A facile process for fabrication of environmentally safe superhydrophobic surfaces

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Abstract Superhydrophobic coatings have opened new vistas in the field of self-cleaning surfaces by having improved performance, robustness and preservation of cleaning agents including water. Presently, fluoropolymers are extensively explored and used for this purpose. However, the major drawback accompanying fluoropolymers is formation of environmentally persistent and toxic compounds, viz. PFOA (perfluorooctanoic acid) and PFOS (perfluorooctanesulfonic acid) on their degradation raising concern on their use. In the present study, an effort has been made to develop a facile process by using an environmentally safe material. A simple dip coating technique is reported to fabricate superhydrophobic surface. SiO_2 nanoparticles of size 25–30 nm, prepared by sol–gel route, were dip-coated on glass substrate in multilayers followed by coating of a surfactant to achieve homogeneity of SiO_2 layers and enhanced binding with subsequent layer of NUVA-2114 [a commercially used fluorotelomer with chemical composition $C_2F_6(CF_2CF_2)_nX$]. It was observed that SiO_2 nanoparticles and sodium dodecyl sulfate (SDS) surfactant exhibit a synergistic effect on interface stability at optimized SDS concentration. A water contact angle of 152° is achieved. The established method is simple, scalable, environmentally safe and cost-effective.

Keywords Nanosilica, Superhydrophobic coatings, Self-cleaning, Dip coating, Fluoropolymers, NUVA-2114, PFOA, PFOS

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Introduction

Superhydrophobic surfaces with a water contact angle (WCA) higher than 150° have lately fascinated researchers due to their prospective application in various fields such as antireflection,[1] self-cleaning,[2] antisticking,[3] lenses and windows,[4] antifogging,[5] anticorrosion,[6–8] oil–water separation,[9–11] and selective transportation of microdroplets.[12–14] Several methods have been reported to attain superhydrophobic surfaces including plasma method,[15] template method,[16] chemical vapor deposition,[17] sol–gel processing,[18–20] wet chemical reaction,[21–23] lithography, electrospinning,[24,25] and solution immersion. Among these, layer-by-layer (LbL) deposition is a simple, accessible, broadly applicable and reliable method to obtain superhydrophobic surfaces. On the basis of the previous studies, the conventional approach of fabricating superhydrophobic surfaces involves two steps: creation of a hierarchical rough surface to prepare essential small surface topographies (≤ 100 nm) and further treatment of the surface in order to reduce the surface energy.[26–28] The antisticking and anticontamination properties obtained by self-cleaning surfaces are of great significance for applications including antifouling surfaces, automobile parts, stain resistance textiles, dust-free coatings for glasses in buildings and PV solar cells. Superhydrophobicity can be achieved by either roughening the surface or lowering of the surface energy or both. Surface energy and surface roughness are the dominant factors influencing the wettability. By lowering the surface energy, the hydrophobicity of surfaces is enhanced. CF_3 having the lowest surface energy (6.7 mJ/m^2) gives a water contact angle of around 120°.[29] However, to achieve higher hydrophobicity, appropriate surface roughness is desirable. Surfaces with water contact angles of more than 150° were developed by introducing appropriate roughness on materials having low surface energies. Nanostruc-

tured surfaces are preferably prepared by self-assembly, chemical or electrochemical deposition, or sol–gel process followed by further surface modification using low-surface-energy materials. The most important material used in such type of coatings is fluoropolymers. Since the fluoropolymers are generally synthesized from monomers with carbon chain lengths of eight or greater, these materials produce perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic (PFOS) acid on degradation.[30] PFOA and PFOS are proven biopersistent[31] and therefore a major cause of concern. In recent years, efforts are being made to develop alternatives to longer perfluoro chain length alcohols which degrade to perfluorooctanoic acid (PFOA) and perfluorooctanesulphonic (PFOS) acid and higher homologue perfluoro acids. Fluorotelomers (C-6 or lower products) such as NUVA-2114 are short-chain molecules and do not produce PFOA on decomposition. However, they exhibit similar characteristics of larger-chain fluoropolymers. Therefore, these are environmentally acceptable alternatives which could be promising candidates for superhydrophobic coating applications.

Experimental

Materials

The chemicals used in the study are tetraethylorthosilicate (TEOS; Merck 99%), aqueous ammonia (NH$_4$OH), (Merck 25%), hydrochloric acid, (Merck 37%), and ethanol (Merck 99%). NUVA-2114, used in the study, was obtained from M/s. Clariant, New Delhi. Sodium dodecyl sulfate (SDS), HPLC grade, was employed as surfactant.

Preparation of SiO$_2$ NPs by sol–gel route

SiO$_2$ NPs were prepared by the hydrolysis of tetraethylorthosilicate (TEOS). Aqueous ammonia was added to a solution containing 74 ml ethanol and 10 ml of deionized water which was stirred for an hour, and pH was maintained at 8–9 by using NH$_4$OH. 5 ml of TEOS was added to this solution with stirring. The temperature was maintained between 65 and 70°C, and stirring was continued for 3 h for complete hydrolysis and condensation. Formation of silica NPs takes place by condensation of the partially hydrolyzed species.

Deposition of SiO$_2$ NPs on glass substrate

For fabrication of hydrophobic coatings on glass substrate, strips of glass of size 10 mm × 20 mm × 2 mm were used. The glass substrate was cleaned by acetone for 30 min followed by DI water in an ultrasonic cleaner. The glass substrates were etched by immersing in 1:1 aqueous HCl for 1 h, washed with deionized water and dried. Glass substrate was then immersed in the above prepared nanosilica sol for 5 min and withdrawn at the rate of 3 mm s^{-1}. The samples were partially dried in ambient conditions. Second layer of nanosilica was subsequently coated by a similar process followed by drying.

Deposition of SDS and NUVA 2114 layers over SiO$_2$ NPs

A layer of SDS (sodium dodecyl sulfate) was coated over SiO$_2$ NPs layer to improve the adhesion of final layer of NUVA coating. 2% (w/v) solution of SDS in ethanol was used, and the layer was deposited by dip coating in a similar fashion as described above. A layer of NUVA was finally deposited by preparing a solution of NUVA in water (1:1 v/v). The samples were left in the solution for 20 min. The coated samples were then washed with ethanol and dried in ambient conditions followed by heating at 100°C for 30 min with heating rate of 5°C.

Characterization

Silica NPs obtained by centrifugation were characterized by an X-ray diffractometer (Rigaku Mini Flex II) using Cu $K\alpha$ radiation; λ = 0.154 nm, at a scan rate of 8° min^{-1}. The particle size distribution was obtained using dynamic light scattering (DLS) instrument, Model Zetasizer Nano-S90. The morphology of silica NPs was studied using scanning electron microscope (FE-SEM; Hitachi S-4500). The particle size and crystallinity of silica NPs were studied using transmission electron microscopy (TEM; Model Jeol-2010), and the orientation of SiO$_2$ NPs was studied using high-resolution transmission electron microscopy (HR-TEM). Fourier transform infrared spectroscope, (FT-IR; Perkin Elmer PE-1600) was used to study the interaction of subsequent layers of coatings with each other. Water contact angles of the coatings were measured using optical contact angle goniometer (model SL150) with a drop shape analyzer at ambient temperature. Surface roughness of coatings was measured by atomic force microscopy (AFM) (VECCO DICP2) with SPM software.

Results and discussion

Particle size and morphology of SiO$_2$ NPs

The hierarchical structure of a surface contributes significantly to its hydrophobic character. The size of nanoparticles plays an important role in formation of nanohierarchical structure of SiO$_2$ particles. Figure 1c indicates the uniform and spherical nature of SiO$_2$ NPs.
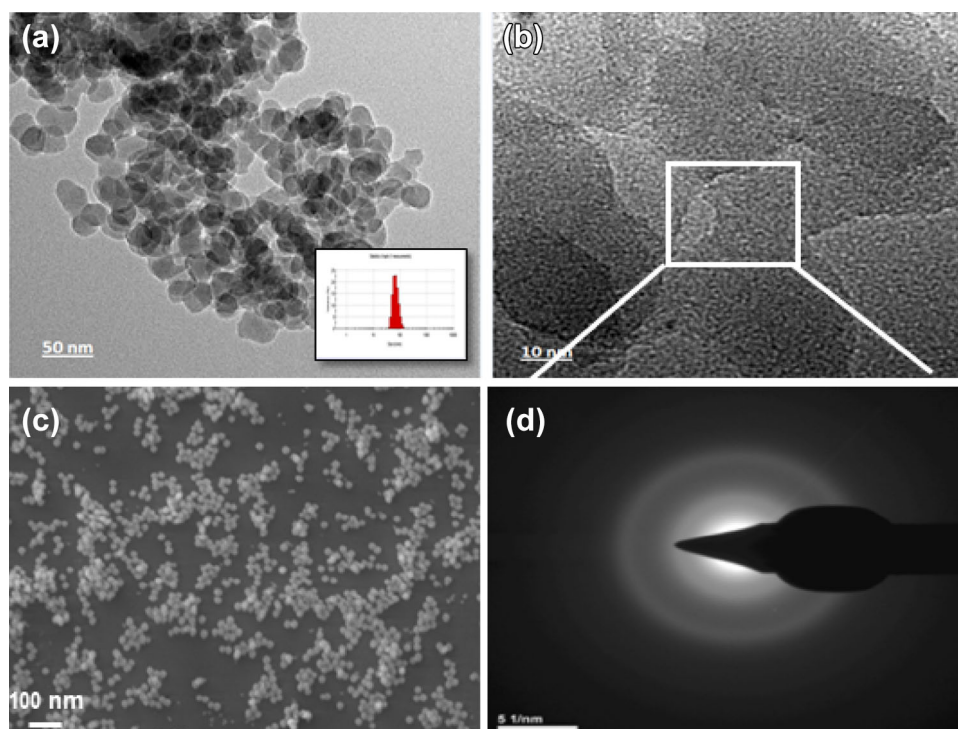
Fig. 1: (a) TEM micrographs of SiO_2 NPs and the inset showing DLS pattern, (b) HR-TEM micrographs of SiO_2 NPs, (c) SEM images of SiO_2 NPs, (d) SAED pattern of SiO_2 NPs

The particles appear as spherical nanostructures with well-defined boundaries. The size of the particles as observed in the SEM image is 25–30 nm. The TEM images of SiO_2 NPs and inset showing particle size distribution, obtained using dynamic light scattering (DLS) technique, can be seen in Fig. 1a. The particle size of 25–30 nm was observed by TEM which is predictably less than the particle size range obtained by DLS (50–53 nm). This can be attributed to the fact that DLS gives hydrodynamic radius which is always higher than the actual particle size.[32] Figure 1b shows the high-resolution transmission electron microscopy (HR-TEM) micrographs of SiO_2 NPs that indicate lack of orientation in SiO_2 NPs (highlighted in micrographs). Selected area electron diffraction (SAED) pattern for SiO_2 NPs can be seen in Fig. 1d which confirms the amorphous nature of SiO_2 NPs. It is inferred that the particle size obtained by SEM is in accordance with the results obtained by DLS and TEM.

SiO_2 NPs deposition on glass substrate

SEM analysis was carried out to study the deposition pattern of SiO_2 NPs layer on glass after single- and double-layer coating. Figures 2a and 2b show SEM images of single-layer coating of SiO_2 NPs on glass substrate at two different magnifications. Double-layer coating of SiO_2 NPs at different magnifications is shown in Figs. 2c and 2d.

In case of single-layer coating, the particles are uniformly distributed. In double-layered coating, a more uniform layer completely covering the substrate is visible. The deposition of SiO_2 NPs is uniform and the particles are closely packed, thereby providing the essential nanoroughness to the coating.

Role of SDS in stabilization of interfaces between various layers

Figure 3 gives a schematic diagram for the interface interaction between various layers which accounts for its stabilization. When the layer of SDS is applied on SiO_2 NPs, the SDS molecules adhere on nanoparticle surface, rendering it amphiphilic and thereby enhancing the stability of the coatings and its adhesion to the subsequent layers. The adsorption of nanoparticles is usually irreversible, and its adsorption energy enhances the stability of interfaces.[33] At specific SDS concentration, a more uniform layer of SiO_2 is adsorbed on the surface. The SDS molecules attach to the layer of SiO_2 NPs through their hydrophilic end. It renders the opposite surface hydrophobic thus amenable for adhesion of the subsequent layer of NUVA 2114. To obtain best results, the concentration of SDS was taken slightly above its critical micelle concentration (CMC). At this concentration, the adsorbed surfactant molecules help in pulling particles together to the air/water interface.[34]
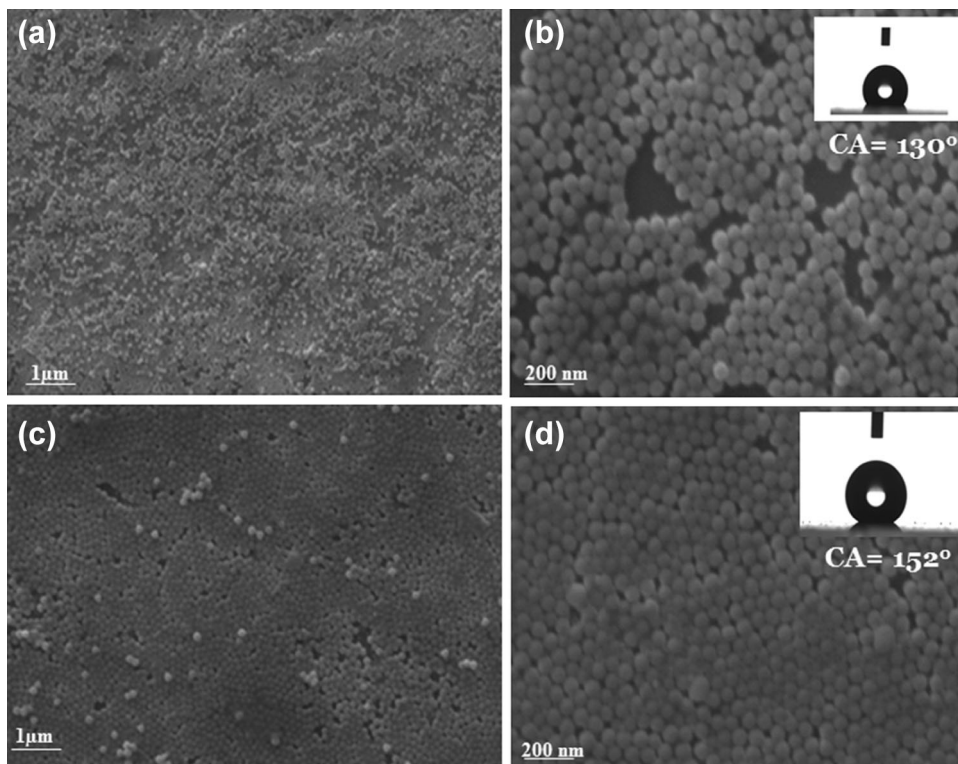
Fig. 2: (a) SEM micrograph of single layer of silica nanoparticles, (b) single layer of silica nanoparticles at higher magnification, (c) SEM micrograph of double layer of silica nanoparticles, (d) double layer of nanoparticles at higher magnification; the insets show the water contact angle of single and double layer, respectively
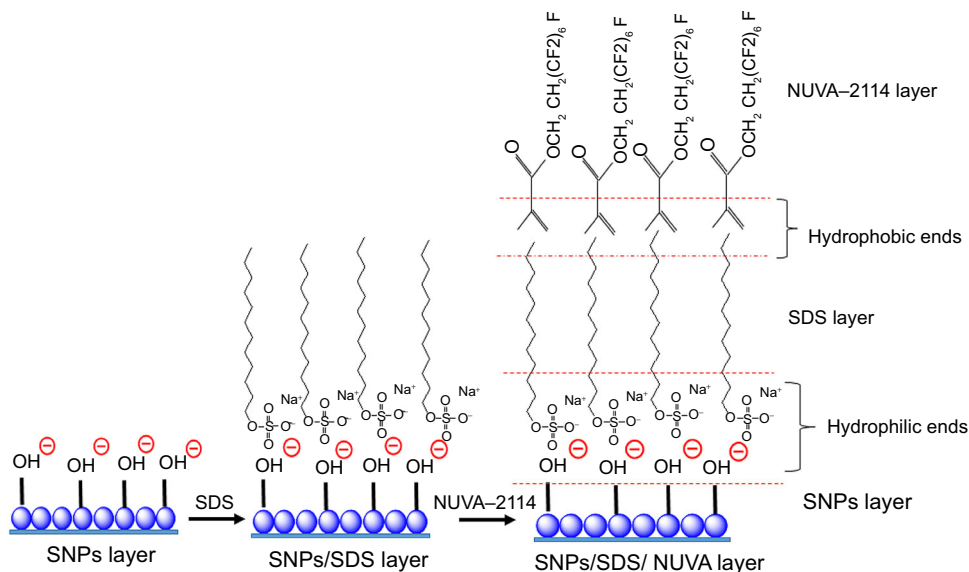

Fig. 3: Schematic diagram for interface interactions between various layers of the coating

To further understand the interface interactions, IR spectra of SiO_2 NPs (Fig. 4a), SDS surfactant (Fig. 4b) and NUVA 2114 (Fig. 4c) and nanoparticles was recorded after deposition of each layer. Figure 4d shows IR spectra for SDS-coated SiO_2 NPs, and

Fig. 4e shows IR spectra for NUVA coated over SiO_2 NPs/SDS layer. A comparison of IR spectra for all the above samples is depicted in Fig. 4.

Characteristic peaks of SDS (1030 cm^{-1}, 819 cm^{-1})[35] and SiO_2 (1086 cm^{-1}, 800 cm^{-1})[36] are
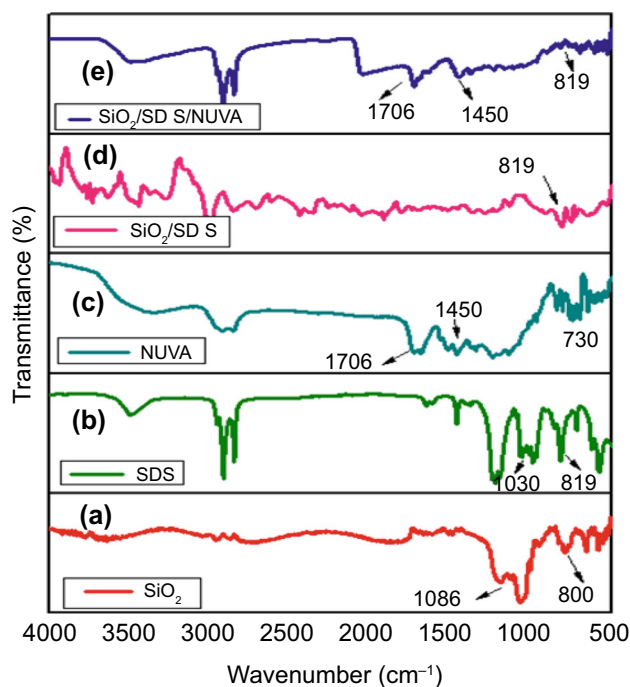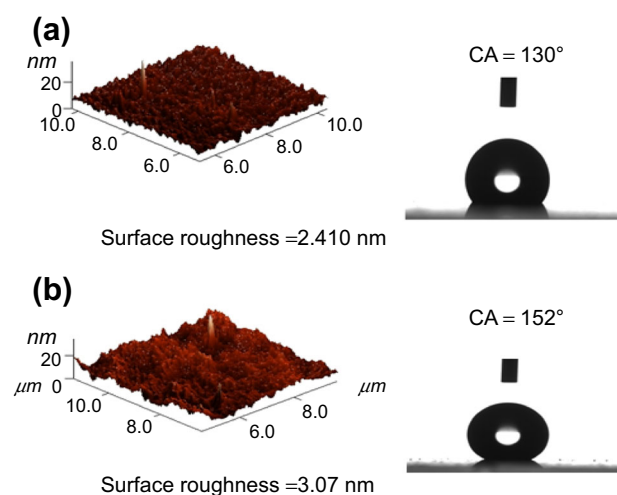
Fig. 4: (a) FTIR spectra of SiO_2 NPs, (b) SDS surfactant, (c) NUVA 2114, (d) SDS over two subsequent layers of SiO_2 NPs, (e) final coat of NUVA

Fig. 5: (a) 3D AFM topographical images silica single layer, (b) silica double layer

observed in IR of SDS-coated SNPs. This indicates the ionic nature of the interaction thus ruling out any chemical reaction between the two layers. In NUVA-coated SDS/SNP layer, low-intensity peaks of SDS ($819\ cm^{-1}$) can be seen while characteristic peaks of NUVA ($1706\ cm^{-1}$, $1450\ cm^{-1}$) appear prominent in IR spectra. The IR studies support ionic interaction between the layers. The peaks of SiO_2 are not clearly visible in NUVA-coated sample which appears to be suppressed by the two subsequent layers of SDS and NUVA. From these results, it is evident that ionic interaction between various layers is responsible for the stability of coatings.

Contact angle and AFM analysis

Surface roughness is acknowledged to be utmost important for imparting superhydrophobicity. Surface roughness and contact angle of the coatings with single and double layers of silica were determined. All measurements were made in static contact angle mode using Laplace–Young calculation method. CA measurements were conducted at five different places for layers of SiO_2 NPs to establish the uniformity of the coating and consistency of the CA values. The standard deviation of WCA was found to be ± 2 and ± 1,

respectively, for recorded values of double layer and single layer of silica coatings. Figure 5 shows single-layer coating of SNPs with a root mean square (RMS) roughness value of 2.41 nm and a contact angle of $130° \pm 1°$. With double layer of SNPs, the RMS value is increased to 3.07 nm with a corresponding increase in the contact angle to $152° \pm 2$, thus converting the surface superhydrophobic. The nanoroughness plays an important role in imparting superhydrophobicity. Jianmen Chen et al.[37] reported a CA of $163°$ with a micrometer roughness. In the present work, the nanoroughness obtained is appropriate for achieving superhydrophobicity.[38,39] The higher hydrophobicity reported by Chen is due to the use of C-8 fluorocompound which in general has better hydrophobicity. The superhydrophobicity obtained in this work is because of the combination of both C-6 fluorocompound and nanoroughness achieved through nanosilica multilayers. Thus, surface chemistry and roughness of coatings together are seen to have a significant impact on the apparent contact angles which leads to superhydrophobicity.[40,41]

Optical characterization

Transmission spectra were recorded on UV–Vis spectrophotometer to evaluate the transparency of the coatings. The coatings of single layer (A) and double layer (B) show 90% transmission in the wavelength range of 300–800 nm. The images of water droplets on the prepared coatings are shown in Fig. 6b. As can be seen, the letters beneath the superhydrophobic glass coatings are visible clearly. Therefore, the prepared coatings retain a significant transparency.

(a)

(b)
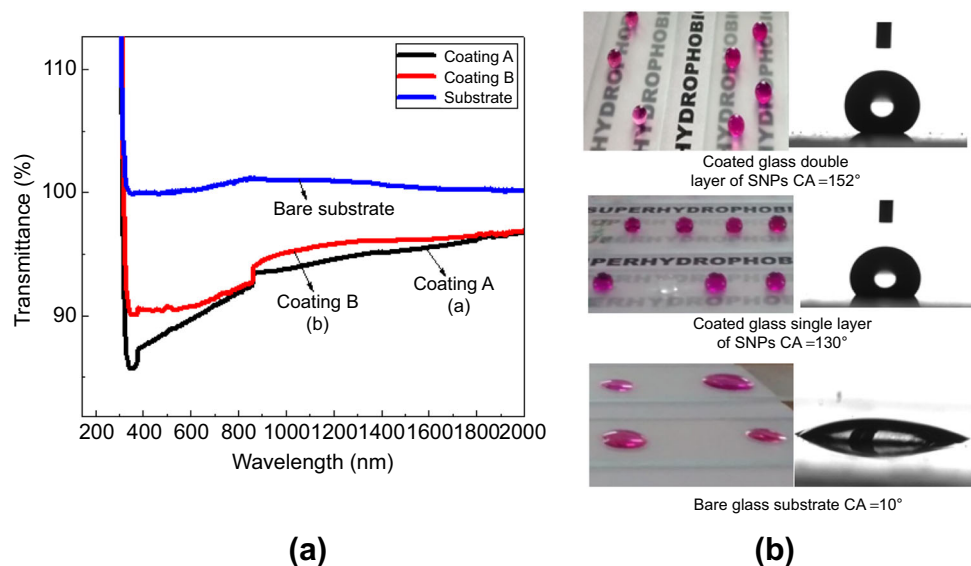
Fig. 6: (a) Transmission spectra of coatings: single-layer SNPs/SDS/NUVA (Coating A), double-layer SNPs/SDS/NUVA (Coating B), (b) images of coated and uncoated surfaces

Conclusions

In the present study, a facile way of obtaining super-hydrophobic surfaces is developed. The method involves fabrication of multilayer coating on glass substrate by adopting layer-by-layer (LBL) deposition approach using dip coating technique. Nanoroughness is obtained by deposition of nano-SiO_2 in bilayers. NUVA-2114, an environmentally safe alternative to fluorosilanes, has been used to lower the surface energy. A layer of SDS is used between the layers of SiO_2 and NUVA to facilitate better adhesion at the interface, thereby stabilizing the multilayered coating. Use of a short-chain telomere as an ecofriendly alternative to longer perfluoro chain length alcohols in obtaining superhydrophobic coating has been successfully demonstrated. By combining bilayers of SiO_2 NPs and NUVA-2114, we are able to produce super-hydrophobic coatings, which exhibit similar characteristics as those of larger-chain fluoropolymers. The imparted stability is explained by ionic interactions and van der Waals forces of attraction between the various layers of the coating. A reasonable optical transparency of 90% is achieved. Environmental acceptability, ready availability of all components and ease of fabrication are the highlights of the developed process for obtaining these superhydrophobic coatings.

References

1. Feng, L, Zhang, YN, Xi, JM, Zhu, Y, Wang, N, Xia, F, Jiang, L, "Petal Effect: A Superhydrophobic State with High Adhesive Force." *Langmuir*, **24** 4114–4119 (2008)
2. Ragesh, P, Ganesh, VA, Nair, AS, "A Review on Self-Cleaning and Multifunctional Materials." *J. Mater. Chem. A*, **2** 14773–14787 (2014)
3. Yu, S, Guo, Z, Liu, W, "Biomimetic Transparent and Superhydrophobic Coatings: From Nature and Beyond Nature." *Chem. Commun.*, **51** 1775–1794 (2015)
4. Li, J, Yan, L, Ouyang, Q, Zha, F, Jing, Z, Li, X, Lei, Z, "Facile Fabrication of Translucent Superamphiphobic Coatings on Paper to Prevent Liquid Pollution." *Chem. Eng. J.*, **246** 238–243 (2014)
5. Darmanin, T, Guittard, F, "Recent Advances in the Potential Applications of Bio Inspires Superhydrophobic Materials." *J. Mater. Chem. A*, **2** 16319–16359 (2014)
6. Wang, P, Zhang, D, Qui, R, Wan, Y, Wu, J, "Green Approach to Fabrication of a Super-Hydrophobic Film on Copper and the Consequent Corrosion Resistance." *Corros. Sci.*, **80** 366–373 (2014)
7. Xu, WJ, Song, JL, Lu, Y, Yu, Z, "Rapid Fabrication of Large Area Corrosion Resistant Superhydrophobic Mg Alloy Surfaces." *ACS Appl. Mater. Interfaces*, **3** 4404–4414 (2011)
8. Shubha, HN, Venkatesha, TV, Vathsala, K, Pavitra, MK, Punith Kumar, MK, "Preparation of Self Assembled Sodium Oleate Monolayer on Mild Steel and its Corrosion Inhibition Behavior in Silane Water." *ACS Appl. Mater. Interfaces*, **5** 10738–10744 (2013)
9. Li, J, Yan, L, Li, H, Li, W, Zha, F, Lei, Z, "Underwater Superoleophobic Palygorskite Coated Mesh for the Efficient Oil/Water Separation." *J. Mater. A*, **3** 14696–14702 (2015)
10. Li, J, Yan, L, Li, JP, Zha, F, Lei, Z, "A Facile One Step Spray-Coating Process for the Fabrication of Superhydrophobic Attapulgite Coated Mesh Used in Oil/Water Separation." *RSC Adv.*, **5** 53802–53808 (2015)
11. Li, J, Yan, L, Zhao, Y, Zha, F, Wang, Q, Lei, "One-Step Fabrication of Robust Fabrics with Both-Faced Superhydrophobicity for Separation and Capture of Oil from Water." *Phys. Chem. Chem. Phys.*, **17** 6451–6457 (2015)
12. Li, J, Jing, Z, Zha, F, Yang, Y, Wang, Q, Lei, Z, "Facile Spray Coating Process for the Fabrication of Tunable Adhesive Superhydrophobic Surfaces with Heterogeneous Chemical Composition Used for Selective Transportation of Micro Droplets with Different Volumes." *ACS Appl. Mater. Interfaces*, **6** 8868–8877 (2014)

13. Chen, Z, Du, M, Lai, H, Du, Y, Zhang, N, Sun, K, "Selective Transportation of Micro Droplet Assisted by a Superhydrophobic Surface with pH- Responsive Adhesion." *Chem. Asian J.*, **8** 3200–3206 (2013)

14. Li, J, Jing, Z, Yang, Y, Wang, Q, Lei, Z, "From Cassie State to Gecko State: A Facile Hydrothermal Process for the Fabrication of Superhydrophobic Surfaces with Controlled Sliding Angles on Zinc Substrates." *Surf. Coat. Technol.*, **258** 973–978 (2014)

15. Han, D, Moon, SY, "Development of Superhydrophobic Surface on Glass Substrate by Multi Step Atmospheric Pressure Plasma Treatment." *Thin Solid Films*, **587** 34–38 (2015)

16. Li, KQ, Zeng, XR, Li, HQ, Lai, XJ, "A Study on the Fabrication of Superhydrophobic Iron Surfaces by Chemical Etching and Galvanic Replacement Methods and Their Anti-Icing Properties." *Appl. Surf. Sci.*, **346** 458–463 (2015)

17. Sasan, R, Rostam, M, "One Step Chemical Vapor Deposition and Modification of Silica Nanoparticles at the Lowest Possible Temperature and Superhydrophobic Surface Fabrication." *Chem. Eng. J.*, **252** 11–16 (2014)

18. Cheng, SJ, Liu, XL, Yun, S, Luo, HJ, Gao, YF, "SiO$_2$/TiO$_2$ Composite Aerogels: Preparation via Ambient Pressure Drying and Photocatalytic Performance." *Ceram. Int.*, **40** 13781–13786 (2014)

19. Garav, AB, Lathe, SS, Vhatkar, RS, Lee, JG, Kim, DY, Park, JJ, Yoon, SS, "Superhydrophobic Surfaces Decorated with Vertical ZnO Nanorods Modified by Steric Acid." *Ceram. Int.*, **40** 7151–7160 (2014)

20. Lie, YL, Wang, QR, Huo, JC, "Fabrication of Durable Superhydrophobic Coatings with Hierarchical Structure on Inorganic Radome Materials." *Ceram. Int.*, **40** 10907–10914 (2014)

21. Raza, MA, Zandvliet, HJW, Poelsma, B, Kooji, ES, "Hydrophobic Surfaces with Tunable Dynamic Wetting Properties via Colloidal Assembly of Silica Microspheres and Gold Nano Particles." *J. Sol-Gel Sci. Technol.*, **74** 357–367 (2015)

22. Wang, HX, Zhou, H, Niu, HT, Zhang, J, Du, Y, Lin, T, "Dual Layer Superhydrophobic/Superhydrophobic-Oleophilic Nanofibrous Membranes with Unidirectional Oil-Transparent Ability and Strengthened Oil-Water Separation Performance." *Adv. Mater. Interfaces*, **2** 1400506 (2015)

23. Avinash, B, Mojtaba, A, Seeram, R, "Bio-Inspired Electrospun Micro/Nanofibers with Wettability." *J Nanosci. Nanotechnol.*, **14** 4781–4798 (2014)

24. Zhang, LB, Chen, H, Sun, JQ, Shen, JC, "Layer-by-Layer Deposition of Poly(diallyldimethylammonium chloride) and Sodium Silicate Multilayers on Silica-Sphere-Coated Substrate; Facile Method to Prepare a Superhydrophobic Surface." *Chem. Mater.*, **19** 948–953 (2007)

25. Manabg, K, Nishizawa, S, Kyung, KH, Shiratori, S, "Optical Phenomena and Antifrosting Property on Biomimetics Slippery Fluid-Infused Antireflective Films via Layer-by-Layer Comparison with Superhydrophobic and Antireflective Films." *ACS Appl. Mater. Interfaces*, **6** 13985–13993 (2014)

26. Garav, AB, Xu, QF, Lathe, SS, Vhatkar, RS, Liu, SH, Yoon, H, "Superhydrophobic Coatings Prepared from Methyl-Modified Silica Particles Using Simple Dip-Coating Method." *Ceram. Int.*, **41** 3017–3023 (2015)

27. Zhang, X, Shi, F, Niu, J, Jiang, Y, Wang, Z, "Superhydrophobic Surfaces: from Structural Control to Fundamental Application." *J. Mater. Chem.*, **18** 621–633 (2008)

28. Bhusan, B, Jung, YC, "Natural and Biomimetic Artificial Surfaces for Superhydrophobicity, Self-Cleaning Low Adhesion and Drag Reduction." *Prog. Mater. Sci.*, **56** 1–108 (2011)

29. Nishino, T, Meguro, M, Nakamae, K, Matsushita, M, Ueda, Y, "The Lowest Surface Free Energy Based on –CF3 Alignment." *Langmuir*, **15** 4321 (1999)

30. Giesy, JP, Kannan, K, "Global Distribution of Perfluorooctane Sulfonate and Related Perfluorinated Compounds in Wildlife." *Environ. Sci. Technology*, **35** 1339–1342 (2001)

31. Giesy, JP, Kannan, K, "Perfluorochemical Surfactants in the Environment." *Environ. Sci. Technol.*, **36** 47A–152A (2002)

32. Bogren, S, Fornara, A, Ludwig, F, Steinhoff, U, Hansen, MF, Kazakova, O, Johanssom, C, "Classification of Magnetic Nanoparticle Systems-Synthesis, Standardization and Analysis Methods in the NanoMag Project." *Int. J. Mol. Sci.*, **16** 20308–20325 (2015)

33. Binks, BP, Horozov, TS, "Aqueous Foams Stabilized Solely by Silica Nanoparticles." *Angew Chem.*, **117** 3788–3791 (2005)

34. Yusuf, S, Manan, M, Jaafar, MZ, "Aqueous Foams Stabilized by Hydrophilic Silica Nanoparticles via In-Situ Physisorption of Nonionic TX100 Surfactant." *Iran. J. Energy Environ. (Special Issue on Nanotechnology)*, **4** (1) 08–16 (2013). doi:10.5829/idosi.ijee.04.01.02

35. Latthe, SS, Imai, H, Ganesan, V, Rao, AV, "Superhydrophobic Silica Films by Sol-Gel Co-Precursor Method." *Appl. Surf. Sci*, **256** 217–222 (2009)

36. Brassard, JD, Sarkar, DK, Perron, J, "Synthesis of Monodisperse Fluorinated Silica Nanoparticles and Their Superhydrophobic Thin Films." *ACS Appl. Mater. Interfaces*, **3** 3583–3588 (2011)

37. Li, J, Wan, H, Ye, Y, Zhou, H, Chen, J, "One-Step Process to Fabrication of Transparent Superhydrophobic SiO$_2$ Paper." *Appl. Surf. Sci.*, **261** 238–243 (2012)

38. Barthlott, W, Neinhuis, C, "Purity of the Sacred Lotus, or Escape from Contamination in Biological Surface." *Planta*, **202** 1–8 (1997)

39. Lafuma, A, Quéré, D, "Superhydrophobic States." *Nat. Mater.*, **2** 457–460 (2003)

40. Zheng, QS, Yu, Y, Zhao, ZH, "Effects of Hydraulic Pressure on the Stability and Transition of Wetting Modes of Superhydrophobic Surfaces." *Langmuir*, **21** 12207–12212 (2005)

41. Raspal, V, Awitor, KO, Massard, C, Feschet-Chassot, E, Bokalawela, RSP, Johnson, MB, "Nanoporous Surface Wetting Behavior: The Line Tension Influence." *Langmuir*, **28** 11064–11071 (2012)