. TEM. TEM micrographs of ZnO-C and ZnO-nt are shown in Figure 2. Figure 2(a) confirms the formation of ZnO nanotriangles with diameter in the range of 45–60 nm. ZnO-C consists of a mixture of irregular hexagonal and rectangular particles (Figure 2(b)). The average diameter of rectangle/hexagonal particle is in the range of 90–100 nm (Figure 2(b)). TEM results revealed that the nanotriangles are smaller when compared to hexagonal or rectangular particles. The small size of ZnO-nt would display high surface energy, which makes it thermodynamically unstable or

TABLE 2: WCA, SA, and water drop behavior of glass substrate coated with different hydrophobic mixtures.

Substrate	WCA (°)	SA (°)	Water drop behavior
Bare glass	44 $\pm$ 2	—	Wetted
DMDEOS	72 $\pm$ 2	—	Wetted
PDMS	134 $\pm$ 2	12 $\pm$ 1	Pinned
ZnO-nt/PDMS	165 $\pm$ 1	3 $\pm$ 1	Roll off
ZnO-C/PDMS	153 $\pm$ 2	5 $\pm$ 1	Pinned

metastable as compared to ZnO-C [41]. Consequently, ZnO-nt is highly beneficial to fabricate a hierarchical structure with low surface energy and improved hydrophobicity.

3.3. FT-IR. FT-IR spectra of ZnO-nt, DMDEOS, PDMS, and ZnO-nt/PDMS are shown in Figure 3. For ZnO-nt (Figure 3(a)), the peak observed at 3392 cm^{-1} is attributed to O-H stretching vibration of adsorbed water on the ZnO surface [31]. A strong peak noticed at ~ 500 cm^{-1} is ascribed to Zn-O stretching vibration [42]. The additional absorption bands identified at 2973 cm^{-1} and 2848 cm^{-1} are attributed to CH₃ and C-H band, respectively, which might be resulting from the acetate precursor [43]. The existence of bands near 1578 cm^{-1} and 1422 cm^{-1} is associated with the C=O stretching vibration of the acetate group [8], indicating the presence of acetate, which is deduced to be the possible functional group to anchor with silanol group of glass substrate.

For DMDEOS (Figure 3(b)), the band observed at 3389 cm^{-1} is ascribed to the OH group, indicating that the silane group of DMDEOS is hydrolyzed by acid [44]. Two peaks centered at 2973 cm^{-1} and 1257 cm^{-1} are attributed to CH₃ stretching and bending vibrations from DMDEOS. The bands located at 1077 cm^{-1} , 838 cm^{-1} , and 790 cm^{-1} are assigned to the Si-O-Si, Si-C, and Si-O vibrations, respectively [16].

For PDMS (Figure 3(c)) and ZnO-nt/PDMS (Figure 3(d)), the peaks are almost similar. An additional peak observed at 3374 cm^{-1} for ZnO-nt/PDMS is associated to the OH group at the ZnO surface [31]. Two strong peaks observed at 2970 cm^{-1} and 2881 cm^{-1} are ascribed to anti-symmetric and symmetric $-\text{CH}_3$ stretching, confirming the presence of Si-(CH₃)₃ and Si-O-CH₃ groups [23]. A series of absorption peaks in the range of 600 cm^{-1} –2000 cm^{-1} are ascribed to the vibrations of various silane groups (Si-O in Si-O-Si backbone and Si-CH₃) on the ZnO-nt/PDMS surface [16]. A weak peak located at 946 cm^{-1} is attributed to Zn-O-Si, confirming the reaction between zinc acetate and the residual silanol (Si-OH) group (at 804 cm^{-1} in Figure 3(c)) [8]. The hydrophobic properties of a coating are greatly influenced by the existence of methyl groups [38, 45]. FTIR analysis affirms the presence of more methyl groups in ZnO-nt/PDMS as compared to ZnO-nt/DMDEOS. Thus, it can be inferred that PDMS is a more prominent silylating agent to attain maximum hydrophobicity.

3.4. Surface Roughness and Wettability. 2D topographic mapping, FE-SEM and AFM line profile images of bare glass, DMDEOS, PDMS, ZnO-nt/PDMS, and ZnO-C/PDMS-

FIGURE 5: WCA (a) and SA (b) of ZnO-nt/PDMS-coated and UV-cured glass substrates at various pH after 90 days. Error bars are the standard deviation of the contact angles from five repeating tests.

FIGURE 6: FESEM image and photograph (appearance of 10 μL water droplet on the glass surface) of ZnO-nt/PDMS-coated and UV-cured glass substrate (a) before and (b) after 10 peel-off tape tests.

coated glass substrates are shown in Figure 4. WCA, SA, and water drop behavior are tabulated in Table 2. Bare glass has a uniform and smooth surface (Figure 4(a)) with a R_a /RMS value of about 310 nm (Figure 4(a)) and WCA of $44 \pm 2^\circ$, indicating the hydrophilic nature. After coating with DMDEOS, the R_a /RMS roughness is increased to 410 nm (Figure 4(b)) with a WCA of $72 \pm 2^\circ$. FE-SEM (Figure 4(b)) and AFM line profile (Figure 4(b)) images reveal that the surface roughness of a glass is increased by the addition of DMDEOS. Similarly, when coated with PDMS, the WCA is increased to $134 \pm 2^\circ$ with a R_a /RMS roughness of 589 nm (Figure 4(c)). The results are in good agreement with the FE-SEM image (Figure 4(c)) and AFM line profile (Figure 4(c)), which reveals a rough surface with cavities. It is also noted that the chemical mixture with low surface energy plays a major role in improving the hydrophobicity. PDMS has low surface energy (7.16 N/m) as compared to DMDEOS (40.44 N/m). Besides, PDMS has a long chain of $(\text{Si}-(\text{CH}_3)_2-\text{O}-)$ group and sterically closed structure. Thus, it minimizes the Van der Waals contact and enhances the hydrophobic behavior. ZnO-nt/PDMS-coated glass substrate exhibits a maximum WCA of $165 \pm 1^\circ$ with a surface roughness of 791 nm (Figure 4(d)). More protrusions are

FIGURE 7: WCA of ZnO-nt/PDMS-coated glass substrate during 10 peel-off tape tests. Error bars are the standard deviation of the contact angles from five repeating tests.

3.5. Stability Test. Figure 5 displays the relationship between pH and hydrophobicity (WCA (Figure 5(a)) and SA (Figure 5(b))) of ZnO-nt/PDMS-coated glass substrate. There is no remarkable change in the WCA at pH 7 and 4 [18]. These results confirm that the coating has a strong tolerance to acid rain and tap water and sustain the rolling properties. However, the WCA is slightly decreased at pH 10, and SA is increased from 3° to 6° , indicating the alkaline solution can corrode the superhydrophobic coating. This is mainly ascribed to the dissolution of ZnO at high alkaline pH [39].

3.6. Peel-Off Tape Test. The adherence of the coating was assessed according to Cholewinski et al.'s [15] work (peel-off tape test at 4 tape applications). In this present work, the peel-off tape test was extended up to 10 times to evaluate the adherence of the coating [15]. The appearance of water droplets and FE-SEM images of ZnO-nt/PDMS-coated glass substrate before and after the peel-off tests are shown in Figure 6. The FESEM images showed that there are no major changes in the surface morphology before and after the peel-off tape test. Figure 7 shows the WCA of ZnO-nt/PDMS-coated glass substrate during 10 peel-off tape tests. There is no significant drop in the WCA after 10 (160°) peel-off tape tests, indicating the excellent adherence of the superhydrophobic coating. Nevertheless, we noticed that some nanoparticles were transferred onto the tape surface, suggesting the loss of unbound particles from the glass surface.

Based on the crystal structure and functional group, the excellent adherence of the superhydrophobic coating is explained schematically in Figure 8. An oxygen in the solvated zinc acetate forms a hydrogen bond with the OH group of glass (the area labelled as "A" in reaction (1)), while the oxygen of PDMS forms a hydrogen bond with $-H$ of the solvated zinc group (the area marked as "B" in reaction (1)). Solvated zinc acetate acts as a "bridge" between the glass substrate and PDMS. In the meantime, the $-O$ group from tetrahedral ZnO forms a hydrogen bond with the $-H$ group of PDMS (the area labelled as "C" in reaction (1)). After heat treatment at 80°C and UV exposure, this bridge provides a better adhesion due to the formation of Si-O-Zn linkages (the area marked as "D" in reaction (2)). This is further confirmed by the appearance of a band at 946 cm^{-1} in FTIR results. Upon heat treatment, zinc acetate is decomposed into interstice of the inorganic silica network. This is clearly affirmed by the FTIR results, which shows the presence of Si-O-Zn and Si-O-Si bands, corresponding to a strong bonding interaction between the glass substrate, ZnO, and silylating agent.

4. Conclusion

Superhydrophobic glass substrates with excellent adhesion have been successfully developed using PDMS and ZnO-nt via a facile spray coating and UV-curing techniques. The surface free energy, surface roughness, and morphology are the influencing factors to achieve the maximum superhydrophobicity. The ZnO-nt/PDMS-coated glass substrate exhibited a high surface roughness (791 nm with WCA of $165 \pm 1^\circ$) when

compared to ZnO-C/PDMS (658 nm with WCA of $153 \pm 2^\circ$). The superhydrophobic coating is chemically stable in acid and neutral pH environment. This kind of superhydrophobic coating would have promising applications in self-cleaning cloths, glass, windows of high-rise buildings, optical devices, solar panels, and electronic devices.

Data Availability

The raw/processed data used to support the findings of this study have not been made available because the data is a part of an ongoing study.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

The figure describes about the preparation method and chemical bonding responsible for sample adherence. The first picture shows the facile spray method on glass substrate with ZnO-nt/PDMS mixture. The second picture describes about bonding that occurred between glass substrate and mixture. The final picture shows the water droplet on the coated glass substrate coated with ZnO-nt/PDMS mixture. (*Supplementary Materials*)

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