

Electronic Supplementary Information:

Spectroscopic characterizations:

XPS experiments were recorded on a K-Alpha Thermo Scientific spectrometer using Al K α (1486.6 eV) radiation (USA) monochromatized by a twin-crystal monochromator. It yielded a focused X-ray spot with a diameter of 400 μ m at 3 mA \times 12 kV, at a pressure greater than 1×10^{-9} Torr (1 Torr = 1.333 \times 10² Pa). The general scan and the Si 2p, C 1s, O 1s, and Cu 2p core-level spectra for the samples were recorded with un-monochromatized Mg K α radiation (photon energy of 1253.6 eV) at 20 eV pass energy and 90° electron take-off angle. The overall resolution for the XPS measurements was 0.1 eV. The spectra background were subtracted using a Shirley fit algorithm and a Powell peak-fitting algorithm within the spectrometer software.

Real test methods:

Surface roughness measurements:

Surface roughness measurements were obtained by using a profilometer (Mitutoyo SurfTest SJ-301) with a stylus device standard. The measuring speed, pin diameter, and pin top angle of the tool were 10 mm/min, 4 μ m, and 90°, respectively. The points of roughness measurement were randomly marked on the surface of the samples. Each point recorded is the mean of three readings.

Also the roughness ratio was calculated from surface free energy by means of contact angles and surface free energy of solids [1].

Field test in sea water:

At the Arsenal Marine Suez Canal, Suez, Egypt, the field test panels were applied (for unfilled PDMS and 0.1% nanofiller PDMS composites) for 6 months in red sea water. Three layer coatings (anticorrosive layer, tie coat layer and then our designed PDMS/0.1Cu₂O nanocomposites) were applied on the steel sheets (30 cm \times 20 cm) after sand blast cleaning to Sa 2½. Suez Canal was chosen for test application of our design patterns, where the larvae of fouling organisms are ready to attach the surfaces at all seasons of the year. The panels were tested at water temperature 23-30°C, pH 8.5-9.1 and salinity 40‰ from April to September, 2014.

Results and discussion

Vinyl-terminated PDMS was prepared via anionic ring opening polymerization of octamethylcyclotetrasiloxane (D₄). The reaction proceeds via three possible routes. The silanolate reactive species can react with other cyclics to propagate the polymer chain, backbite to form different cyclics, or react with other linear analogs. The anion is responsible for the initial attack on the ring, but the counter cation has been shown to have important effects on the rate of polymerization, the degree of polymerization, and the polydispersity of the final product. Developing new, high-performance materials require the synthesis of well-defined, cyclic-free polymers with narrow molecular weight distribution. The mechanism of reaction can be summarized as shown in Scheme S1. The FTIR characterization figures of the prepared vinyl-terminated PDMS are shown in Figure S1. The FTIR of the prepared Cu₂O NPs is indicated in Figure S2.

The curing of vinyl-terminated PDMS follow the hydrosilation curing mechanism, in which vinyl end-blocked polymers react with the SiH groups carried by functional oligomers. The mechanism of platinum hydrosilation was proposed by Chalk and Harrod [2], and the catalytic cycle was also discussed before [3] and proposed here as described in Scheme S2.

The PDMS/Cu₂O nanocomposites were prepared following the same hydrosilation curing mechanism used for vinyl-terminated

PDMS. The FTIR spectra of PDMS and Cu₂O nanocomposites provide evidence for the interaction between the polymer and the NPs, as shown in Figure S3.

The SEM micrographs of the unfilled and filled polymer nanocomposites are shown in Figure S4. The surface properties of Cu₂O nanocubes were analyzed using XPS (Figure S5a and b). The photopeaks located at 530.2 and 932.5 eV are assigned to the characteristic peaks of O 1s (the lattice oxygen of Cu₂O) and Cu 2p (the Cu(I) in Cu₂O), respectively, showing the existence of Cu₂O NPs according to the reported literature on Cu₂O [4,5]. The photopeaks at 932.5 and 952.9 eV that correspond to Cu 2p_{3/2} and Cu 2p_{1/2} are clearly observed. Two Cu 2p_{3/2} peaks at 932.5 eV can be assigned to Cu₂O. To understand the chemical interactions of nanofillers with the PDMS matrix, XPS was performed on a fractured surface of unfilled PDMS and nanocomposite films. The general scan spectra of the unfilled film at room temperature (Figure S5 c, d, and e) show the presence of C 1s, Si 2p, O 1s, and core levels with no evidence of impurities. For the unmodified PDMS, a single peak at 284.1 eV is observed, consistent with C in a methyl environment in the PDMS polymer. This peak undergoes only limited broadening upon oxidation. Again, this result is consistent with previous studies on oxidized PDMS and suggests that the oxidation of the Si sites, as opposed to C, predominates during the oxidation process [6,7]. Herein, upon depositing the Cu₂O nanofillers in PDMS, no evidence of free Cu₂O in the nanocomposites is seen in the XPS spectra, presumably because the more reactive nature of the prepared nanocomposites led to a thick layer over the surface, which was larger than the escape depth Cu₂O photoelectrons, and ensured the complete dispersion of the nanoparticles in the polymer matrix.

The average surface roughness (Ra, μ m) and the surface ratio (r) measurements were illustrated in Table S1. The results show the following:

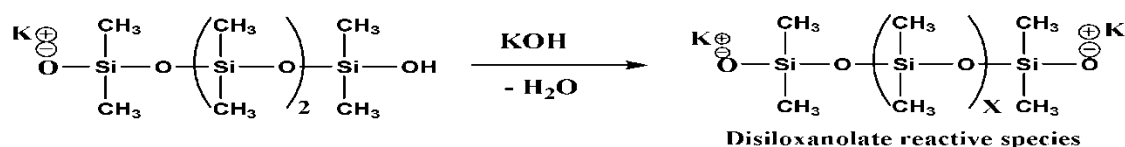
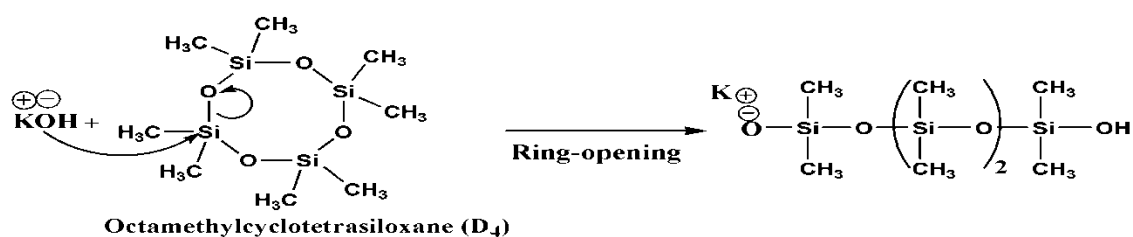
- 1) the higher microroughness for unfilled PDMS than PDMS/Cu₂O nanocomposites,
- 2) the lowest microroughness caused by addition of 0.1% Cu₂O nanofillers

Finding indicates that the addition of Cu₂O nanofillers, particularly with 0.1% loading, into surface pattern leads to low adhesion of microorganisms and facile fouling-release performance. By contrast, the roughness gradually increases with increasing filler loadings of up to 5% due to the NP agglomeration and aggregation. The latter patterns are proven to be non-practically used, as a result of the fouling adhesion which usually led to increased fuel consumption of ships. Furthermore, the (r) results indicated that the surface smoothness increases from the unfilled up to (0.1%), and then decreases with filler loading increased up to 5%.

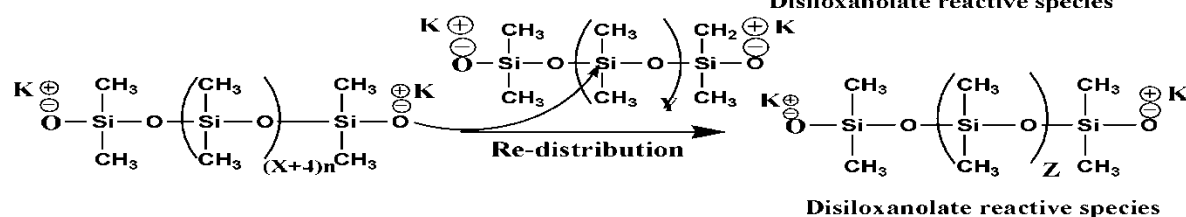
It is important to note that the practical field test (raft testing) was carried out in natural environments, leading to that various micro and microorganisms can attack to settle on the surface and form fouling colonization's. Figure S6 shows the superior fouling resistance of micro and macrofouling organisms and prevention of macrofouling organism's settlements. Therefore, the optimal time-test condition for foul release performance was measured after 180 days.

Schemes:

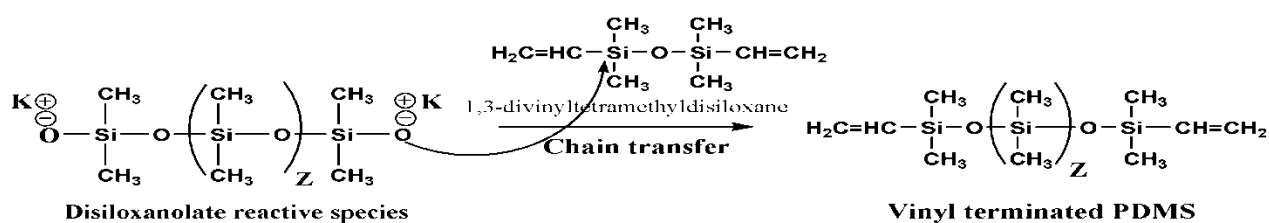
Initiation

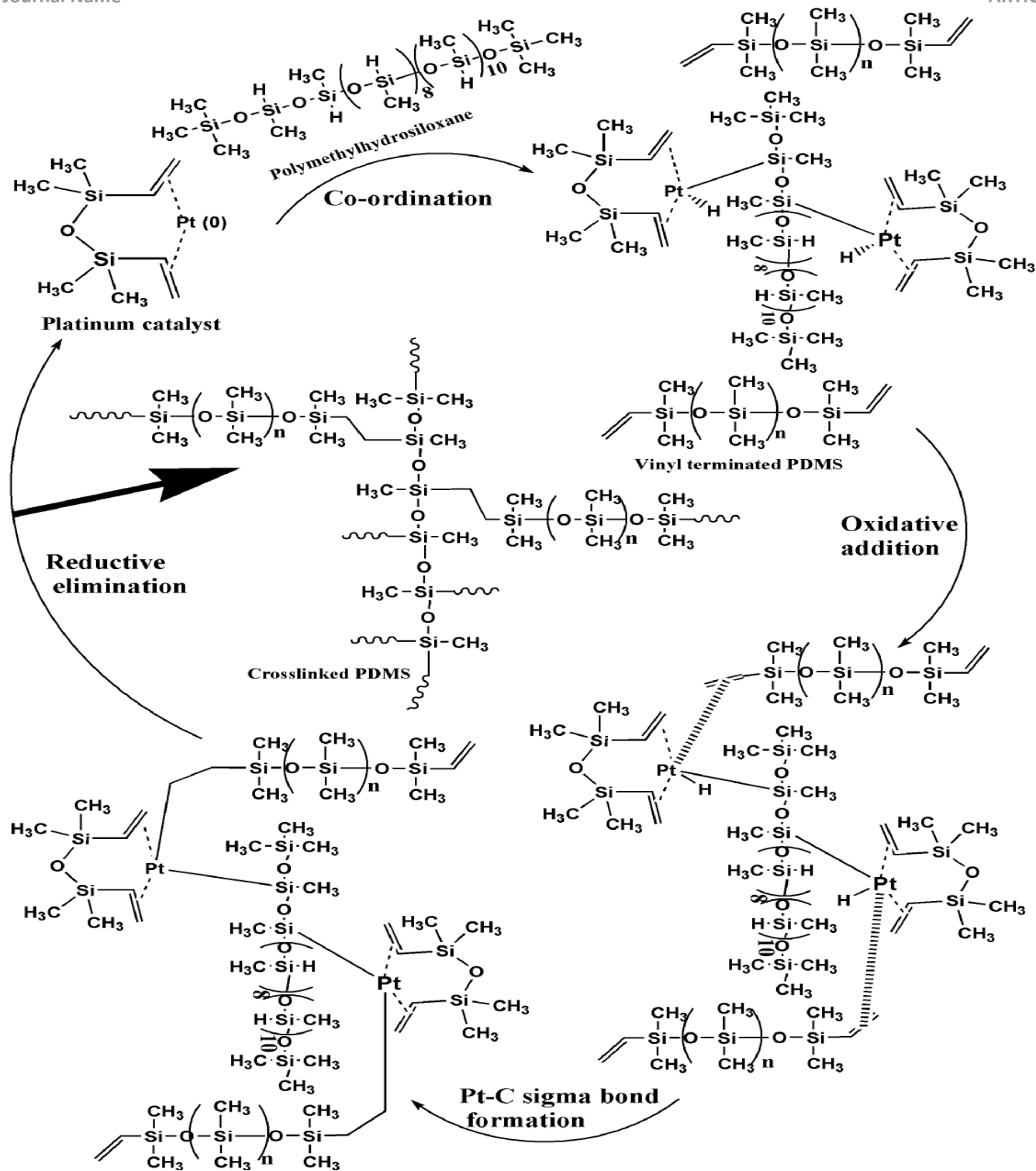


Propagation



Termination

Scheme S1: Mechanism of the anionic ring opening polymerization of D_4 with KOH catalyst.



Scheme S2: Chalk-Harrod mechanism for hydrosilation using Karstedt catalyst.

Figures:

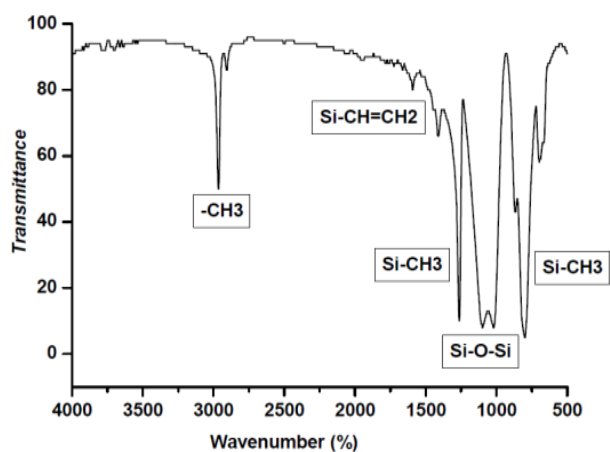


Figure S1: FTIR spectrum of vinyl-terminated PDMS

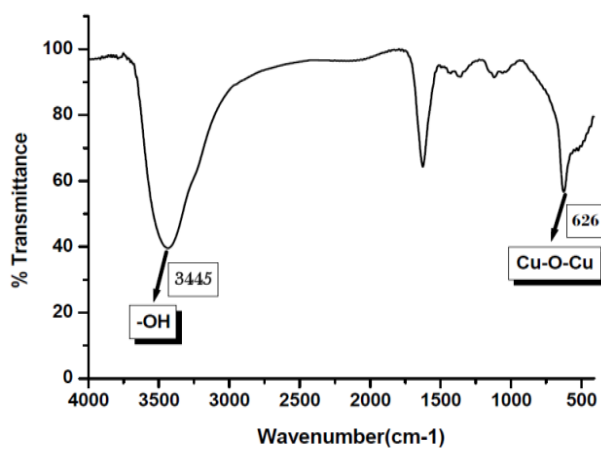


Figure S2: FTIR spectrum of Cu₂O nanoparticles

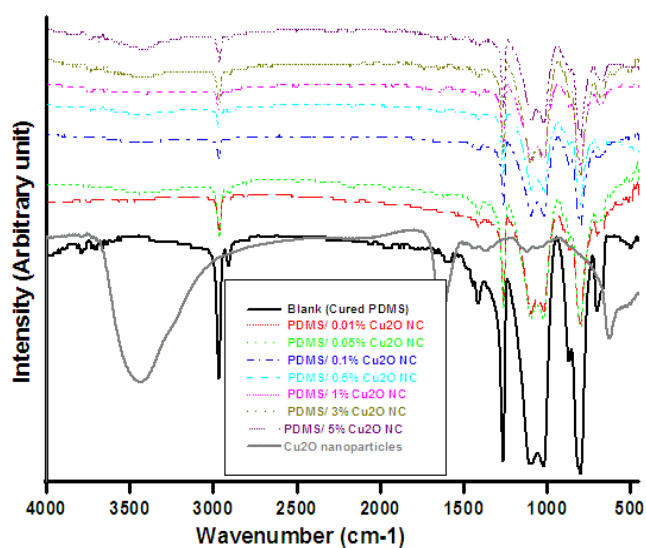


Figure S3: Comparison of the FTIR plots of unfilled PDMS, Cu₂O-filled PDMS nanocomposites, and Cu₂O.

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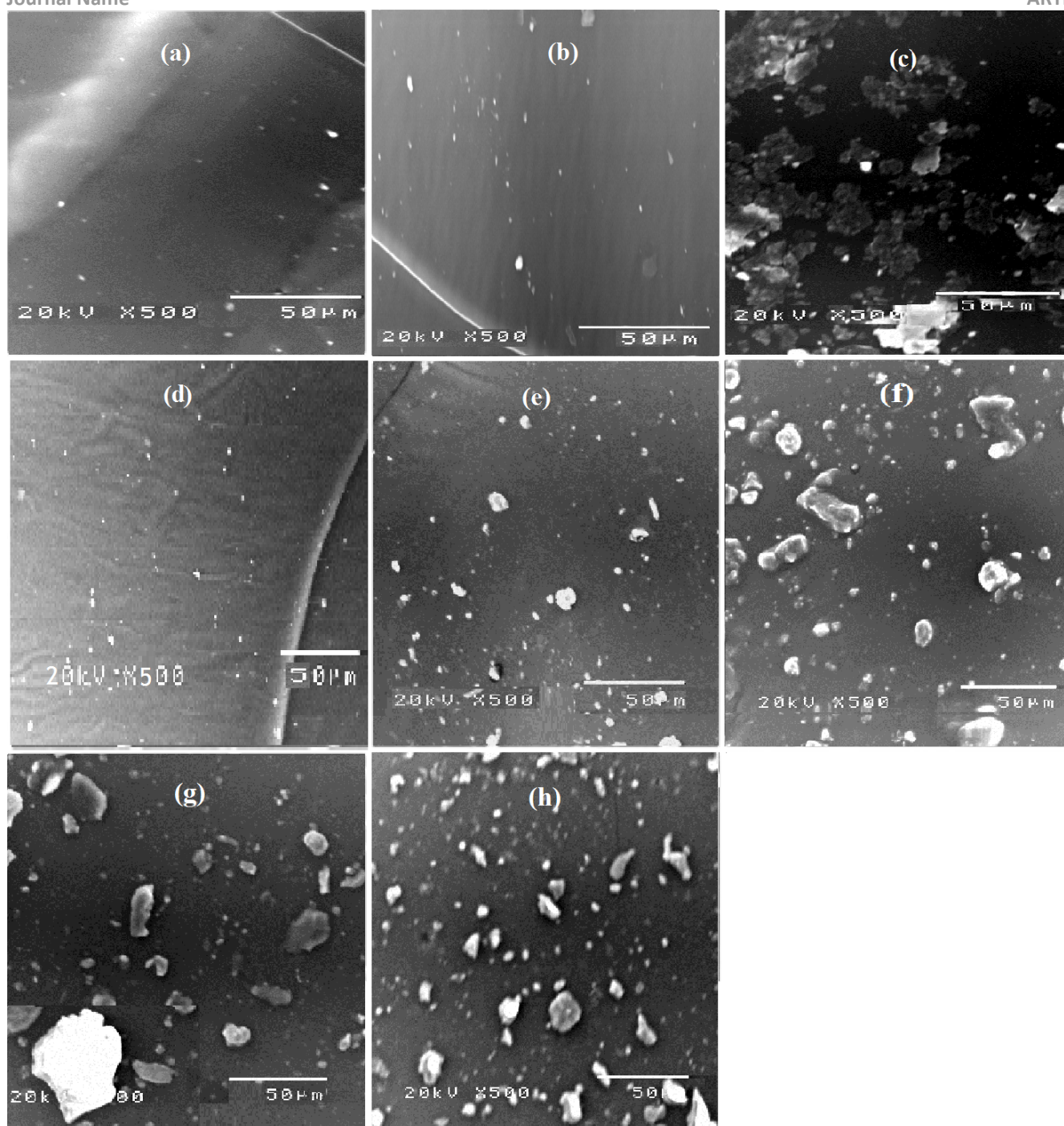


Figure S4: SEM image of (a) unfilled PDMS, (b) 0.01%, (c) 0.05%, (d) 0.1%, (e) 0.5%, (f) 1%, (g) 3%, and (h) 5% PDMS/Cu₂O nanocomposites.

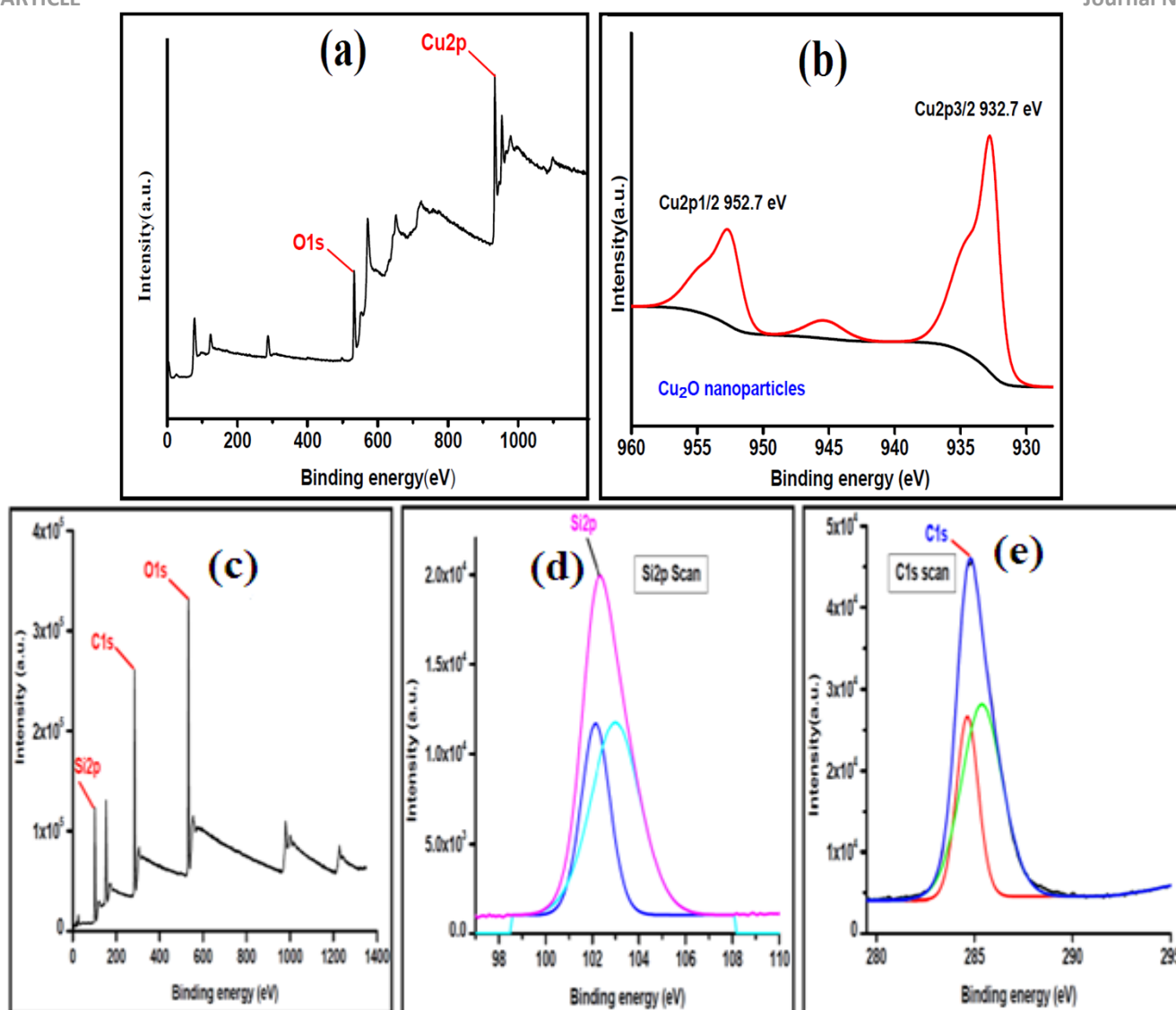


Figure S5: (a) Survey XPS spectra of the Cu₂O nanoparticles, (b) curve fitting of Cu 2p spectra, (c) survey XPS spectra of PDMS, (d) curve fitting of Si 2p spectra, and (e) curve fitting of C 1s spectra.



Figure S6: Field test of PDMS/Cu₂O nanocomposites for 6 months of immersion.

Table S1: Average roughness and roughness ratio measurements

Sample Design	Ra (μm)	r
PDMS blank	0.76	1.0
PDMS/ Cu ₂ O (0.01%)	0.53	0.67
PDMS/ Cu ₂ O (0.05%)	0.31	0.40
PDMS/ Cu ₂ O (0.1%)	0.21	0.067
PDMS/ Cu ₂ O (0.5%)	0.46	0.34
PDMS/ Cu ₂ O (1%)	0.56	0.60
PDMS/ Cu ₂ O (3%)	0.66	0.94
PDMS/ Cu ₂ O (5%)	0.72	1.26

Comparable key factors of foul-release performance

Previously, two commercial FR silicone coatings, namely, Sylgard® 184 (hydrosilation-cured PDMS) and RTV11 (condensation-cured PDMS), were used, and their FR performance were studied¹⁸. These compounds were proven to be effective against certain bacterial growth and attachments^{18,91}. Furthermore, Wynne et al. (2000) evaluated these two types of PDMS coatings according to their surface hydrophobicity and surface free energy¹⁹. These studies found that Sylgard 184 was more hydrophobic and fairly stable in water. On the contrary, RTV11 showed low

hydrophobicity and was not stable in water. By comparing the static contact angle data for control samples, Sylgard®184 silicone has slightly higher contact angles than RTV11 coatings, which were 106° and 100°, respectively^{18,91}. In addition, the surface energy of RTV11 is 23.3 mJ/m², which is slightly higher than that of Sylgard® 184 silicone (≈ 20 mJ/m²). Thus, RTV11 had a higher tendency for biofilm formation than Sylgard® 184. Therefore, Sylgard®184 is more effective than RTV11.

Sylgard 184 was modified with multi-wall carbon nanotubes (MWCNT) (up to 0.2% nanofillers) and with speolite (from 0 to 10%) to enhance the surface energy and FR properties. Upon modifications, the surface free energy decreased to 18 mJ/m², with a slight change in the water contact angle. Filled coatings were more hydrophobic than unfilled coatings.

However, in this work, the fabricated PDMS/Cu₂O nanocomposites (0.1% Cu₂O nanofiller) were found to be more

effective in FR performance compared with RTV11 and modified Sylgard®184. Herein, the contact angle increased up to 130°, and the surface free energy dropped ($\approx 14.1 \text{ mJ/m}^2$), as shown in Table S2. Consequently, the prepared PDMS/Cu₂O (0.1% nanofillers) nanocomposites can be a promising candidate as an environment-friendly solution for FR coatings. The biological results of the prepared nanocomposites showed their resistance to fouling

organisms to a high extent, as shown if Figure 5 A and B. The promising antibacterial attachment results of the designed FR nanocomposites coupled with the simplicity of varying the preparation conditions supported the nanocomposites to be an environment-friendly alternative to the existing antifouling systems.

Table S2: Comparison of the prepared PDMS/Cu₂O nanocomposites and other commercial or sounded FR coatings.

Sample Design	Static contact angle (°)	Surface free energy (mJ m ⁻²)
RTV11 (GE co.)	100°	23.3
Sylgard 184 (Dow corning co.)	102° -106°	20
Sylgard 184/MWCNT-speolite nanocomposites	102±2°	~18
Our developed FR nanocomposites (0.1% Cu ₂ O NPs)	130°	14.096

References:

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