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Electrostatic Layer-by-Layer Self-Assembly for Tuning Hydrophilic ITO glass to Wenzel Super Hydrophobic Surface

Channapura Halappa Chandrashekhar
Department of PG Studies in Chemistry, Kadur, Kuvempu University, 577548, Karnataka, India

Abstract: Layer-by-Layer self assembly concept was designed for the construction of films from electrostatic polymers, we have fabricated nano hybrid organic/inorganic surfaces by alternating various different layers of electrostatic polymers and silica nano particles (10nm diameter). The obtained molecular structure leads to a nanoscale textures. Then hydrophobization of the final layer by Azobenzene and OTMS -functionalized silica particles was carried out by grafting technique highly fluorinated azobenzene, creating a monolayer with the formation of an azo function. The fluorinated surfaces (contact angle-133.7^0) and OTMS- SAM (contact angle-124^0) was shown a wenzel model super hydrophobic surfaces were obtained with the alternate of nine layers. This result demonstrates the possibility to construct LBL of polymers with functionalized silica nanoparticles for superhydrophbic surface on ITO glass surface.

Keywords: Self assembly, Contact angle , Electrostatic, Layer-by-Layer, Superhydrophobic

I. INTODUCTION

Since the promising work of Decher et al., [1] layer-by-layer (LBL) method has emerge as one of most possible and precious technical tool to construct very thin multilayer films. [2-4] The importance of this technique is very simple, versatile, and promising and convenient control over the structure and thickness, roughness of the resulting film. [5] Recently, the LBL films with the thickness in the range from hundreds of nanometers to dozens of micrometers have gained attention because thick LBL films can possess some particular advantages over thin films, such as exceptional mechanical properties, [6-9] high loading capacity for guest molecules, [10,11] highly nano textured surface with superhydrophobicity, [12-14] and so on. However, well known, the conventional LBL method is quite time-consuming.

Large variety of materials including macromolecules, inorganic nanomaterials and biomaterials of thin films and coating surfaces can be fabricated by most popular technique was LBL assembly. [15-25]

In the conventional LBL process, we deposited the polyelectrolytes by dipping the substrate alternately into the corresponding polyanion and polycationic solutions. Between the deposition steps, rinsing steps are taken by dipping the substrate into water to remove the residue and loosely bound polymers.

It is indicated by some study that the polymer deposition consists of initial adsorption and subsequent reconfiguration, which take several tens and hundreds of seconds, respectively.[26,27] The result of most polymers are deposited on the substrate in the initial several seconds, it is still necessary to extend the deposition time to 5 to 20 min to reach the equilibrium thickness. Meanwhile, to avoid cross-contamination of polymer solutions, the rinsing steps are normally repeated more than three times and 1 min each at least. The attempt to deposit the LBL fabricated film by simply decreasing deposition and rinsing time has been tried, [28] but the results show that when the deposition and rinsing time is shortened to 30 and 15 s (three times and 5 s each), respectively, the film quality becomes rather poor.

Therefore, it is very difficult to decrease the assembly time per layer to <1 min by conventional LBL, which has impeded the further exploration and development of thick LBL films. The superhydrophobic states such as Cassie and Wenzel have minimum surface energy of a drop yields its apparent contact angle θ^* on a rough (hydrophobic) substrate, as a function of the Young's contact angle θ (determined on a flat surface of the same nature).In the Wenzel model, the surface roughness *r* is defined as the ratio of the actual over the apparent surface area of the substrate (*r* is a number larger than unity),and we have: $\cos\theta^* = r \cos\theta$. (1)

For a Cassie drop, the contact angle is an average between the value on air (that is, 180°) and on the solid (that is,θ), which can be calculated for a simple geometric texture such as posts, or parallel channels7. Denoting φ_s as the fraction of solid in contact with the liquid (there again φ s is dimensionless, but smaller than unity), we find: $\cos\theta^* = -1 + \varphi_s (1 + \cos\theta)$. (2)

Equation 2 should hold good for substrates with very rough (large *r*) or very hydrophobic (large θ) [29-31] In both these limits, the Wenzel formula predicts a total drying of the surface (θ*=180°), which is not physical because of the contact that must exist between a drop and its substrate. Similarly, we expect the Wenzel equation to hold for solids that are slightly hydrophobic (θ just above (90°): then, air pockets, which imply that many liquid/vapour interfaces of high surface energy exist, should not be favored. [32]

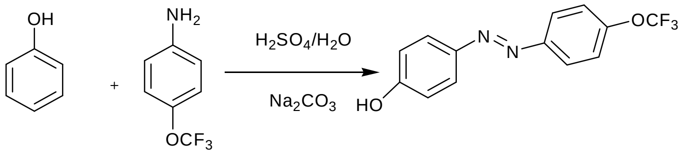
II. EXPERIMENTAL SECTION

A. Materials

Phenol (99%), 4-(Trifluoromethoxy)aniline (99%), sodium nitrite (99%), acetic acid (glacial, 99.8%), 5-bromopentyl(trimethoxy)silane (99%) , sodium carbonate (99%), were supplied by Sigma- Aldrich and used as received. Poly(styrene sulfonate) (PSS, mol. wt. 70,000), poly(ethylene imine) (PEI, mol. wt. 25,000), Poly(allylamine hydrochloride) (PAH, mol. wt. 70,000), and nanosilica particles (SiO2 Nanoparticles, d~10 nm) were provided from Aldrich. All water was Millipore Milli-Q grade with a resistivity about 18MΩ/cm obtained from a Milli-Q purification system (Millipore, USA). All chemicals and solvents were used directly without further purification and of reagent grade.

B. Synthesis of 4-(4-trifluoromethoxyphenylazo) Phenol (1).

4-(Trifluoromethoxy)aniline (75mmol) was dissolved with heating a mixture of 21 ml concentrated sulfuric acid and 21 ml water in a beaker and cool the solution after it was diazotized by dropping a solution of 7g sodium nitrite in 40 ml water at 0-5^{0}C to the acid mixture. Then the coupling was carried out by slowly adding the diazotized solution to a solution of 7.5g phenol, 3g sodium hydroxide and 47g sodium carbonate in 270 ml water at 0-5^{0}C The yellow-orange colored precipitate of **1** was filtered off, dried and recrystallized from n-hexane.[33,34]



C. Treatment of Substrates.

Indium Tin Oxide glass was used as the substrate in this study. The surface size is 3 cm in length and 1 cm in width. The substrate surface was tailored with OH group prior to LBL assembly. In brief, the substrate was first kept in a UV-Ozone chamber for about 20min. Then the substrate was measured contact angle the surface is get converted into hydrophilic in a water. After cleaned up with toluene, acetone. and chloroform, the substrate with OH-tailored surface was obtained.

D. Film Preparation.

A nanostructure of Organic-inorganic hybrid films were easily prepared by using the electrostatic self-assembly method with SiO2 nanoparticles of size 10nm. The ITO glass was treated with UV-Ozone followed by rinsing with excess Milli-Q water and drying under nitrogen gas. Before to the first deposition of SiO2 nanoparticles, a layer of PEI was dip coated after alternate layer of PAH and PSS polymers [(PAH/PSS)5/PEI] was deposited onto each freshly treated ITO glass with five cycles. In order to prepare a dense SiO2 nanoparticles layer. The clean ITO glass was immersed in 40 mM PEI solution for 5 min and rinsed with DI water separate bottles. The substrate was then softly dried using a nitrogen stream. The PEI-modified ITO glass was alternately dipped in 40 mM PSS solution and 40 mM pH 7.0 PAH solution for 5 min, and then rinsed with Milli-Q water in separate bottles, each for 1 min. The ITO glass was then dried under a nitrogen gas stream and these procedures were repeated 5 times. The (PAH/PSS)5/PEI-coated ITO glass was then immersed in 0.05 wt% SiO2 nanoparticles solution and PAH solution for 5 min alternately and washed three times with Milli-Q water, each for 1 min. The roughness of the films can be satisfactorily controlled by varying the number of PAH and SiO2 nanoparticles deposition cycles. The roughness and porosity of the surface after 5 deposition cycles are distinctly greater than after 1 deposition cycle. Further, after 7 deposition cycles the surface of the ITO glass is almost covered by PAH/SiO2 bilayers and the use of 9 deposition cycles was found to be sufficient to significantly increase the nanoporosity and surface roughness.[35] The variation of surface roughness was find out by contact angle measurement for different layers of deposition indicated that change in contact angle in Figure.1

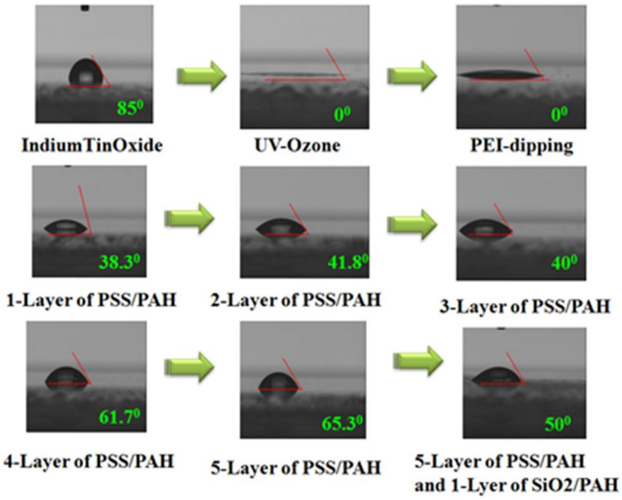


Figure 1. Contact angle change from ITO glass to different layers of PSS/PAH deposition and SiO$_2$/ PAH.

E. Self Assembly of Azobenzene onto rough Substrate

The substrates were incubated in 0.5 vol% of 5-bromopentyl(trimethoxy)silane in dry toluene solution for about 1h before being removed from the solution and washed well in toluene to remove excess reagent. Then the substrates were dried at 100^{0}c for 20 min and washed well in toluene and water. The bromo-modified ITO substrates were placed in an ethanolic solution of CF3AZO (1mM) in the presence of catalytic amount triethylamine. This was carried out in an air glow box, at room temperature, with gentle stirring for 10 h in nitrogen atmosphere. The substrates were then removed from solution, washed sequentially with ethanol and water to remove unbound azobenzene, and dried under vacuum for 1 h. The same process was repeated for OTMS, which was shown in below Figure-2

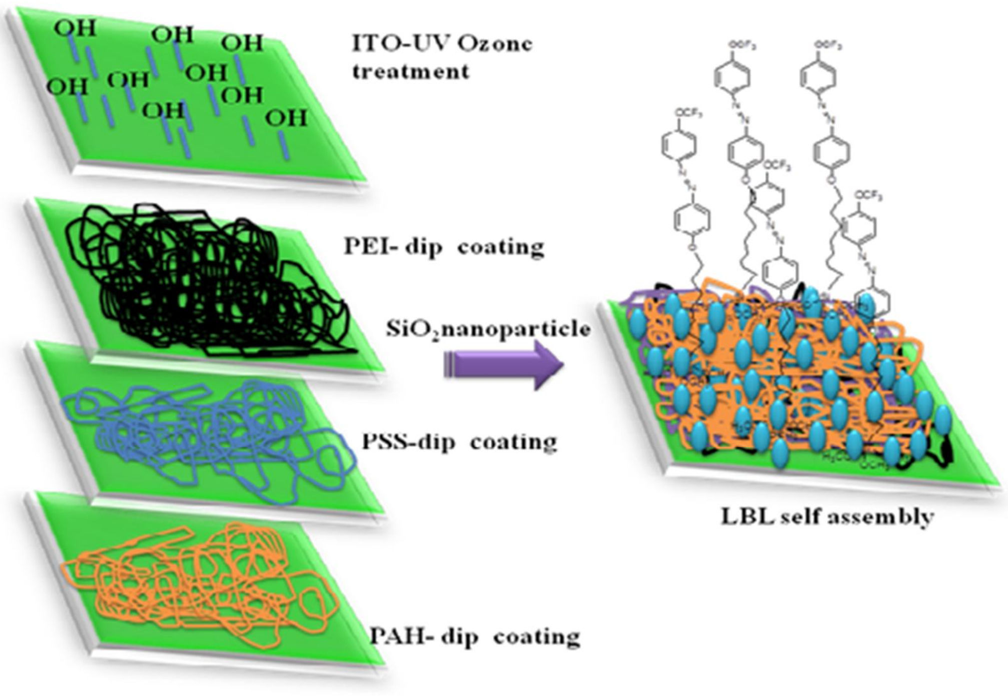


Figure 2. Surface modification of hydrophilic ITO glass to LBL – Self assembly Organic –Inorganic hybrid layer

F. Measurement.

UV-Ozone treatment was carried out on a PSD, PSDP and Thermal Series Nova scan UV Ozone Cleaner.

The contact angle was measured with a DSA100 contact angle system (Data Physics, KRUSS) at room temperature by using a 5-μL drop of water for the static contact angle (θ_s).

III. RESULTS AND DISCUSSION

The procedure of LBL assembly significance mainly depends on vigorously agitated dipping solutions and short dipping time of 5min. In this study, the dipping time in polymer solutions and each rinsing bath was set up respectively, and the agitation was produced by hand shaking. Between two polymer deposition steps, rinsing in water bath was repeated three times to remove the surface residue as much as possible. In addition, the ITO glass substrate was dipped along the beaker edge so as to obtain high flow rate and maintained paralleled with the solution flow so that the surface got fully flushed.

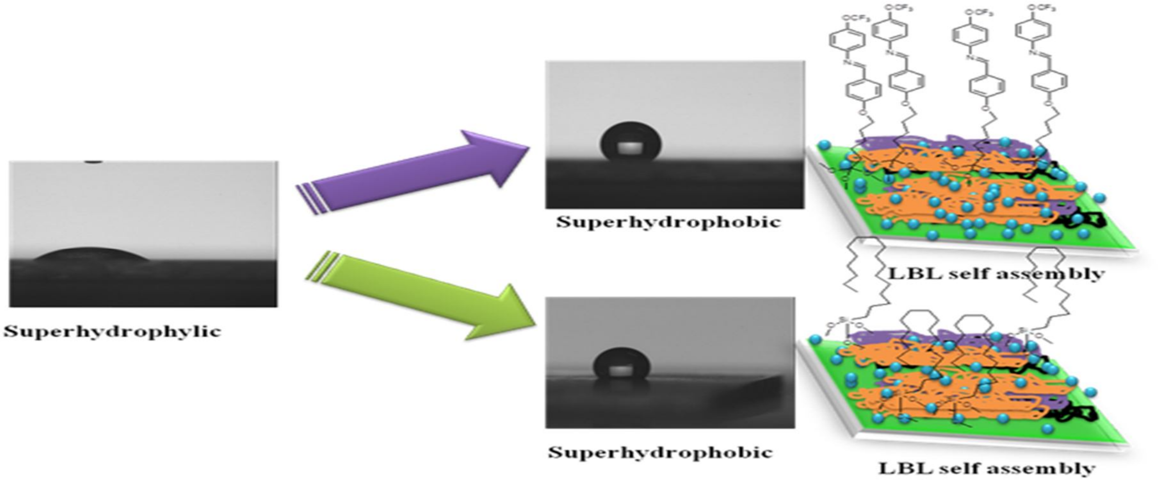


Figure 3. Wenzel model of superhydrophobicity shown by Azobenzene and OTMS modified self assembly.

As a combination in LBL electrostatic assembly, PAH and PSS were employed to deposit alternately by LBL. The LBL process of PAH and PSS was monitored by contact angle instrument. Figure 2 shows the contact angle of different bilayer numbers which can used to confirm the uniformity of LBL, It is clear that the thickness also increases linearly with the bilayer numbers, Meanwhile, the surface roughness was changed on depositing charged electrolytic polymers. Fabrication Process of LBL of the polymer deposition and represent the rinsing steps. remarkable regular variation with the bilayer. The **Figure3** indicates that the fluorinated surfaces (contact angle-133.7^0) and OTMS- SAM (contact angle-124^0) was shown a wenzel model super hydrophobic surfaces were obtained with the alternate of nine layers. If we increase number of PAH/SiO2 layer we can get more superhydrphobicity

IV. CONCLUSIONS

We have used a new method called Agitated deposition of LBL to fabricate LBL films rapidly by employing continuously agitated solutions as dipping solutions. When the samples are dipped in polyanion and the polycation there may be a change in the contact angle for 1-layer deposition of PSS/PAH the contact angle is 38^o the number of deposition cycle increases the contact angle 68^o for 5 cycles (CA changes can be shown in figure2), In particular, the CA of the (PAH/SiO2)9 film was found to be dramatically reduced from superhydrophobic to superhydrophilic The enhanced hydrophilicity is strongly dependent on the surface roughness and also of hydrophilic silica nanoparticles. Since azobenzene molecules have a cis form on the porous substrates, the imbibition of water into the inner pores occurs, and water will fill the inner pores below the droplets owing to the 3D capillary effect[35]. These results indicate that the wettability from superhydrophobic can easily be achieved by using photoresponsive azobenzene molecules on a nanostructured surface fabricated with simple LBL assembly and just nine cycles of deposition of PAH and SiO2 nanoparticles. We repeatedly irradiated a (PAH/SiO2)9 multilayer film and a flat substrate without degradation occurring after formation and obtain a contact angle-133.7^0 and OTMS- SAM , the contact angle-124^0 was shown a wenzel model super hydrophobic surfaces. The surface roughness plays the most important role in intensifying hydrophobicity. Therefore, these indicate that the surface roughness can be used to greatly intensify the hydrophobicity of a hydrophilic surface.

REFERENCES

[1] G. Decher, J. D. Hong, Makromol. Chem., Macromol. Symp. 1991, 46, 321–327.
[2] J. A . Jaber, J. B. Schlenoff, Curr. Opin. Colloid Interface Sci. 2006, 11, 324–329.
[3] K. Ariga, J. P.Hill, Q. M. Ji, Phys. Chem. Chem. Phys. 2007, 9, 2319– 2340.
[4] J. F.Quinn, A. P. R. Johnston, G. K.Such, A. N. Zelikin, F. Caruso, Chem. Soc. Rev. 2007, 36, 707–718.
[5] G. Decher, Science , 1997, 277, 1232–1237.
[6] Z. Y.Tang, N. A. Kotov, S. Magonov, B. Ozturk, Nat. Mater. 2003, 2, 413–418.
[7] J. L. Lutkenhaus, K. D. Hrabak, K . McEnnis, P. T. Hammond, J. Am. Chem. Soc. 2005, 127, 17228–17234.
[8] Y.Ma, J.Sun, J. Shen, Chem. Mater. 2007, 19, 5058–5062.
[9] P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, B. S. Shim, J. D Xu,. H. Nandivada, B. G. Pumplin, J. Lahann, A. Ramamoorthy, N. A. Kotov, Science, 2007, 318, 80–83.
[10] S. Srivastava, V. Ball, P. Podsiadlo, J. Lee, P. Ho, N. A. Kotov J. Am. Chem. Soc. 2008, 130, 3748–3749.
[11] L. Zhang, J. Sun, Chem. Commun, 2009, 3901– 3903.
[12] L. Zhai, F. C. Cebeci, R. E.Cohen, M. F. Rubner, Nano Lett. 2004, 4, 1349–1353.
[13] L. Zhai, M. C.Berg, F. C .Cebeci, Y. Kim, J. M. Milwid, M. F. Rubner, R. E.Cohen, Nano Lett. 2006, 6, 1213–1217.
[14] X.Liu, B.Dai, L.Zhou, J.Sun, J. Mater. Chem. 2009, 19, 497–504.
[15] R. K. Iler, .J. Colloid Interface Sci. 1966, 21, 569-594.
[16] G. Decher, Science, 1997, 277, 1232-1237.
[17] G. Decher, J. D . Hong, J. Schmitt, Thin Solid Films, 1992, 210, 831-835.
[18] Y. Lvov, K. Ariga, M. Onda, I. Ichinose, T. Kunitake, Langmuir, 1997, 13, 6195-6203.
[19] J. Park, L. D. Fouche, P. T. Hammond, Adv. Mater. 2005, 17, 2575-2579.
[20] J. Schmitt, G. Decher, W. J. Dressick, S. L. Brandow, R. E. Geer, R. Shashidhar, J. M. Calvert, Adv. Mater. 1997, 9, 61-65
[21] Tang, Z. Y. Kotov, N. A. Magonov, S. Ozturk, .Nat. Mater. 2003, 2, 413-418.
[22] S. Srivastava, N. A. Kotov, Acc. Chem. Res. 2008, 41, 1831-1841.
[23] P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, S. Shim, J. D. Xu, H. Nandivada, B. G. Pumplin, J. Lahann, A. Ramamurthy, N. A. Kotov, Science, 2007, 318, 80-83
[24] D. Lee, M. F.Rubner, R. E. Cohen, Nano Lett. 2006, 6, 2305-2312.
[25] C. Q. Peng, Y. S.Thio, R. A. Gerhardt, Nanotechnology, 2008, 19, 505603.
[26] R. A. McAloney, M. C. Goh, J. Phys. Chem. B, 1999, 103, 10729–10732.
[27] O. Mermut, C. J. Barrett, J. Phys. Chem. B, 2003, 107, 2525–2530.
[28] A. Izquierdo, S. S. Ono, J. C.Voegel, P. Schaaff, G. Decher, Langmuir, 2005, 21, 7558–7567.
[29] J. Bico, C. Marzolin, D. Quéré, Europhys. Lett. 1999, 47, 220–226.
[30] J. Bico, U. Thiele, D.Quéré, Colloids Surf.A, 2002, 206, 41–46.
[31] N. Patankar, Langmuir , . 2003, 19,1249–1253.
[32] L.Aurelie,Q. David, Nature materials, 2003, 2(7), 457-460,
[33] D. Prescher, T. Thiele, R. Ruhmann, G. Schulz, J. Fuorine Chem. 1995, 74, 185-189.
[34] S.Furumi, K. Ichimura, Adv. Funct. Mater. 2004, 14, 247-254.
[35] H.S.Lim, J. T.Han, D. Kwak, M. Jin, K.W.Cho, J. Am. Chem. Soc. 2006, 128, 14458-14459