

Review article

Superhydrophobic Surface Based Silica Nanoparticle Modified with Diisocyanate and Short and Long Normal Chain Alcohols

Hamed Saeedi^a, Mohammad Javad Taghizadeh^{b,*}, Seyed Salman Seyed Afghahi^c

^aDepartment of Polymer Chemistry, Faculty of Chemistry, University of Isfahan, Isfahan, Iran

^bDepartment of Organic Chemistry, Faculty of Science, Imam Hossein University, Tehran, Iran

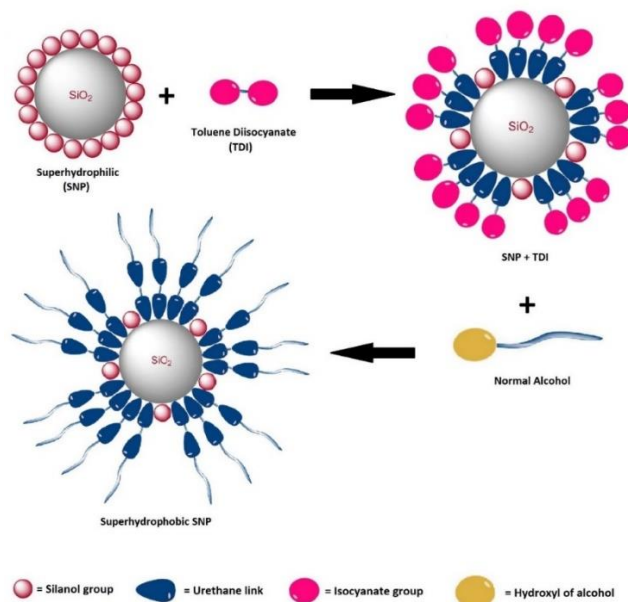
^cDepartment of Advance Materials, Imam Hossein University, Tehran, Iran

Received: 28 January 2018, Revised: 11 April 2018 and Accepted: 14 April 2018.

ABSTRACT: A superhydrophobic (SH) surface is a nanoscopic coating layer that repels water. SH materials are essential for a myriad of applications such as anti-icing and selfcleaning due to their extreme water repellency. However, simple, cost-effective and environmental-friendly approach and using nonhazardous chemicals can be considered as its deficiencies. We demonstrated a unique class of modification of silica nanoparticle with toluene diisocyanate and grafting long alkyl chains on silica nanoparticles surface by a facile two-step method. The modified nanoparticles showed very well SH property. This kind of coating and modification, hitherto undisclosed, is expected to be a breakthrough method in the field non fluorine and cost effective industrial SH coatings.

KEYWORDS: Superhydrophobic, Cost Effective, Silica Nanoparticle, Flourine Free, Grafted Modification.

GRAPPHICAL ABSTACT:



Introduction

SH surfaces have been of considerable interest in both academic and commercial communities [1-4], because of their different applications such as anticorrosion, self-cleaning, antifogging, anti-icing, oil-water separation, medicine, drag reduction, water harvesting, and other fields [5-

14]. The SH materials' behaviour of lotus leaf which contained micro and nano roughness on its surface structure has caused high water contact angle and water rolling properties. It showed that surface roughness and surface chemistry are two main factors for SH property [15-17].

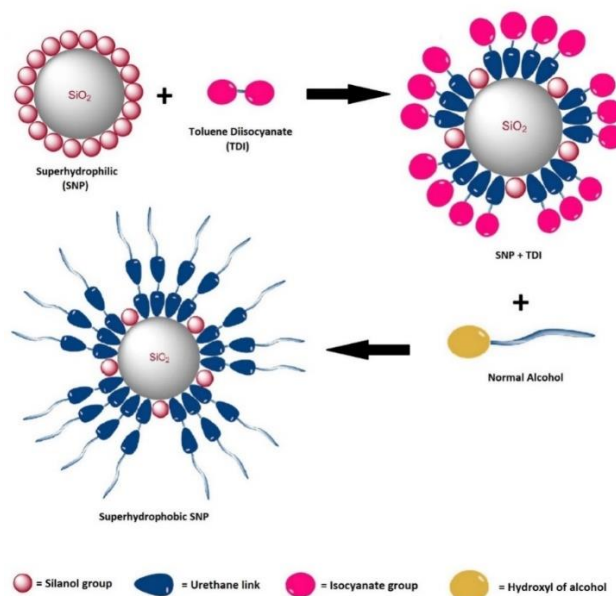
There are various methods, such as electrospinning [18], microlithography [19], photolithography [20, 21] and etching techniques [22] for preparation of SH surfaces. But these methods entail the hard conditions and intricate treatment.

Therefore, it is consequential to develop simple and cost effective methods for preparing the SH surface in large scale for industrial usage. The most promising method to fabricate SH coating is thought to spray deposition of hydrophobic nanoparticles [23-25]. Moreover, respraying the SH nanoparticles are used to repair degraded surfaces.

The most commonly low surface energy materials for fabricating SH surface are fluorocarbons. In this sense, nanoparticles modified by fluor-alkylsilanes have been used to prepare SH coating [5, 26-31]. But the use of long-chain polyfluorinated materials are costly and toxic [32-34]. For this reason, many researchers have tried to find methods for preparing SH surfaces with non-fluorinated materials, which were affordable and eco-friendly. Some methods for constructing non-fluorinated SH coating have been improved by using the hydrophobic modified nanoparticles,

which were done through the reaction between the hydroxyl on the surface of nanoparticles and the carboxyl or silanol groups from low-surface-energy materials. But, the materials for improving the SH surfaces are restricted commercially [35-41]. In spite of the various methods for fabricating non-fluorinated SH coating, it is still required to improve new and more efficient strategies.

In this study, we have developed the synthesis of SH nanoparticles, without using fluoride groups, which are resistant to acidic and basic condition and also the commercially available raw materials for extending formulation at industrial scale. To achieve this goal we modified hydroxile group on silica nanoparticle with toluene diisocyanate, then, we added alcohols of varying lengths. Hydroxyl group of alcohols react with another isocyanate groups on the silica surface and form a urethane bond (Scheme 1). A two-step synthesis method has been used to make this nanoparticle without the need of a catalyst. Synthesized SH nanoparticle with high contact angle, acid and base resistance, and affordability can be used in practical applications.



Scheme 1. preparation of SH nanoparticles by modifying with toluene diisocyanate and alcohol.

Experimental

Material and methods

Silica Nanoparticle (10-20 nm), 1-butanol, 1-octanol, cetyl alcohol, toluene diisocyanate

(TDI) and toluene were purchased from Merck Company. The SH nanoparticles were analyzed by FT-IR (Fourier transform infrared spectroscopy, Nicolet-Impact 400D spectrophotometer in KBr pellets and reported in cm^{-1}), and also Contact angle (CA) measurement was performed using CA-ES10 (Fars EOR TechCo.) apparatus at ambient temperature. The morphologies and size of the SH nanoparticles were observed using field emission scanning electron microscope (FE-SEM, MIRA3TESCAN-XMU) and transmission electron microscopy (TEM, Philips CM30 unit operated at 150 kV). The sonication was performed in PARSONIC 11s (Pars Nahand Engineering Co.) ultrasonic bath.

Surface modifier preparation

A mixture of silica nanoparticles (1 g) and toluene (15 ml) was irradiated in the ultrasonic bath for 30 min at 60°C . Then, TDI (3 ml) was added drop wisely, and the resulting suspension was heated at 110°C for 18 h under nitrogen atmosphere. Silica nanoparticles modified by TDI (SNP+TDI) was filtered and washed with toluene and dried in oven at 70°C .

Preparation of SH silica nanoparticles

Hydrophobic silica nanoparticles were synthesized by incorporating the surface

modifier (alcohol) to modify SNP+TDI. Firstly, SNP+TDI were dispersed in toluene by ultrasonic treatment. Under stirring, the 1-Octanol was added in dropwise, and the suspension was heated at 110°C for 18 h. The mixture was filtered and washed with toluene and dried to obtain SH silica nanoparticles (SH-SNP).

Results and discussion

The SH-SNP, was characterized by means of fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM). Figure 1 illustrates the FT-IR spectrums of SNP+TDI (a), SNP+TDI+1-octanol (b), SNP+TDI+1-butanol (c), and SNP+TDI+cetyl alcohol (d) respectively. The appearance of the peak at 2277 cm^{-1} indicates the $-\text{N}=\text{C}=\text{O}$ stretching band in Figure 1a while this peak did not exist in Figure 1b, c and d. The FT-IR spectrum of SNP+TDI+1-octanol, SNP+TDI+1-butanol and SNP+TDI+cetyl alcohol showed absorption bands at, 1105 cm^{-1} (O-Si-O stretching band), 1650 cm^{-1} (C=O), 2930 cm^{-1} (C-H stretching band), and 3450 cm^{-1} (N-H bending vibration), respectively.

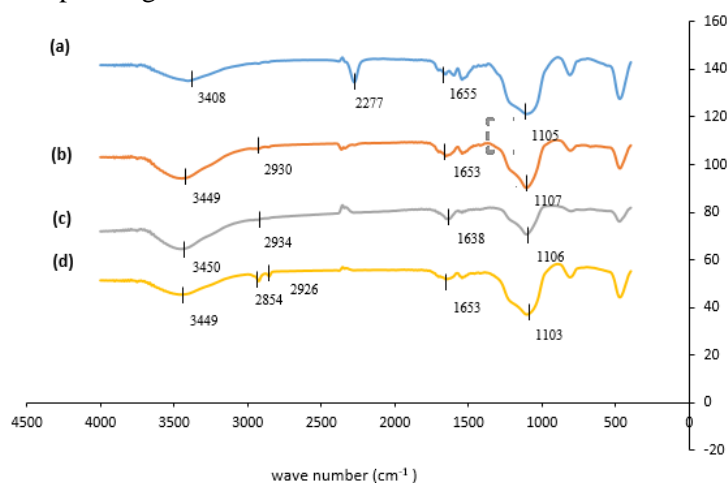


Fig. 1. Comparison of FT-IR spectrums of SNP+TDI (a), SNP+TDI+1-octanol (b), SNP+TDI+1-butanol (c), and SNP+TDI+cetyl alcohol (d)

TEM images of SH-SNP revealed that it appears to have almost a spherical structure

with the average size about 26-30 nm (Figure 2).

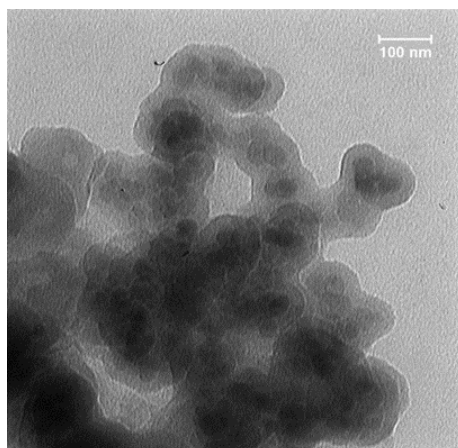


Fig. 2. TEM image of SH nanoparticles(a) and SH nanoparticles particle size distribution histogram (b)

The surface morphology and nanostructure of silicananoparticles modified with diisocyanate and different alcohols were examined by FESEM, and the representative

images are shown in Figure 3 respectively. The SEM image of SH-SNP indicates aspherule-like structure with surface roughness.

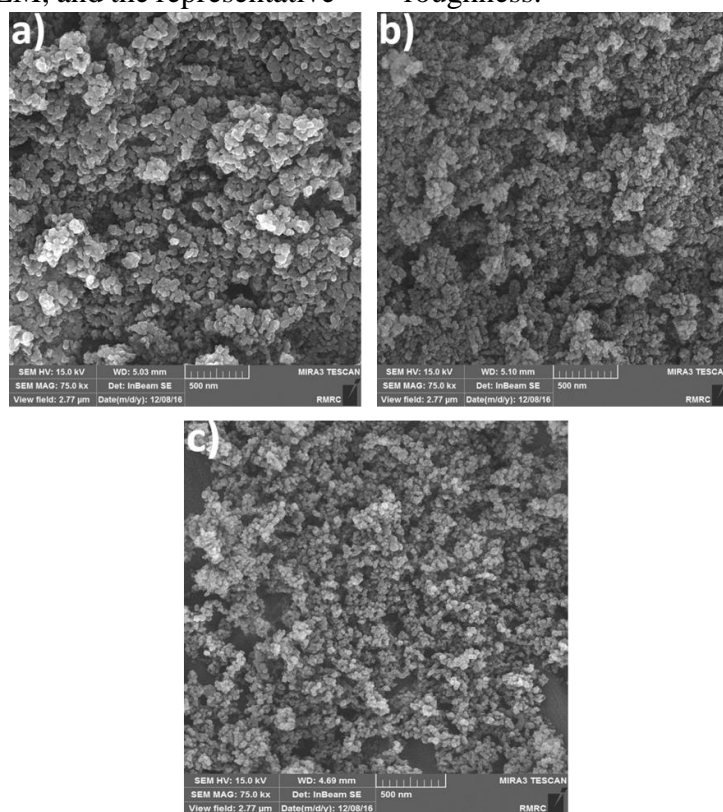


Fig. 3 FESEM images of SHnanoparticles, (a) SNP+TDI+1-octanol, (b) SNP+TDI+1-butanol, and (c) SNP+TDI+cetyl alcohol

After structure characterization of the nanoparticles and in order to examine the contact angle of SH-SNP, we have the water repellency of the nanoparticles highlighted

in Figure 4. Water droplets exhibit typical and spherical shapes on the nanoparticles and the bright, reflective surface visible underneath the water droplets is a signature

of trapped air. This state allows the nanoparticles surface to display a high apparent contact angle (159°) with water droplets placed on it. The SH-SNP can retain its superhydrophobicity for at least 6 months under atmospheric conditions, indicating its

long-term stability. We also found that the SH coating was very stable in wide range of pH (4-12), where the CA values were $>140^\circ$ (Figure 4). The representative results of this investigation are summarized in Table 1.

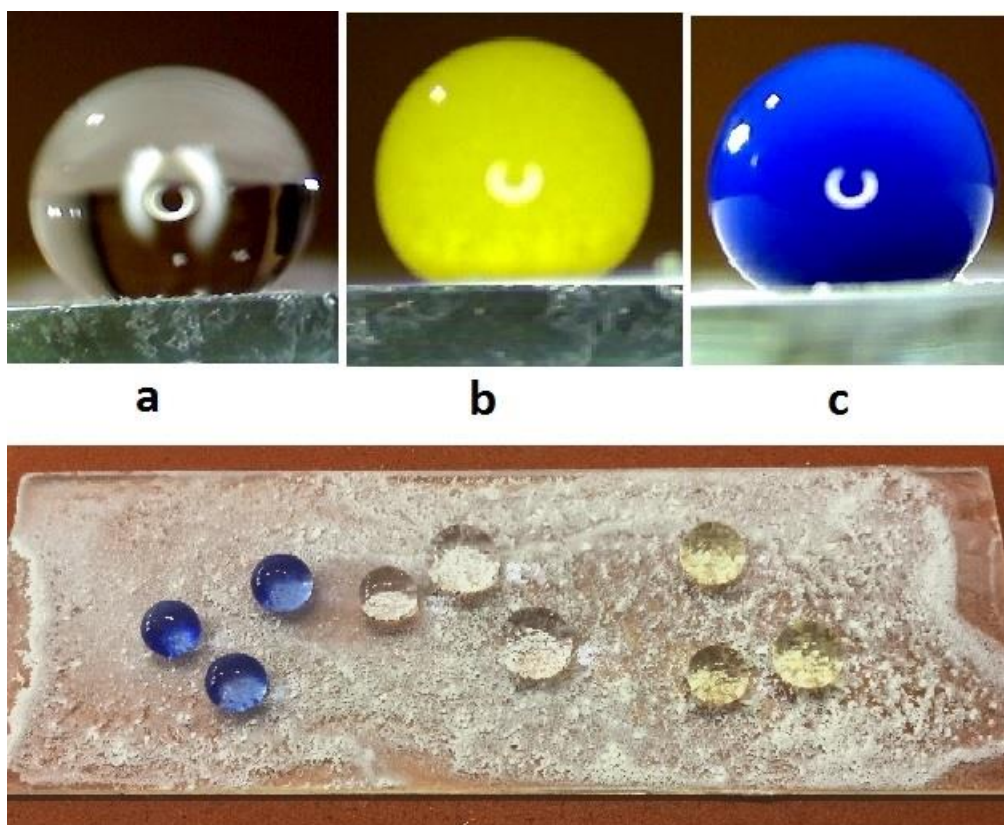


Fig. 4. (a) Comparison of a water, (b) acidic (pH=4; yellow), (c) and basic (pH=12 blue) droplet on SH-SNP coating (colored for visualization).

Table 1. Contact angle measurements of SH-SNP at different pH.

Entry	Product	pH=4	pH=7	pH=12
1	Silica + TDI + 1-butanol	145.56°	143.89°	155.23°
2	Silica + TDI + 1-octanol	160.58°	162.65°	166.73°
3	Silica + TDI + cetyl alcohol	148.26°	159.98°	163.41°

Conclusions

We demonstrated a sustainable, straightforward, efficient and practical way to the synthesis of SH coating without using catalyst and fluorine compound using silica nanoparticles and modifying with toluene diisocyanate and alcohols. Achemically and

acid-base durable SH nanoparticles material with self-cleaning and self-regenerating features and with low surface energy and high surface roughness at the nano-scales was demonstrated. Novel SH systems can be developed by varying the chain length of grafted alkyl groups over the surface. The

approach can be extended to different micro-nanomaterials (like metal oxides and others) and also for achieving practical applications. It is so because of its satisfactory low-cost, environmental friendly, weather durability and scalable fabrications.

Acknowledgments

We gratefully acknowledge financial support from the Research Council of Imam Hossein University.

References:

- [1] Feng, X. J., & Jiang, L. (2006). *Adv. Mater.*, 18: 3063–3078.
- [2] Blosssey, R. (2003). *Nat. Mater.*, 2: 301.
- [3] Gao, X., Yan, X., Yao, X., Xu, L., Zhang, K., Zhang, J., Yang, B., & Jiang, L. (2007). *Adv. Mater.*, 19: 2213–2217.
- [4] Li, X.-M., Reinhoudt, D., & Crego-Calama, M. (2007). *Chem. Soc. Rev.*, 36: 1350–1368.
- [5] Wang, S., Liu, K., Yao, X., & Jiang, L. (2015). *Chem. Rev.*, 115: 8230–8293.
- [6] Wen, L., Tian, Y., & Jiang, L. (2015). *Angew. Chemie Int. Ed.*, 54: 3387–3399.
- [7] Simpson, J. T., Hunter, S. R., & Aytug, T. (2015). *Reports Prog. Phys.*, 78: 86501.
- [8] Lai, Y., Tang, Y., Gong, J., Gong, D., Chi, L., Lin, C., & Chen, Z. (2012). *J. Mater. Chem.*, 22: 7420–7426.
- [9] Sun, Z., Liao, T., Liu, K., Jiang, L., Kim, J. H., & Dou, S. X. (2014), 10: 3001–3006.
- [10] He, Q., Yu, W., Wu, Y., & Zhou, C. (2012). *Soft Matter*, 8: 2992–3001.
- [11] Chu, Z., Feng, Y., & Seeger, S. (2015). *Angew. Chemie Int. Ed.*, 54: 2328–2338.
- [12] Wang, B., Liang, W., Guo, Z., & Liu, W. (2015). *Chem. Soc. Rev.*, 44: 336–361.
- [13] Li, J., Shi, L., Chen, Y., Zhang, Y., Guo, Z., Su, B., & Liu, W. (2012). *J. Mater. Chem.*, 22: 9774–9781.
- [14] Li, A., Sun, H.-X., Tan, D.-Z., Fan, W.-J., Wen, S.-H., Qing, X.-J., Li, G.-X., Li, S.-Y., & Deng, W.-Q. (2011). *Energy Environ. Sci.*, 4: 2062–2065.
- [15] Onda, T., Shibuichi, S., Satoh, N., & Tsujii, K. (1996), 12: 2125–2127.
- [16] Sun, T., Feng, L., Gao, X., & Jiang, L. (2005). *Acc. Chem. Res.*, 38: 644–652.
- [17] Feng, L., Li, S., Li, Y., Li, H., Zhang, L., Zhai, J., Song, Y., Liu, B., Jiang, L., & Zhu, D. (2002). *Adv. Mater.*, 14: 1857–1860.
- [18] Ganesh, V. A., Raut, H. K., Nair, A. S., & Ramakrishna, S. (2011). *J. Mater. Chem.*, 21: 16304–16322.
- [19] Sogaard, E., Andersen, N. K., Taboryski, R., & Smistrup, K. (2012). *In: Nanotech 2012*.
- [20] Gao, S. J., Shi, Z., Zhang, W. Bin, Zhang, F., & Jin, J. (2014). *ACS Nano*, 8: 6344–6352.
- [21] Notsu, H., Kubo, W., Shitanda, I., & Tatsuma, T. (2005). *J. Mater. Chem.*, 15: 1523–1527.
- [22] Qian, B., & Shen, Z. (2005), 21: 9007–9009.
- [23] Yang, J., Zhang, Z., Men, X., Xu, X., & Zhu, X. (2010). *Colloids Surfaces A Physicochem. Eng. Asp.*, 367: 60–64.
- [24] Xu, X., Zhang, Z., & Liu, W. (2009). *Colloids Surfaces A Physicochem. Eng. Asp.*, 341: 21–26.
- [25] Yang, J., Zhang, Z., Men, X., & Xu, X. (2009). *Appl. Surf. Sci.*, 255: 9244–9247.
- [26] Lu, Y., Sathasivam, S., Song, J., Crick, C. R., Carmalt, C. J., & Parkin, I. P. (2015). *Science* (80-.), 347: 1132–1135.
- [27] Chen, K., Zhou, S., Yang, S., & Wu, L. (2015). *Adv. Funct. Mater.*, 25: 1035–1041.
- [28] Zhou, H., Wang, H., Niu, H., Gestos, A., & Lin, T. (2013). *Adv. Funct. Mater.*, 23: 1664–1670.
- [29] Xu, L., Karunakaran, R. G., Guo, J., & Yang, S. (2012). *ACS Appl. Mater. Interfaces*, 4: 1118–1125.

- [30] Zhou, H., Wang, H., Niu, H., Gestos, A., Wang, X., & Lin, T. (2012). *Adv. Mater.*, 24: 2409–2412.
- [31] Liu, K., Cao, M., Fujishima, A., & Jiang, L. (2014). *Chem. Rev.*, 114: 10044–10094.
- [32] Darmanin, T., & Guittard, F. (2013). *Soft Matter*, 9: 5982–5990.
- [33] Begley, T. H., White, K., Honigfort, P., Twaroski, M. L., Neches, R., & Walker, R. A. (2005). *Food Addit. Contam.*, 22: 1023–1031.
- [34] Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). *Environ. Sci. Technol.*, 40: 32–44.
- [35] Zhang, X., Cai, S., You, D., Yan, L., Lv, H., Yuan, X., & Jiang, B. (2013). *Adv. Funct. Mater.*, 23: 4361–4365.
- [36] Alexander, S., Eastoe, J., Lord, A. M., Guittard, F., & Barron, A. R. (2015). *ACS Appl. Mater. Interfaces*, 8: 660–666.
- [37] Park, E. J., Sim, J. K., Jeong, M.-G., Seo, H. O., & Kim, Y. D. (2013). *RSC Adv.*, 3: 12571–12576.
- [38] Kulkarni, S. A., Ogale, S. B., & Vijayamohan, K. P. (2008). *J. Colloid Interface Sci.*, 318: 372–379.
- [39] Ogihara, H., Xie, J., & Saji, T. (2013). *Colloids Surfaces A Physicochem. Eng. Asp.*, 434: 35–41.
- [40] Wu, L., Zhang, J., Li, B., & Wang, A. (2013). *J. Mater. Chem. B*, 1: 4756–4763.
- [41] Li, L., Li, B., Dong, J., & Zhang, J. (2016). *J. Mater. Chem. A*, 4: 13677–13725.

How to cite this manuscript: Hamed Saeedi, Mohammad Javad Taghizadeh*, Seyed Salman Seyed Afghahi. Superhydrophobic Surface Based Silica Nanoparticle Modified with Diisocyanate and Short and Long Normal Chain Alcohols. *Asian Journal of Nanoscience and Materials*, 2018, 1, 71-77.