

Fluorine-Free Multifunctional Hybrid Coatings with Enhanced Hydrophobic, Antibacterial and Antifogging Performance

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Abstract: Transparent coatings that repel water, resist bacterial colonisation and stay clear under condensation are much needed for glass and other surfaces that are touched or exposed often. In this work, a fluorine-free organic-inorganic hybrid coating was prepared on glass from tetraethyl orthosilicate (TEOS), methyltrimethoxysilane (MTMS), 3-glycidoxypyltrimethoxysilane (GPTMS), polydimethylsiloxane (PDMS) and ZnO nanoparticles by a sol-gel-assisted dip-coating route. TEOS formed the main silica network, MTMS and PDMS supplied low-surface-energy methyl groups, GPTMS improved network compatibility and adhesion, and ZnO provided antibacterial action and surface texture. FTIR spectra confirmed the siloxane network, the methyl groups and the Zn-O bond. SEM showed that the surface changed from a compact film carrying ~75 nm grains (S0) to a textured surface built from ~0.9 μm particulates (S3, S4), while the AFM roughness (R_a) rose from about 9 nm to about 28–31 nm. The water contact angle increased from 96° for S0 to ~150° for S3 and dropped slightly to ~142° for S4, where aggregation and cracking became evident. All ZnO-containing coatings produced clear inhibition zones against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus subtilis*; the clear-zone width reached 3.7 mm for S4 (2.0–3.0 mm for S3), whereas the ZnO-free S0 showed none. Coatings S2–S4 remained clear under condensation while uncoated glass fogged heavily. Controlled addition of PDMS and ZnO to a silica hybrid matrix therefore gives a fluorine-free route to coatings that combine water repellency, antibacterial activity and fog resistance.

Keywords: Fluorine-free hybrid coating; TEOS-MTMS-GPTMS; PDMS; ZnO nanoparticles; surface wettability; hierarchical morphology; antibacterial coating; antifogging coating; sol-gel dip coating

I. INTRODUCTION

Multifunctional surface coatings [1] have attracted growing attention because one coating that performs several jobs is more useful than a stack of single-purpose layers. Water repellency [2], self-cleaning [3], optical transparency, mechanical durability and antibacterial activity [4] are all wanted on glass, optical components, medical equipment [5], electronic displays, vehicles and many other surfaces where dirt and microbial growth have to be kept under control. Combining these properties is not easy, because the chemistry and structure that favor one property often work against another. A highly hydrophilic surface, for example, spreads condensed water into a thin film and so suppresses fogging, whereas a hydrophobic surface keeps liquid water and contaminants away. Surface chemistry and morphology therefore have to be tuned together if a workable balance is to be reached.

Organic-inorganic hybrids are a convenient platform for this purpose, since the organic and inorganic parts can be combined in one material. Sol-gel silica [5] is attractive because it forms under mild conditions and gives transparent, chemically stable films that adhere well to glass. Tetraethyl orthosilicate (TEOS) [6] is the most common precursor: its



hydrolysis and condensation produce a three-dimensional Si–O–Si network, and the properties of that network can be adjusted by adding organosilanes that carry organic groups.

Methyltrimethoxysilane (MTMS) [7] is widely used for hydrophobic films. It takes part in hydrolysis and condensation like TEOS but keeps a non-polar methyl group on silicon, which lowers the surface energy [8] and improves water repellency. Too much of it, however, weakens the film and its adhesion to the substrate, so the inorganic and organic contributions have to be balanced.

3-Glycidoxypolytrimethoxysilane (GPTMS) [9] is another useful component. Its methoxysilane end joins the silica network, while the glycidoxypoly chain improves interfacial interaction and adhesion. Using TEOS, MTMS and GPTMS together is therefore a reasonable way to obtain a mechanically stable, hydrophobic hybrid network.

Polydimethylsiloxane (PDMS) [10] is a fluorine-free silicone with low surface energy, good chemical stability and flexibility. Adding it to a sol–gel silica matrix lowers the surface energy further without perfluorinated compounds, and this is the main reason it is attractive for fluorine-free hydrophobic coatings. Unlike fluorinated silanes, PDMS gets its water repellency from the methyl groups on its siloxane backbone, and in a hybrid it can be combined with the mechanical and chemical stability of the silica network.

Antibacterial function is equally important for surfaces in healthcare, food packaging, water treatment, protective equipment and frequently touched devices. ZnO nanoparticles [11] are a popular additive here because they are antimicrobial, chemically stable, inexpensive and compatible with inorganic matrices. A controlled amount of ZnO in a silica coating can add antibacterial activity and, at the same time, surface roughness. Too much, however, leads to aggregation and light scattering, which reduces transparency and coating uniformity.

Wetting is also governed by surface morphology. According to the classical Wenzel and Cassie–Baxter models, low surface energy combined with suitable micro/nanoscale roughness can raise the contact angle considerably. A hybrid that contains a silica network, methyl and PDMS groups and a controlled amount of ZnO is therefore a sensible candidate for a multifunctional surface.

In the present work, a fluorine-free TEOS–MTMS–GPTMS–PDMS/ZnO hybrid coating was deposited on glass by sol–gel-assisted dip coating. Water repellency comes from PDMS and methyl-functionalized siloxane groups rather than from fluorinated compounds. TEOS is the main network former, MTMS provides hydrophobicity, GPTMS improves network integrity and adhesion, and ZnO supplies antibacterial activity and surface texture. Five compositions were prepared, and the effect of PDMS and ZnO content on their structure, morphology, wetting, antibacterial activity and fog resistance was examined.

II. EXPERIMENTAL SECTION

2.1 Materials

Tetraethyl orthosilicate (TEOS), methyltrimethoxysilane (MTMS) and 3-glycidoxypolytrimethoxysilane (GPTMS) served as the silica-forming and surface-modifying precursors. Polydimethylsiloxane (PDMS) was the fluorine-free low-surface-energy component, and ZnO nanoparticles provided antibacterial activity and surface roughness. Absolute ethanol was the solvent, deionised water was used for hydrolysis, and hydrochloric acid (HCl) acted as the catalyst. All the aforementioned materials were acquired from Sigma-Aldrich, India and used as received. Microscope glass slides were the substrates. They were cleaned ultrasonically in acetone, ethanol and deionised water for 10 min in each solvent, dried at 80 °C and stored in a dust-free place until coating.

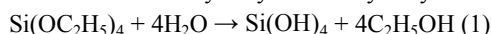
2.2 Overview of the coating procedure

The coatings were prepared by a modified sol–gel process followed by dip coating and thermal curing, in four stages: (i) hydrolysis of TEOS and MTMS; (ii) formation of the hybrid silica network by condensation; (iii) addition of GPTMS, PDMS and ZnO nanoparticles; and (iv) deposition of the hybrid sol on glass by dip coating, followed by thermal curing.

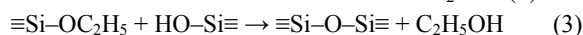
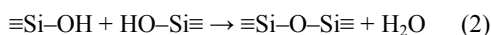


2.3 Preparation of the sol-gel precursor

A calculated amount of TEOS was dissolved in absolute ethanol under continuous magnetic stirring. Deionised water containing a small amount of dilute HCl was then added slowly under vigorous stirring, and the mixture was stirred for about 60 min at room temperature to allow controlled hydrolysis. The hydrolysis of TEOS is represented by



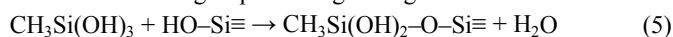
The silanol groups formed then condense, either with each other (water condensation) or with unhydrolysed ethoxy groups (alcohol condensation):



Repeated condensation builds up the three-dimensional silica network. MTMS was next added to the partially hydrolysed TEOS sol, where it hydrolyses according to



and the methylsilanol condenses with silanol groups of the growing network:



The methyl groups stay attached to silicon throughout and are responsible for the hydrophobic character of the coating.

2.4 Incorporation of GPTMS

After partial hydrolysis of TEOS and MTMS, the required amount of GPTMS was added slowly under continuous stirring. Its methoxy groups hydrolyse as follows:



where $\text{R} = -(\text{CH}_2)_3-\text{O}-\text{CH}_2-\text{CH}(\text{O})\text{CH}_2$, the glycidoxypropyl group containing the epoxy ring. The hydrolysed GPTMS then condenses with silanol groups derived from TEOS and MTMS:



This is expected to give an interconnected organic-inorganic network and better adhesion to the glass. Under acidic conditions and during curing, part of the epoxy ring may also open, so the epoxy group should not be assumed to survive intact in the final film.

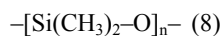
2.5 Incorporation of ZnO nanoparticles

A predetermined amount of ZnO nanoparticles was dispersed separately in ethanol and sonicated for 30–60 min to reduce agglomeration. The dispersion was added slowly to the partially condensed TEOS–MTMS–GPTMS sol under continuous stirring, and stirring was continued until a homogeneous suspension was obtained.

ZnO is not expected to take part directly in the siloxane condensation. It is more likely embedded in, or associated with, the growing hybrid network at the interface, where it adds surface heterogeneity and antibacterial activity. Different ZnO contents were used to find the best nanoparticle loading (Table 1).

2.6 Incorporation of PDMS

PDMS was introduced as the fluorine-free hydrophobic component. The required amount, dissolved in xylene, was added gradually to the TEOS–MTMS–GPTMS/ZnO sol under continuous stirring. PDMS is built from repeating dimethylsiloxane units:



The methyl groups on silicon give PDMS its low surface energy. During drying and curing the PDMS is expected to become incorporated in, or associated with, the hybrid network. In the resulting composite, the silica network provides structural integrity, MTMS and PDMS provide hydrophobicity, GPTMS improves adhesion and network compatibility, and ZnO contributes antibacterial activity and nanoscale texture. The sol was stirred for a further 30 min and allowed to equilibrate before deposition.



2.7 Dip coating and curing

The cleaned substrates were immersed vertically in the coating sol and, after a short residence 5 min, withdrawn at a constant rate of 2 mm per second. The withdrawal speed was kept constant because it controls film thickness and uniformity. The coated slides were dried at room temperature for 15–30 min, and three layer coatings were made by repeating the dipping after partial drying of the previous layer. Curing was carried out at 80 °C for 1 h followed by 150⁰ for 2 h. The coatings were named according to their PDMS and ZnO contents (Table 1).

Table 1. Designation and composition of the coatings. TEOS, MTMS and GPTMS are given in mol %; PDMS and ZnO in wt % relative to the coating solids.

Sample	TEOS (mol %)	MTMS (mol %)	GPTMS (mol %)	PDMS (wt %)	ZnO (wt %)
S0	80	10	10	0	0
S1	70	20	10	3	0.5
S2	70	20	10	6	0.5
S3	70	20	10	6	0.75
S4	70	20	10	8	1.0

Note that S0 also differs from S1–S4 in its TEOS:MTMS ratio (80:10 versus 70:20), so the change between S0 and S1 reflects the matrix composition as well as the additives.

2.8 Characterisation

FTIR spectra were recorded from 4000 to 400 cm⁻¹ using (Bruker Tensor 27) using the attenuated total reflectance(ATR). Surface morphology was examined by SEM at 10 kV (S-3000M, Hitachi, Tokyo, Japan) and by AFM in tapping mode (AFM) (MULTIMODE 5, Bruker Corporation, Billerica, MA, USA) over a 0.5 × 0.5 μm² area. Particle and domain sizes were obtained from the SEM micrographs by image analysis: each micrograph was calibrated with its own scale bar, features were segmented by thresholding, and the equivalent circular diameter of each feature was calculated. The AFM roughness parameters R_a (arithmetic mean roughness), R_q (root-mean-square roughness) and R_{max} (maximum peak-to-valley height) were calculated over the whole scan area. Water static contact angle (SCA) measurements were conducted at room temperature via the sessile drop method using a drop shape analysis system (DSA 100, Krüss GmbH, Hamburg, Germany). For each measurement, a 5.0 μL water droplet was dispensed at a rate of 600 μL/min using a 500 μL syringe equipped with a needle (0.5 mm diameter, 38 mm length).

2.9 Antibacterial assay

Antibacterial activity was evaluated by the agar diffusion (zone-of-inhibition) method [12] against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus subtilis*. Square coated coupons of about 10 × 10 mm² were placed on agar plates spread with the test organism. The clear-zone width was defined as the distance from the coupon edge to the edge of the zone, and the zone area as the cleared area around the coupon excluding the coupon itself. Both were obtained from photographs of the plates, calibrated using the coupon dimensions and checked against the plate diameter.

2.10 Antifogging test

Antifogging behaviour was assessed by visual observation. Coated and uncoated slides were exposed to identical condensation conditions in warm-water vapour chamber for 60 second and placed over printed text, and the legibility of the text was recorded photographically.



III. RESULTS AND DISCUSSION

3.1 FTIR analysis

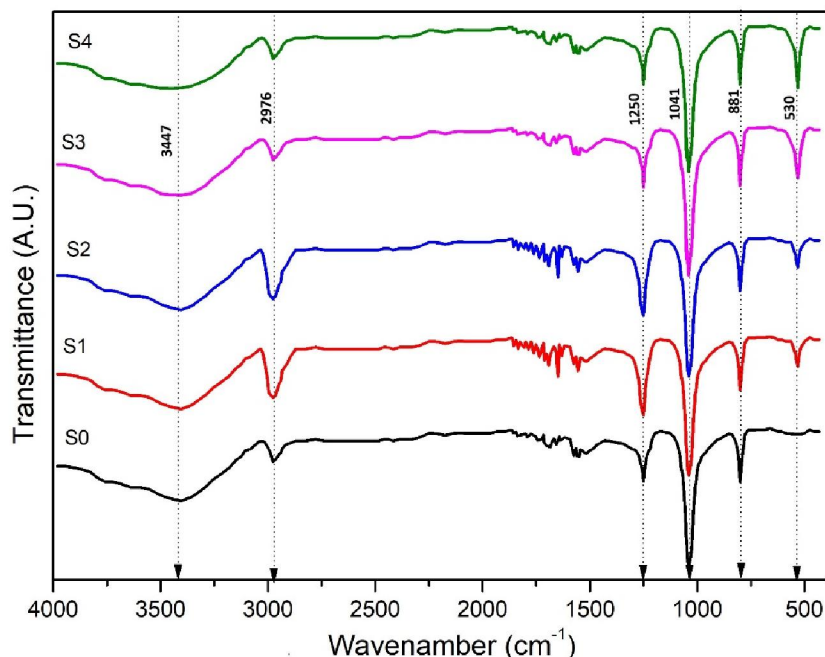


Fig. 1. FTIR spectra of coatings S0–S4.

The FTIR spectra of S0–S4, recorded from 4000 to 400 cm^{-1} , are shown in Fig. 1. They show the vibrations of the silica/siloxane network together with those of the groups introduced through MTMS, GPTMS, PDMS and ZnO.

A broad band centered at 3447 cm^{-1} appears in all samples and is assigned to O–H stretching of residual Si–OH groups and adsorbed moisture [13, 14]. The band at 2976 cm^{-1} comes from C–H stretching of methyl groups [15–17], mainly from MTMS and PDMS. It is weak but present in S0, which contains 10 mol % MTMS, and stronger in the PDMS-modified coatings (most clearly in S1 and S2). The band at 1250 cm^{-1} is assigned to the Si–CH₃ deformation [2, 18] and follows the same pattern, supporting the presence of the methylated siloxane component that lowers the surface energy. Because the spectra are stacked and not normalized, the intensities of these two bands cannot be compared quantitatively, and they do not increase steadily with PDMS content.

The strongest band, at 1041 cm^{-1} , is the asymmetric Si–O–Si stretching vibration [19, 20] and confirms that a condensed siloxane network has formed. It remains strong in every sample, so adding PDMS and ZnO does not disturb the basic sol–gel network. The sharp band that the spectra show at about 800 cm^{-1} (labelled 881 cm^{-1} in the original figure, but located near 800 cm^{-1} on the wavenumber axis) is characteristic of Si–O–Si symmetric stretching and Si–C (Si–CH₃) rocking of the methylated siloxane [21, 22]. Finally, a band at 530 cm^{-1} is present in the ZnO-containing coatings (S1–S4) and is assigned to Zn–O stretching [23, 24]; it is absent in S0 and appears stronger in S3 and S4 than in S1 and S2, in line with the higher ZnO content.

The spectra therefore confirm the formation of the TEOS–MTMS–GPTMS–PDMS/ZnO hybrid: bands at 3447, 2976, 1250, 1041, ~800 and 530 cm^{-1} correspond to O–H, C–H, Si–CH₃, Si–O–Si, siloxane/Si–CH₃ and Zn–O vibrations, respectively. No separate band of the epoxy ring (expected near 910 cm^{-1}) can be resolved, which is consistent with ring opening or reaction of the epoxy group during processing.



3.2 SEM analysis

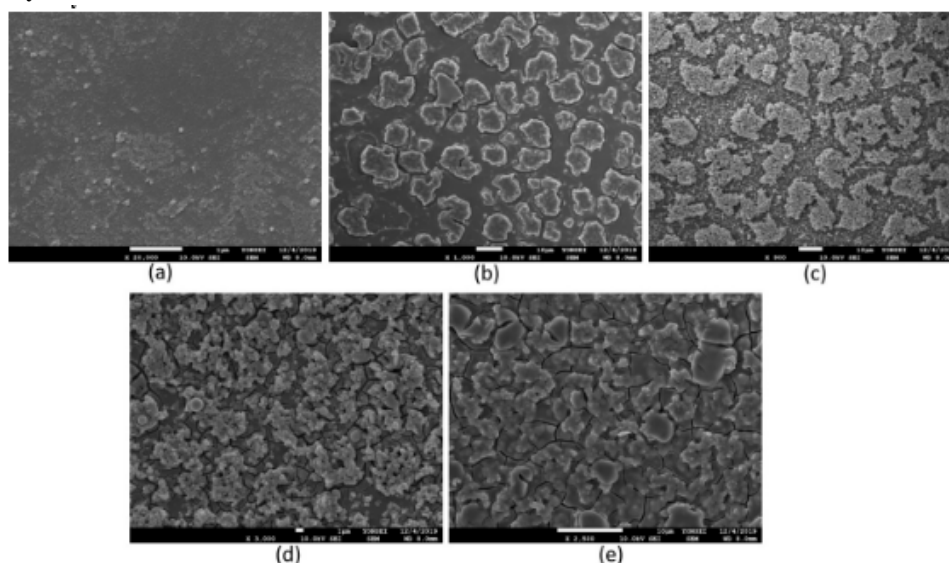


Fig. 2. SEM micrographs of (a) S0 ($\times 20,000$; scale bar 1 μm), (b) S1 ($\times 1,000$; 10 μm), (c) S2 ($\times 900$; 10 μm), (d) S3 ($\times 3,000$; 1 μm) and (e) S4 ($\times 2,500$; 10 μm).

The surface morphology of S0–S4 is shown in Fig. 2, and the particle and domain sizes measured from the micrographs are collected in Table 2. S0 has a compact, fairly homogeneous surface covered with fine granules of about 75 nm (75 ± 32 nm), which indicates a continuous TEOS–MTMS–GPTMS matrix. Adding PDMS and ZnO changes the morphology markedly. S1 carries discrete, irregular aggregates with an average equivalent diameter of about 8 μm (8.1 ± 3.8 μm) on the surrounding film, and S2 is more heterogeneous, with larger particulate clusters (11 ± 7 μm , though fewer clusters could be counted, so this value is less certain).

Table 2. Particle/domain sizes of the coatings estimated from the SEM micrographs (mean $\pm$ SD of the equivalent circular diameter; n = number of features).

Sample	Magnification	Feature analyzed	Size	n
S0	$\times 20,000$	Fine surface granules	75 ± 32 nm	~ 1280
S1	$\times 1,000$	Irregular aggregates	8.1 ± 3.8 μm	40
S2	$\times 900$	Particulate clusters	11.2 ± 6.9 μm	15
S3	$\times 3,000$	Fine particulates/agglomerates	0.85 ± 0.49 μm	~ 810
S4	$\times 2,500$	Fine particulates / large domains	0.94 ± 0.45 μm / 3.6 ± 2.2 μm	~ 840 / 24

The micrographs were taken at different magnifications, so sizes are best compared within the same feature type. Sizes below about 3 pixels are near the resolution limit of the images.

The change is most pronounced for S3, where fine particulates of about 0.85 μm are spread over the whole surface and form a fairly uniform, hierarchical texture. This follows from the combined effect of PDMS modification and ZnO incorporation, which alters the organization of the siloxane matrix and adds nanoscale features. The texture increases roughness, while the methyl-rich PDMS/MTMS component keeps the surface energy low, and both are expected to raise water repellency and self-cleaning ability. A network of fine cracks is also visible in the matrix between the particulates in S3 and, more clearly, in S1.



S4, which contains the most PDMS and ZnO, shows a different picture. Its surface consists of large plate-like domains ($3.6 \pm 2.2 \mu\text{m}$) separated by pronounced cracks, with local particle aggregation on top, although the fine particulates ($0.94 \pm 0.45 \mu\text{m}$) are of similar size to those of S3. Too much modifier evidently makes the coating more heterogeneous and coarser. S3 therefore gives the best balance between surface texture and uniformity among the compositions studied.

The morphology agrees with the FTIR results: the Si–O–Si (1041 cm^{-1}), C–H (2976 cm^{-1}), Si–CH₃ (1250 cm^{-1}) and Zn–O (530 cm^{-1}) bands all support the formation of the modified siloxane/ZnO coating, and S3 shows the most favourable morphology for a hydrophobic multifunctional surface.

3.3 AFM surface topography

The AFM images (Fig. 3) support the SEM observations, and the roughness parameters derived from them are given in Table 3. S0 is comparatively smooth, with a limited height variation ($R_a \approx 8.6 \text{ nm}$), while S1 and S2 show progressively more surface asperities ($R_a \approx 13.4$ and 18.9 nm). S3 has a well-defined three-dimensional texture of closely spaced nanoscale protrusions ($R_a \approx 27.5 \text{ nm}$, $R_q \approx 35.8 \text{ nm}$), in keeping with the granular morphology seen by SEM. S4 has the highest values ($R_a \approx 31.2 \text{ nm}$) and larger, more coalesced features, which agrees with the aggregation seen in its micrograph.

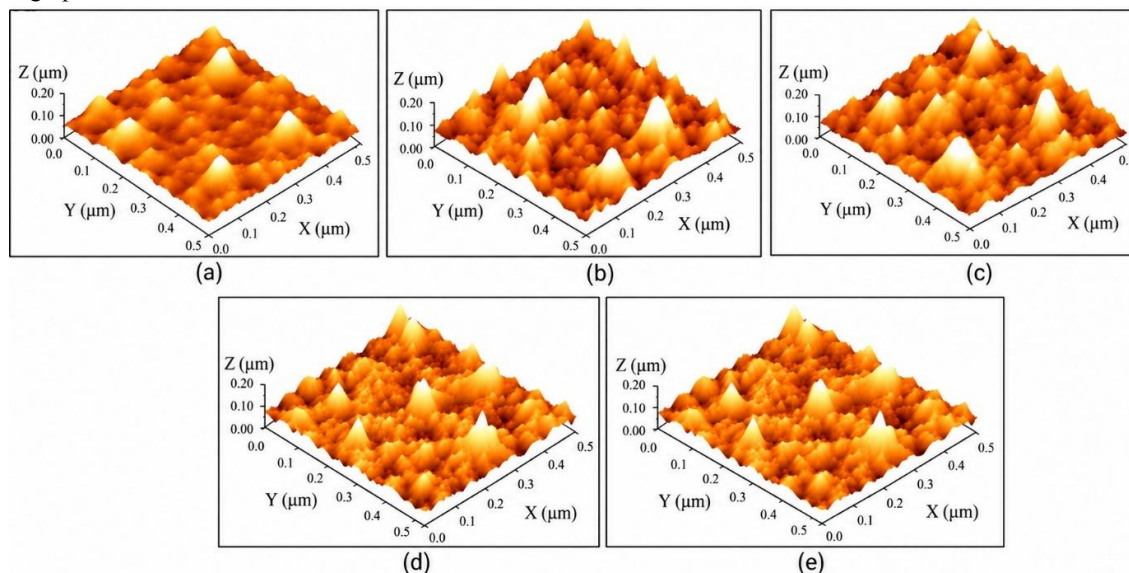


Fig. 3. Three-dimensional AFM topography ($5 \times 5 \mu\text{m}^2$) of (a) S0, (b) S1, (c) S2, (d) S3 and (e) S4.

Table 3. AFM roughness parameters of the coatings (scan area $0.5 \times 0.5 \mu\text{m}^2$).

Sample	R_a (nm)	R_q (nm)	R_{max} (nm)
S0	8.6	11.2	112
S1	13.4	17.5	141
S2	18.9	24.6	163
S3	27.5	35.8	186
S4	31.2	40.5	194



The AFM window (0.5 μm) is much smaller than the features seen by SEM (0.85–11 μm), so the two techniques probe different length scales. SEM shows the micrometre-scale particulates and aggregates, and AFM shows the nanometre-scale texture (asperities tens of nanometres wide and up to about 200 nm high) superimposed on them. Together they justify calling the surface hierarchical, with S3 and S4 the most developed. The roughness values are small in absolute terms, so the transparency of the coatings is not expected to suffer from surface scattering, although this should be confirmed by UV–vis transmittance measurements.

3.4 Contact angle analysis

Static water contact angles are shown in Fig. 4. The angle rises from 96° for S0 to 109° for S1 and 136° for S2, i.e. from a marginally hydrophobic to a strongly hydrophobic surface. This is attributed to the growing contribution of methyl groups from MTMS and PDMS and to the surface texture introduced with ZnO. S3 reaches about 150° , which is close to the superhydrophobic limit. This result is explained by the low-surface-energy PDMS/MTMS components together with the hierarchical texture seen by SEM and AFM. The FTIR bands at 2976 cm^{-1} (C–H) and 1250 cm^{-1} (Si–CH₃) confirm that methyl groups are present in the network.

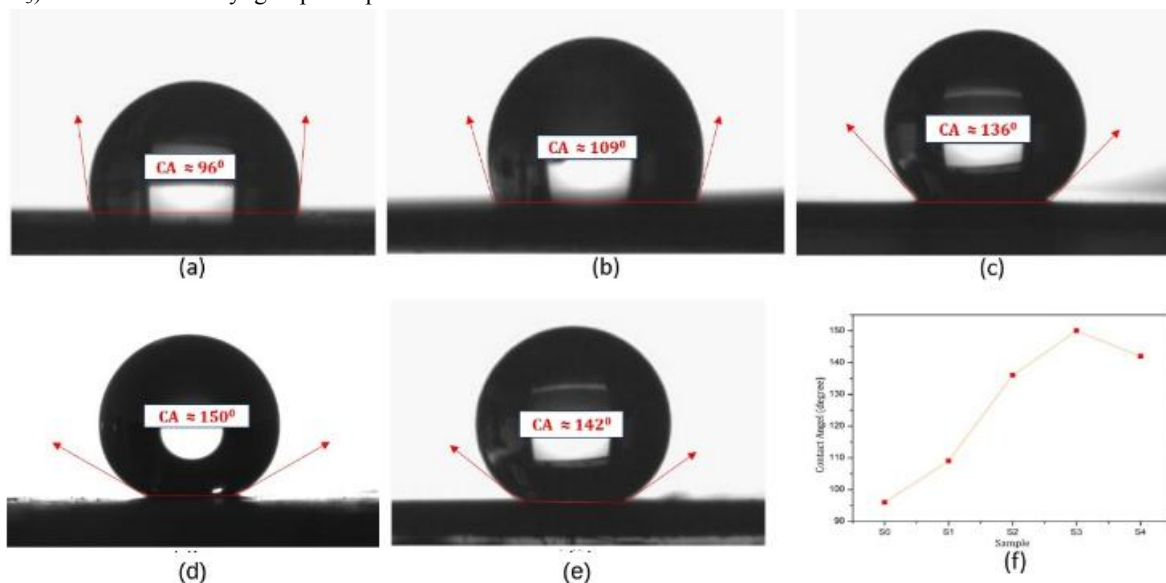


Fig. 4. Water contact angle images of (a) S0, (b) S1, (c) S2, (d) S3 and (e) S4, and (f) the variation of contact angle with sample.

Two classical models help to interpret the roughness effect. In the Wenzel model [25], the apparent contact angle θ_w on a rough surface satisfies

$$\cos \theta_w = r \cos \theta_Y \quad (9)$$

where r is the ratio of true to projected surface area and θ_Y is the intrinsic (Young) angle on the flat surface. In the Cassie–Baxter model [26], in which air is trapped beneath the drop,

$$\cos \theta_{CB} = f_s (\cos \theta_Y + 1) - 1 \quad (10)$$

where f_s is the fraction of the projected area in contact with the liquid. Because θ_Y is greater than 90° for these coatings, roughening in the Wenzel state would only make the surface more hydrophobic by a limited amount. For low-amplitude texture such as that measured by AFM ($R_q \approx 36\text{ nm}$ over a 500 nm scan), r is only about 1.1–1.3, so even with $\theta_Y = 110^\circ$ a Wenzel state would give an apparent angle of roughly 115° , well below the 150° observed. The high angle of S3 is therefore better described by a Cassie–Baxter-type state with entrapped air. Taking θ_Y between 96° (the S0 value) and 110° , Eq. (10) gives $f_s \approx 0.15$ – 0.20 for S3, i.e. only about 15–20 % of the drop base is in contact with the solid. Sliding-angle and contact-angle-hysteresis measurements would be needed to confirm this state.



For S4 the contact angle falls slightly to about 142° even though it has the most PDMS and ZnO. The same calculation gives a larger solid fraction, $f_s \approx 0.24\text{--}0.32$. This fits the SEM and AFM observations: the coarser domains, wide cracks and local aggregation reduce the uniformity of the texture and allow more of the drop to touch the solid. In addition, ZnO carries polar surface hydroxyl groups, and a higher loading exposes more of them, which works against the low-energy methyl groups. More PDMS/ZnO therefore does not give further improvement in water repellency. Overall, S3 ($\sim 150^\circ$) is the best composition of the series for water repellency, providing the most favourable combination of low surface energy and well-developed surface texture. The contact-angle results are consistent with the FTIR, SEM and AFM data, and show that both chemistry and morphology control wetting of these hybrid coatings.

3.5 Antibacterial activity

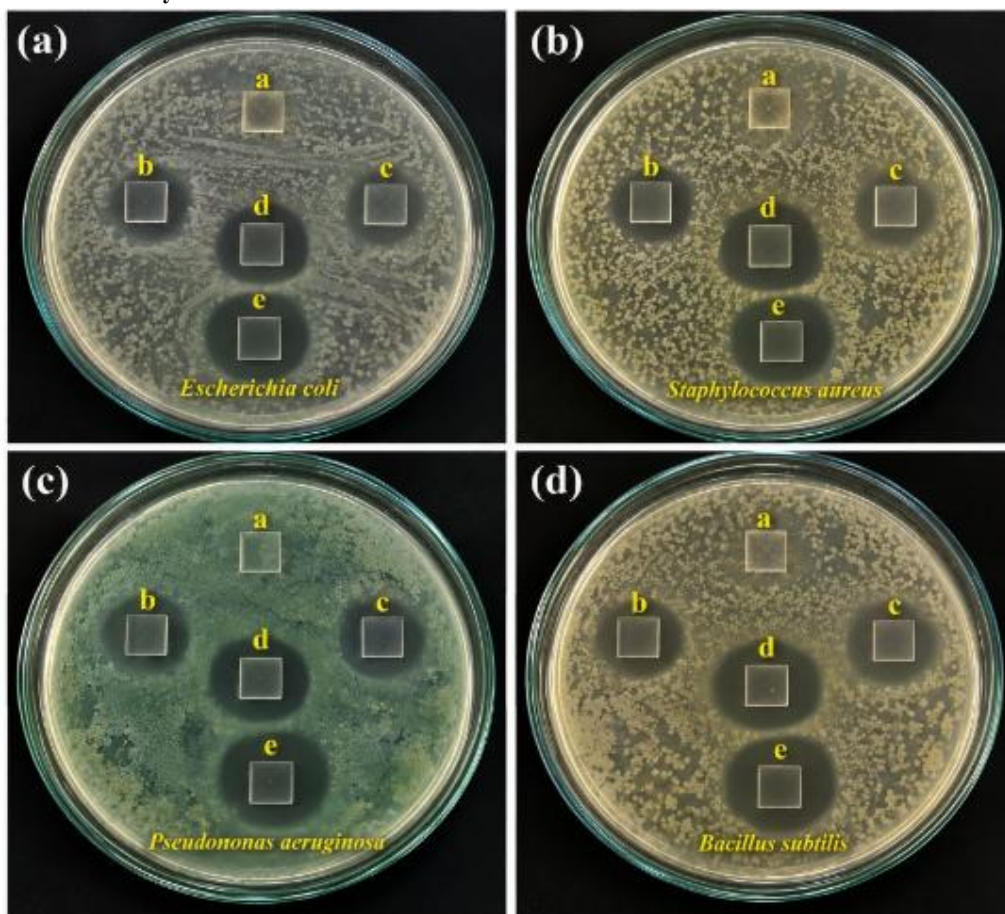


Fig. 5. Zones of inhibition of the coatings against (a) *E. coli*, (b) *S. aureus*, (c) *P. aeruginosa* and (d) *B. subtilis*. On each plate the coupons marked a–e are S0–S4, respectively.

The antibacterial performance against *E. coli*, *S. aureus*, *P. aeruginosa* and *B. subtilis* is shown in Fig. 5, and the measured inhibition-zone widths and areas are listed in Tables 4 and 5. S0, which contains no ZnO, produced no inhibition zone for any of the four organisms, so the TEOS–MTMS–GPTMS matrix itself has no useful antibacterial action.



Table 4. Width of the inhibition zone (mm $\pm$ 0.3, measured from the coupon edge) of the coatings against the four bacteria.

Sample	<i>E. coli</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>B. subtilis</i>
S0	0	0	0	0
S1	0.9	1.2	1.1	1.1
S2	0.7	0.7	1.3	1.1
S3	2.0	2.8	2.6	3.0
S4	2.9	2.9	3.7	3.6

Table 5. Area of the inhibition zone (mm², coupon area excluded) of the coatings against the four bacteria.

Sample	<i>E. coli</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>B. subtilis</i>
S0	0	0	0	0
S1	36	46	43	43
S2	25	28	51	42
S3	81	122	116	135
S4	130	131	174	170

S1 and S2, which both contain 0.5 wt % ZnO, produce narrow but clear zones (0.7–1.3 mm), confirming that ZnO is responsible for the activity. The two coatings give similar results, and the differences between them (S2 is slightly smaller for *E. coli* and *S. aureus* and slightly larger for *P. aeruginosa*) are within the measurement uncertainty, so the PDMS content (3 versus 6 wt %) does not appear to affect the activity at fixed ZnO loading. The zones widen markedly for S3 (0.75 wt % ZnO; 2.0–3.0 mm, 81–135 mm²) and further for S4 (1.0 wt % ZnO; 2.9–3.7 mm, 130–174 mm²). The antibacterial activity therefore increases with ZnO content, and S4 shows the highest overall response. For *S. aureus* the zones of S3 and S4 are nearly equal.

The antibacterial action of ZnO is usually attributed to the generation of reactive oxygen species and the release of Zn²⁺ ions, which damage the cell membrane and disturb cellular processes. Since an inhibition zone forms in the agar around the coupon, some diffusible species (most probably Zn²⁺) must be released from the coating; the assay does not measure contact killing on the surface itself. The differences between the four organisms are modest (at most about 0.8 mm for S4) and do not follow the Gram-positive/Gram-negative division, so the results do not justify a firm conclusion about cell-wall effects. Overall, controlled addition of ZnO to the TEOS–MTMS–GPTMS/PDMS matrix gives the coating clear antibacterial activity against all four organisms, and S3 and S4 are the most effective.

3.6 Antifogging properties

The antifogging behaviour of uncoated and coated glass under identical condensation conditions is shown in Fig. 6. The uncoated glass (a) fogs heavily: condensed droplets scatter light and the text beneath is barely legible. The coated samples are clearly better. S0 (b) reduces the obscuration noticeably, showing that even the silica-based matrix alters how the surface interacts with water, although the text is still hazy. S1 (c) is much clearer but retains a little residual fog at one side, whereas S2 (d), S3 (e) and S4 (f) are essentially free of visible fog and the printed pattern stays sharp.

This behaviour is not the usual hydrophilic film-spreading mechanism, since S2–S4 are strongly hydrophobic (136–150°). A likely explanation is that on these low-energy, textured surfaces condensed water remains as small, nearly spherical drops that coalesce and are shed easily, so that no continuous light-scattering layer builds up; the surface texture seen by SEM and AFM would influence the nucleation and retention of the condensate. This explanation is



tentative. Direct observation of condensation and transmittance measured during fogging would be needed to establish the mechanism and to quantify the transparency of the coatings.

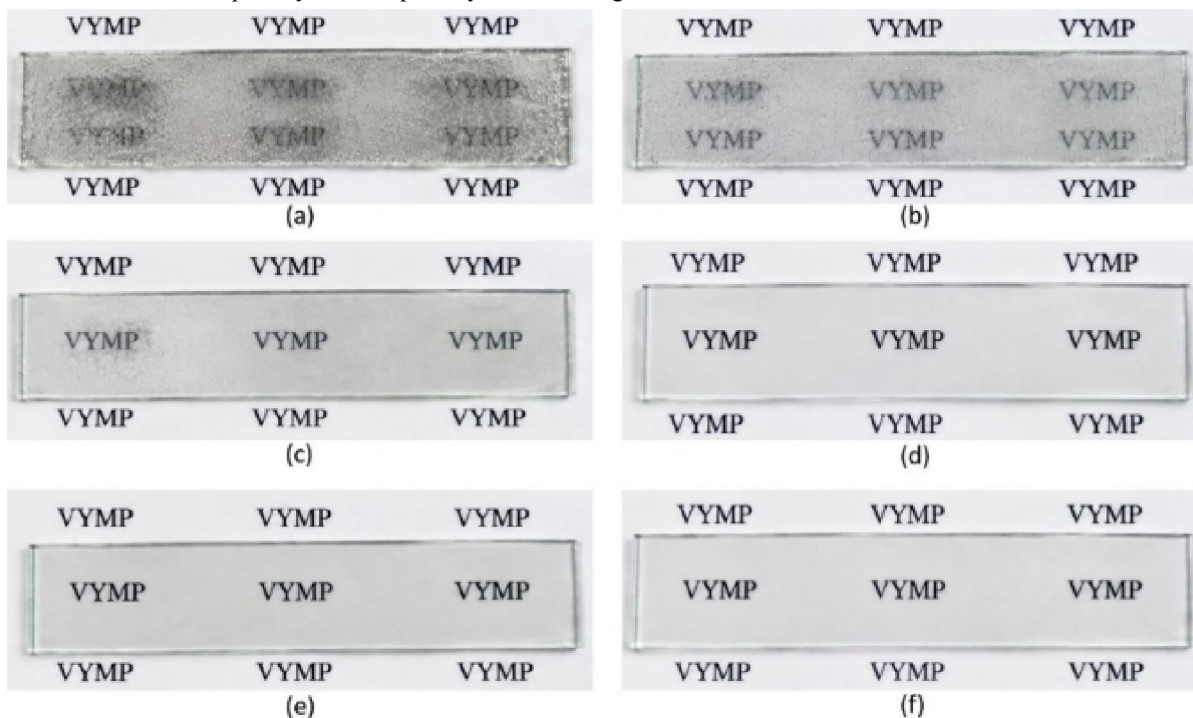


Fig. 6. Antifogging behaviour of (a) uncoated glass, (b) S0, (c) S1, (d) S2, (e) S3 and (f) S4.

The results show that adding PDMS and ZnO to the silica hybrid greatly improves the resistance of the coating to visible fogging while the glass stays optically clear to the eye. This complements the morphological and wetting data and supports the use of these coatings on transparent surfaces.

IV. CONCLUSIONS

A fluorine-free TEOS–MTMS–GPTMS/PDMS–ZnO hybrid coating was prepared on glass by sol–gel-assisted dip coating. FTIR confirmed the siloxane network, methyl groups and Zn–O bonds. SEM and AFM showed a surface that develops from a compact film with ~75 nm grains ($R_a \approx 9$ nm) to a hierarchical texture with ~0.9 μ m particulates and $R_a \approx 28$ –31 nm for S3 and S4, and cracking and coarser domains for S4. The S3 coating had the highest water contact angle (~150°) and the most uniform texture, whereas the contact angle of S4 fell to ~142°. ZnO-containing coatings inhibited *E. coli*, *S. aureus*, *P. aeruginosa* and *B. subtilis*, with clear-zone widths of 2.0–3.0 mm for S3 and 2.9–3.7 mm for S4, while S0 was inactive. Coatings S2–S4 stayed clear under condensation, in contrast to uncoated glass. S3 offers the best overall compromise between water repellency, surface uniformity and antibacterial activity, and controlled incorporation of PDMS and ZnO is an effective fluorine-free route to multifunctional hydrophobic, antibacterial and antifogging glass coatings.

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