pH-sensitive organic diimide materials-based superhydrophobic surface for oil-water separation applications

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Keywords: superhydrophobicity, pH-responsive, oil-water separation, DFT calculations, contact angle

Abstract

pH-responsive superhydrophobic surfaces (SHSs) have recently represented reliable ability in oil-water separation applications. In this work, for the first time we could develop a switchable SHS based on (E)-4-(anthracen-9-ylidiazenyl) benzoic acid (4-ABA) pH-responsive organic molecules and stearic acid (SA) using self-assembly method for oil-water separation applications. Molecular structure of 4-ABA obtains the smart pH sensitive SHS and makes it able to use in oil-water separation process. TiO$_2$ decorated 4-ABA and SA composite (TiO$_2$@4-ABA/SA)-based SHS could tune the surface charge in different pH (2.0–7.0) and subsequently could influence on wettability and contact angle (CA) of surface which makes the surface suitable to represent oil-water separation properties. Density functional theory (DFT) mechanic quantum calculation showed stable absorption of the 4-ABA molecules on TiO$_2$ nanoparticles ($\sim >1.3$ eV) that rely on the reusability (20 cycles) of the surface during oil-water separation. Morphology of switchable SHSs were considered by scanning electron microscopy (SEM) and wettability of the surface has been evaluated by CA. The UV–vis spectroscopy showed packing density ($\Gamma=4.35 \times 10^{-7}$ mol.cm$^{-2}$) of the 4-ABA in TiO$_2$@4-ABA/SA approach which caused to high rate of switching in wettability ($\sim$ 5 s per cycle). Transition between superhydrophobic (CA = $\sim$152.39°) and hydrophilic (CA = $\sim$26.11°) states is the main advantage of this surface obtained from the different charges of the surface in various pH. Therefore, the 4-ABA molecules-based pH-responsive SHS with ability in adjusting the surface wettability can be applied for oil-water separation applications. The mentioned versatile advantages open a new horizon for environmentally friendly applications of this approach which cannot achieved by conventional methods and materials.

1. Introduction

The pH-responsive smart SHSs with water CA > 150° and surface free energy <10 mJ.m$^{-2}$ which represent reversibly changeable interfacial properties in proper pH have recently attracted a lot of attentions because of their broad applications in optoelectronics, cell culture, microfluidic and (photo)catalyst [1–13]. Owing to high capability of SHSs, many different applications have been developed in strategic sciences such as biomedicine [14–17], biosensors [18, 19] biology [20–22], switchable surfaces [23], anti-corrosive/icing/bacterial surfaces and etc [24–28]. While various methods were developed to fabricate the SHSs [29, 30], self-assembly-based approach is as one of the most common method for designing pH-responsive SHSs for oil-water separation applications. Monolayer deposition of pH-responsive organic molecules makes it possible to develop a surface with reversible pH-responsivity for controlling SHS wettability. According to many reports, controlling surface wettability on SHSs as main strategy to design an oil-water separation approach remains as a challenge for many years. Photochromic light-sensitive diimide organic compounds-based switchable SHSs which directly change conformation of molecules structures from trans (Z) to cis (E) isomerization, could adjust the surface wettability...
by converting light energy to molecular mechanical work and subsequently making them as appropriate options for oil-water separation. In previous years, broad efforts have been done to obtain a smart SHS with ion-exchange ability, redox reaction and thermo/pH responsivity of polymers or other types of materials to apply in oil-water separation [23, 31–33]. In this context, for first time we developed an organic diimide-based compounds (TiO₂@4-ABA/SA) to fabricate a pH-responsive SHS. Principally, oil-water separation is highly important because of environmentally friendly effect on water sources. In addition, fabricating SHS with oil-water separation ability working based on the difference in capillary forces of oil and water phase on separator surface have been reported previously using silver nanoclusters-based membranes [34] and superhydrophobic/oleophilic carbon nanotube-based materials [35]. Low efficiency of separation was main disadvantage of these types of oil-water separation approaches. For this reason, charge induced switchable SHSs has been recently developed by Jin and co-workers which could separate various oils from water phase efficiently using poly(methyl methacrylate)-block-poly(4-vinylpyridine) polymer-based nanofibrous membranes using high porosity, adjusting effect on surface charge and surface wettability. Although pyridine pH-responsive part of switchable polymer in various pH plays significant role during separation, unfortunately they extremely suffer from unstable and unadorable superhydrophobic structure [36–38]. In order to solve this challenge, monolayer self-assembly deposited organic molecules-based SHSs have been proposed due to their stable superhydrophobic structures and their outstanding capability in oil-water separation. Up to now, in these approaches various FGs such as carboxylic acids (–COOH), hydroxyl (–OH), amine (–NH₂), and also their combination have been reported to obtain induced charges and hydrogen bond interaction with water phase (in various pH of the water phase) to convert reversibly wettable and stable surface from superhydrophobicity to superhydrophilicity. But majority of these approaches suffer from weak pH-responsivity and more importantly low rate of switching wettability of surface that directly influences on oil-water separation efficiency [32, 39, 40]. In this work, we represent how fast-switchable TiO₂@4-ABA/SA-based pH-responsive, smart and SHS with diimide (–N=N–) FGs acts as vigorous approach for oil-water separation with desired wettability from superhydrophobicity (CA = ~152.39°) to hydrophilic (CA = ~26.11°) states. Oil-water separation efficiency in broad range of pH (2.0–7.0), reusability (>20 cycles), high rate of switchability (~5 s for each cycle of switchability of surface wettability) and chemical stability are main advantages of this new approach that are not achievable in conventional previous approaches. Therefore, we propose this approach as highly-potent option for oil-water separation applications.

2. Computational procedure

All the spin-polarized DFT calculations were performed with the DMol³ [41, 42]. The generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) [43] functional was adopted to treat the exchange-correlation interactions. To accurately describe the weak van der Waals interactions, the PBE + D method the Grimme’s scheme [44, 45] was used in the all calculations. A double-numerical basis set with the polarization function (DNP) was selected as the basis set with a real-space cutoff radius of 4.6 Å. The core electrons were treated with DFT semi-core pseudopotentials [46]. A Fermi smearing parameter of 0.005 Ha was used in the calculations. The convergence tolerance for energy change, maximum force, and maximum displacement were 1 × 10⁻⁵ Ha, 0.001 Ha Å⁻¹, and 0.005 Å, respectively. Vibrational frequencies were calculated on the optimized geometries in order to ensure that the obtained structures are true minima on the corresponding potential energy surface. According to the previous studies [47–49], the surface of anatase TiO₂ thin films is generally terminated at the (101) plane. Hence, in our calculations, the anatase (101) TiO₂ surface was modeled by a periodic (4 × 2) slab containing 32 Ti and 64 O atoms. The Brillouin zone integration was sampled using a 3 × 3 × 1 Monkhorst–Pack grid. To avoid interaction of the periodic images, a vacuum space was added in the z direction such that the lattice constant c = 35.0 Å. The adsorption energy (Eₐₐ₅) of each adsorbate (A) over the TiO₂ surface was calculated as

\[ E_{\text{ads}}(A) = E_A / \text{TiO}_2 - E_A - E_{\text{TiO}_2} \]  

where \( E_A / \text{TiO}_2 \), \( E_A \) and \( E_{\text{TiO}_2} \) are the total energies of the adsorbate/TiO₂ complex, the adsorbate and TiO₂ surface, respectively. By this definition, a negative \( E_{\text{ads}} \) value indicates an exothermic adsorption.

3. Experimental procedure

3.1. Fabrication of TiO₂ substrate

TiO₂-based transparent substrate was prepared according to procedure reported previously [50, 51]. As a summary, glass substrate was cleaned by using concentrated HNO₃/HCl/ethanol three time for ten minutes.
Then dried in room temperature and TiO$_2$ (99% Degussa anatase 25 nm) paste was coated on clean glass using doctor blade deposition method. Subsequently, prepared layer was sintered at 500 $^\circ$C for two hours.

3.2. Synthesis of (E)-4-(anthracene-9-yl)diazenyl benzoic acid

In this stage, 7.0 g anthracene (>96%, Merck Co.) was added in 200 ml of concentrated HNO$_3$/CH$_3$COOH; 1:1 v/v) mixture and was solved at 120 $^\circ$C for ten minutes. Then, 50 ml HCl (37%, Merck Co.) slowly was added to solution and heated at 120 $^\circ$C for 40 min. Subsequently, 100 ml of NaOH aqueous solution slowly was added in solution. Yellowish orange precipitate of 9-nitroanthracene is product of this stage. The precipitate of 9-nitroanthracene washed several times by using DI water and $n$-hexane (96%, Merck Co.). Then the 9-nitroanthracene precipitate was reduced to 9-aminoanthracene in boiled concentrated HCl and tin powder (99.5%, Aldrich Co.) suspension. According to Sandmeyer reactions [52], 9-aminoanthracene and benzoic acid (99.0%, Merck Co.) used in diazonium coupling reaction. In this stage, an icy aqueous solution of NaNO$_2$ (99.0%, Merck Co.) slowly added to mixture of 9-aminoanthracene and benzoic acid in ice bath and high rate stirring conditions. After 30 min, reaction set up was carried in boiling water bath and was heated for 30 min. The yellowish white precipitate of 4-ABA as product of reaction was produced.

3.3. Self-assembly fabrication of switchable SHSs

The TiO$_2$-coated plates (2.0 cm × 2.0 cm) were heated at 80 $^\circ$C for 20 min and then immersed in ethanol (99.9%, Merck Co.) solution of 4-ABA (0.05 M) for 12 h at room temperature. Then the plates washed by using ethanol and DI water several times and was dried at 65 $^\circ$C for 15 min. In continue, the plates were immersed in 0.1 M of ethanol solution of CH$_3$(CH$_2$)$_n$COOH(SA) (99.0%, Merck Co.) for eight hours at room temperature. The plates washed by using toluene (>99.9%, Merck Co.) for several times until the unwanted precipitates have been removed on their surface. Then the plates have been floated in ethanol (99.9%, Merck Co.) for five minutes and finally dried at 80 $^\circ$C for 30 min.

3.4. Switchability testing

For testing switchability of surface ~5 $\mu$l of water droplets in different pHs from 2.0 to 7.0 were prepared by using 2.5 M sulfuric acid (96%, Merck Co.) and CAAs of droplets were measured by using them.

3.5. Fabrication of pH-responsive sponge

In order to prepare pH-responsive surface a piece of commercial polyurethane sponge (5.0 cm × 5.0 cm × 0.5 cm) was immersed in ethanol suspension of TiO$_2$@4-ABA/SA for 30 min. Also, in order to synthesis of TiO$_2$@4-ABA/SA, the 1.0 g TiO$_2$ powder was added into 70.0 ml of the 4-ABA:SA (1:1) ethanol solution and was heated under reflux condition at 60 $^\circ$C for five hours. Then, the mixture was filtered and washed with ethyl acetate (99.5%, Merck Co.) and ethanol and was dried at 70 $^\circ$C for 30 min.

3.6. Separation testing

In order to evaluate separation of organic phase and water mixture, the modified sponge (5.0 cm × 5.0 cm × 0.5 cm) was applied. Toluene (>99.9%, $\rho$ = 867 kg m$^{-3}$, Merck Co.), $n$-hexane (>95.0%, $\rho$ = 673 kg m$^{-3}$, Merck Co.) and p-xylol (>99.0%, $\rho$ = 861 kg m$^{-3}$, Sigma Aldrich Co.) as light organic phase and dichloromethane (99.8%, $\rho$ = 1330 kg m$^{-3}$, Sigma Aldrich Co.) as heavy organic phase and water were combined (1:1 v/v) then for light mixtures the modified sponge was floated on the mixture and the organic phases were collected, while the heavy mixture was placed on the modified sponge. To measure separation efficiency, organic and water phases volume after and before of separation process were determined by using organic phases rejection coefficient (R) which can be written as [53]:

$$R(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100\%$$

Where the $C_p$ and $C_0$ refer to concentration of organic phase in initial mixture and separated mixture, respectively.

3.7. Stability testing

In order to evaluate chemical stability of the modified sponge, it was immersed in 2.5 M sulfuric acid for several hours at room temperature. Then the modified sponge was washed several times with DI-water. The sponge showed the superhydrophobic feature after complete washing that implies to switchability of the modified sponge.

3.8. Characterization

All of CA measurements were considered by CA system (OCA20, Data physics Co., Germany). To measure the CA, receding angle (RA), advancing angle (AA) and hysteresis (H) of CA (difference of advancing and receding
angles, \(\sim 5 \mu l\) of DI-water droplet gently was placed on the modified sponge by using microsyringe (SETonic GmbH Co., Germany) and was measured by CA system at room temperature. SEM image of surfaces were considered by SEM instrument (VEGA-TESCAN inst.). Atomic forced microscopy (AFM) (Ara Co. Iran) was applied to consider mean deviation of roughness \((R_a)\) for samples in various pH. UV–vis spectrometer (mini 1240, Shimadzu Co., Japan) was applied to determine absorbed 4-ABA molecules on TiO\(_2\) nanoparticles and packing density. Concentration was determined using Beer–Lambert equation that can be written as:

\[
A = \varepsilon bc
\]

(3)

Where the \(A\), \(\varepsilon\), \(b\) and \(c\) represent maximum absorption, absorption coefficient, length of vessel and concentration. And the packing density can be calculated as:

\[
\text{Packing density (mole cm}^{-2}) = \frac{\text{mole of absorbate/surface area of NPs}}{4}\]

(4)

4. Results and discussion

Surface chemical structure can be as crucial factor for obtaining switchable surfaces. Changing in charge density of surface has impact on CA of surface. Switchable surfaces that can change their CA, obtained by intelligent applying FGs of deposited materials. Changing in wettability of SHSs are a strategy for designing of switchable surfaces for different applications. Therefore, the alternative charges of FGs of deposited molecules on SHS is a unique strategy for switchable surfaces developing. Organic molecules with diimide FGs have intrinsic ability in designing switchable SHSs because of creation and annihilation of charge on their FGs. According to this fact, the 4-ABA molecules could be able to regulate charges on their diimide FGs and subsequently make the surface more hydrophilic than situation which these molecules are neutral. Figure 1 showed the TiO\(_2\)@4-ABA/SA-based pH-responsive switchable hydrophilic/SHS with suitable structural design and stability on substrate. In order to consider the wettability, the CAs of plate measured using droplets in different pHs from 2.0–7.0. In acidic pH (2.0–3.0) all of deposited 4-ABA molecules are in ionic states on TiO\(_2\) nanoparticle substrate and they have tendency to water molecular absorption on surface. In this state, charge
of diimide FGs reduces hydrophobic effect of SA alkyl chain on TiO2 surface. Therefore, absorption of water molecules on surface could overcome on hydrophobic effect of SA alkyl chains. Moreover, ionic form of 4-ABA molecules facilitates hydration process on surface and make surface more hydrophilic and subsequently can cause to water molecules penetration and spreading on surface. According to these facts, CA remained in minimum amount. In pH (4.0) almost maximum amount of 4-ABA deposited molecules were in ionic state but surface was more hydrophobic than situation in pH (2.0–3.0). In pH (5.0) the population of 4-ABA molecules increases in neutral form and deposited SA hydrophobic tails reduce surface hydrophilicity. Increasing in pH from 2.0 to 5.0 could change CA from ~26.11° to ~34.57° and subsequently ~77.95°. Increasing in pH from 4.0 to 5.0 made an increase in CA from ~34.57° to ~77.95° because of impressive change of deposited 4-ABA molecules from ionic to neutral form. A cooperative effect of deposited neutral 4-ABA and SA molecules on surface and appropriate roughness of surface make the surface more hydrophobic and finally in pH (7.0) almost all of the 4-ABA molecules were in neutral form and subsequently the surface was superhydrophobic (figure 2(B)).

After 20 cycles of switchability testing, stable CA amounts showed stable deposition of 4ABA and SA molecules on TiO2 surface and the reversibility of water CAs which illustrated in figure 2(A). The AA, RA and H measured ~155.0°, ~149.0° and ~6.0°, respectively (see figure 2(C)). As shown in figure 2(C), dynamic CA results of the TiO2@4-ABA/SA-based pH-responsive surface showed high AA (~ >150°) and RA (~ >140°) and low H (~ <10°) at pH (7.0) that imply to superhydrophobic properties of the surface. The stable amounts of the measured WCAs after 20 cycles indicated the stable pH-reversibility of the surface that makes it appropriate to represent good properties to oil-water separation application (see figure 2(A)). As far as molecular design is concerned, mechanism for creation and annihilation of charge for superhydrophobic/hydrophilic transition has potential of application in oil-water separation. Using diimide FGs in 4-ABA molecular structure is an intelligent design for obtaining pH-responsive molecules. Although anthracene part of 4-ABA has cooperative effect on hydrophobicity of surface, possibility of charge transition from diimide FG to anthracene part make surface more hydrophilic. The CA results indicated that the 4-ABA SHS has switchable behaviors in various pHs. The static CAs of superhydrophobic plate were ~26.11°, ~34.57°, ~77.95°, ~98.29° and ~152.39° for 2.0–3.0, 4.0, 5.0, 6.0 and 7.0 pHs, respectively (see figure 2(B)). According to results, increasing in CA after pH (5.0) relate to neutral form of deposited 4-ABA molecules on TiO2 surface. As structural view of the point, in molecular design of 4-ABA three main aims were followed. First, benzoic acid was selected as anchor part of molecule because of strong attaching ability of carboxylic acid on anatase TiO2 nanoparticles. Second, the diimide part of molecule plays a key role in creation and annihilation of charge on molecules in different pHs. The pH-responsive behavior of diimide FG is base of switchable properties of this surface. Third, the anthracene part of molecule with hydrophobic nature has a cooperative effect on hydrophobicity of surface, though the positive charge transfer from diimide functional group to anthracene part can strengthen the water molecules absorption
on surface and hydrophilicity of surface. The stability of the 4-ABA and SA molecules absorption on TiO₂ surface demonstrated by DFT calculations. The results showed the strong covalent bonding between Ti atoms of TiO₂ surface and carboxylic acid functional groups of 4-ABA and SA molecules. According to the results, the absorption energy of carboxylic acid FG in the cationic and neutral form of 4-ABA, and SA molecules on the TiO₂ anatase (101) crystal surface is 1.34, 1.38 and 1.11 eV, respectively. Therefore, 4-ABA molecules in the neutral form at the pH (7.0) can absorb on the TiO₂. The results also showed an acceptable absorption energy for cationic form of the 4-ABA molecules. Hence, absorption of 4-ABA and SA molecules on the TiO₂ nanoparticles makes the surface stable and switchable. The absorption model of 4-ABA and SA molecules, and the covalent bond length of carboxylic acid FGs on TiO₂ crystals were shown in figures 3(A)–(C). In contrast to the absorption of SA on TiO₂ (figure 3(C)), under the condition that the 4-ABA molecule is in neutral form (figure 3(B)), its planar molecular structure could make hyperconjugation of π-electrons and subsequently could increase the absorption energy, while in cationic form, the 4-ABA molecule loses the planar molecular structure that could influence on the hyperconjugation and as subsequent reduction in absorption energy of carboxylic acids FGs on the TiO₂ crystal (figure 3(A)). These results rely on the fact that not only TiO₂@4-ABA/SA-based pH-responsive switchable approach have stable structure for oil-water separation, but also with broad pH-responsivity (2.0–7.0) could obtain the reusability that isn’t accessible in conventional separators. Consideration about surface morphology of switchable SHS showed the TiO₂@4-ABA/SA nanoparticles arrayed on surface randomly and make high roughness to obtain high CA. TiO₂@4-ABA/SA nanoparticles were ~26.8 nm in average size and have a nanometric roughness for switchable SHS figure 4. Ability to oil-water separation considered for TiO₂@4-ABA/SA coated sponge substrates for toluene-water, p-xylol-water, n-hexane-water and dichloromethane-water mixture in various pH (2.0–7.0) of the water phase. The separation process has been done for 10 times and the separation efficiency evaluated for them as the main parameter. As shown in figure 5, the separation process for organic phases showed the close dependence on the pH of the water phase and subsequently the WCA of the surface. According to the results, at pH (7.0) the desired separation efficiency occurred for dichloromethane-water (~97%), p-xylol-water (~94%), n-hexane-water (~98%) and toluene-water (~98%). Moreover, maximum separation efficiencies for dichloromethane-water (~90%), p-xylol-water (~94%), n-hexane-water (~94%) and toluene-water (~97%) have been repeated at pH (2.0–3.0). This finding attributed to the pH-responsivity of the TiO₂@4-ABA/SA and low interaction between organic phases and TiO₂@4-ABA/SA deposited sponge surface. Not only at pH (7.0) the surface separated the organic phase from the water phase, but also at pH (2.0–3.0) the pH-responsivity made the surface stable and switchable.
more hydrophilic and prevents from the organic phase penetration into the modified sponge, while the water phase completely absorbed.

Results obviously showed effect of pH on the separation efficiency. Although increasing in pH of water phase up to 6.0 enhanced the surface CA and separation efficiency significantly, decreasing in pH made the surface more hydrophilic and oleophobic. Low separation efficiency at pH (4.0–6.0) could relate their proportional amount of CA that causes the simultaneous interaction of the organic and water phases with TiO$_2$@4-ABA/SA. Therefore, pH-responsivity and superhydrophobicity of the TiO$_2$@4-ABA/SA with a synergetic effect represented unique interfacial properties for oil-water separation application.

The SEM image of TiO$_2$@4-ABA/SA modified sponge surface was shown in figure 7. According to this, the average size of surface morphology was between 300–400 μm after deposition of TiO$_2$@4-ABA/SA. Deposition of TiO$_2$@4-ABA/SA on sponge caused to increase roughness of smooth sponge micropore and increased the CA. Different resolution of sponge micropores were shown in figures 7(A)–(D). While the organic phase

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**Figure 4.** Surface morphology of TiO$_2$@4-ABA/SA nanoparticle-based SHS.

**Figure 5.** The separation efficiency of (A) dichloromethane/water, (B) p-xylol-water, (C) n-hexanewater and (D) toluene-water versus pH with 10 times of measuring frequency.
absorbed in superhydrophobic sponge (Figure 6), water phase completely accumulated on sponge and the penetrated water into the modified sponge was in minimum amount. All in all, the TiO2@4-ABA/SA-based approach represented reliable properties to use in oil-water separation applications. Principally, the short time to achieve the surface wettability switching plays vital role to obtain high separation efficiency\[54\].

Microscopically, the packing density of the pH-responsive molecules, the kinetics of diimide FGs (de) protonation, desired molecular structure of the pH-responsive approach and mechanism of the wettability switching could be as the main parameters that influenced on the rate of the wettability switching and separation efficiency. For TiO2@4-ABA/SA approach, the 4-ABA and SA molecules with packing density equal to $\Gamma = \sim 4.5 \times 10^{-7}$ mol.cm$^{-2}$ on TiO2 nanoparticles not only represented switchability in wettability of the surface ($\sim 5$ s for each cycle of switchability of surface wettability), but also enhanced the separation efficiency. In one hand, the packing density of the 4-ABA molecules could increase the rate of the pH-responsivity at pH (2.0–3.0). On the other hand, hydrophobic alkyl tails of the SA molecules could facilitate the water molecules rejection from the surface at pH (7.0) and using this mechanism made the surface more efficient for oil-water separation. The kinetics of diimide FGs (de)protonation as second impressive factor in oil-water separation could relate to molecular structure and position of the diimide FGs in behind of the anthracene ring. Therefore,
all of these parameters despaired to foment on conditions to make the TiO$_2$@4-ABA/SA as an efficient approach for oil-water separation.

AFM images showed that $R_a$ for TiO$_2$@4-ABA/SA samples in various pH changed slowly. As shown in figure 8 slow increase in $R_a$ results stable morphological structure of the samples during increasing pH and switchability process.

5. Conclusions

In the present study, a pH-responsive SHS approach (CA = $\sim 152.39^\circ$, $H < 10^\circ$) developed based on (E)-4-(anthracen-9-yl-diazenyl) benzoic acid (4-ABA) pH-responsive organic molecules and stearic acid (SA) (TiO$_2$@4-ABA/SA) using self-assembly method for oil-water separation applications. The mentioned approach used for separation of the toluene-water, $p$-xylol-water, $n$-hexane-water and dichloromethane-water mixture. The results showed that the TiO$_2$@4-ABA/SA approach with broad pH-responsivity is an appropriate option for oil water separation in broad range of pH (2.0–7.0). In one hand, the superhydrophobicity of this approach

![Figure 8. $R_a$ versus pH for TiO$_2$@4-ABA/SA sample during switching process and their AFM images.](image)
showed a high separation efficiency for dichloromethane-water (~97%), p-xylol-water (~94%), n-hexane-water (~98%) and toluene-water (~98%) at pH (7.0). Additionally, at pH (2.0–3.0) the pH-responsivity of the surface which was obtained from diimide FGs of the 4-ABA molecules made it possible to create the positive charges and caused to more hydrophilicity of the surface and subsequently resulted high separation efficiencies for dichloromethane-water (~90%), p-xylol-water (~94%), n-hexane-water (~94%) and toluene-water (~97%). DFT calculation studies showed the stable absorption of the 4-ABA molecules on TiO2 nanoparticles (~ >1.3 eV) that relied on the reusability (>20 cycles) of surface during oil-water separation. Rate of wettability switching (~5 s per cycle), reversible transition between superhydrophobic (CA = ~152.39° at pH = 7.0) and hydrophilic (CA = ~26.11° at pH = 2.0–3.0) states are the other advantages which have been obtained from molecular structure of 4-ABA, different charges of the surface in various pH that make this oil–water separation approach more talent to represents high separation efficiency. Therefore, the 4-ABA molecules-based pH-responsive SHS with ability in adjusting the surface wettability could be a highly potent candidate for oil-water separation applications.

Acknowledgments

The authors would like to acknowledge the Iran University of Science and Technology and Maragheh University’s financial and instrumental supports.

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References

[1] Chen K et al 2017 Transparent smart surface with pH-induced wettability transition between superhydrophobicity and underwater superoleophobicity Mater. Des. 135 69–76
[2] Liu Y et al 2016 Reversibly switchable wettability on aluminum alloy substrate corresponding to different pH droplet and its corrosion resistance Chem. Eng. J. 303 565–74
[3] Ding D et al 2018 Underwater superoleophobic-underoil superhydrophobic janus ceramic membrane with its switchable separation in oil/water emulsions J. Membr. Sci. 565 303–10
[4] Ichimura K, Oh S-K and Nakagawa M 2000 Light-driven motion of liquids on a photoresponsive surface Science 288 1624–6
[5] Auernheimer J et al 2005 Photoswitched cell adhesion on surfaces with RGD peptides JACS 127 16107–10
[6] Liu D et al 2009 Using azobenzene-embedded self-assembled monolayers to photochemically control cell adhesion reversibly Angew. Chem. Int. Ed. 48 84106–8
[7] Stoll R S and Hecht S 2009 Immobilization of a photoswitchable piperidine base Org. Lett. 11 4790–3
[8] Smalii K et al 2010 High on—off conductance switching ratio in optically-driven self-assembled conjugated molecular systems ACS Nano 4 2411–21
[9] Sun Q et al 2016 Superhydrophobicity: constructing homogeneous catalysts into superhydrophobic porous frameworks to protect them from hydrolytic degradation Chem 1 628–39
[10] Liu F et al 2012 Tramsesterification catalyzed by ionic liquids on superhydrophobic mesoporous polymers: heterogeneous catalysts that are faster than homogeneous catalysts JACS 134 16948–50
[11] Eivazadeh-Keihan R et al 2019 Recent advances in the application of mesoporous silica-based nanomaterials for bone tissue engineering Materials Science and Engineering: C 107 110267
[12] Eivazadeh-Keihan R et al 2019 Carbon based nanomaterials for tissue engineering of bone: building new bone on small black scaffolds: a review J. Adv. Res. 18 185–201
[13] Chenab K K et al 2019 Biomedical applications of nanoflakes: targeted intracellular fluorescence probes Nanomed. Nanotechnol. Biol. Med. 17 342–38
[14] Xu L et al 2015 Electrochemically tunable cell adsorption on a transparent and adhesion-switchable superhydrophobic polythiophene film Macromol. Rapid Commun. 36 1265–10
[15] Jokinen V et al 2018 Superhydrophobic blood-repellent surfaces Adv. Mater. 30 1705104
[16] Khammohammadi Chenab K, Sohrabi B and Rahmazadeh A 2019 Superhydrophobicity: advanced biological and biomedical applications Biomaterials Science 7 3110–37
[17] Khammohammadi Chenab K et al 2018 Biological applications of bacterial nano-surface layers: a brief overview Nanomedicine Journal 5 62–6
[18] Xu T et al 2018 Superwettable electrochemical biosensor toward detection of cancer biomarkers ACS Sensors 3 72–8
[19] Eivazadeh-Keihan R et al 2019 Dengue virus: a review on advances in detection and trends—from conventional methods to novel biosensors Microchem. Acta 186 329
[20] Yin B, Liu T and Yin Y 2012 Prolonging the duration of preventing bacterial adhesion of nanosilver-containing polymer films through hydrophobicity Langmuir 28 17019–25
[21] Bartlet K et al 2018 Antibacterial activity on superhydrophobic titania nanotube arrays Colloids Surf. B 166 179–86
[22] Sohrabi B et al 2013 Investigation of DNA–cationic bolaform surfactants interaction with different spacer length Colloids Surf. B 110 29–35
[23] Hua Z et al 2013 Transparent surface with reversibly switchable wettability between superhydrophobicity and superhydrophilicity Langmuir 29 10307–12
[24] Kreder M J et al 2016 Design of anti-icing surfaces: smooth, textured or slippery? Nature Reviews Materials 1 15003
[25] Mishchenko L et al 2010 Design of ice-free nanostructured surfaces based on repulsion of impacting water droplets ACS Nano 4 7699–707
[26] Wang Y et al 2013 Verification of icedophobic/anti-icing properties of a superhydrophobic surface ACS Applied Materials & Interfaces 5 3370–81
[27] Hu C et al 2013 Micro-/nanometer rough structure of a superhydrophobic biodegradable coating by electrospaying for initial anti-bioadhesion Adv. Healthcare Mater. 2 1314–21
[28] Huang T-C et al 2017 Advanced superhydrophobic electroactive fluorinated polyimide and its application in anticorrosion coating Int. J. Green Energy 14 1113–20
[29] Alexander S et al 2015 Branched hydrocarbon low surface energy materials for superhydrophobic nanoparticle derived surfaces ACS Applied Materials & Interfaces 8 860–6
[30] He Z et al 2011 Fabrication of a transparent superamphiphilic coating with improved stability Soft Matter 7 6435–43
[31] Elbert J et al 2013 Ferrocene polymers for switchable surface wettabilities Organometallics 32 5873–8
[32] Ju G, Cheng M and Shi F 2014 A pH-responsive smart surface for the continuous separation of oil/water/oil ternary mixtures NPG Asia Mater. 6 e11
[33] Ou R et al 2016 Robust thermoresponsive polymer composite membrane with switchable superhydrophilicity and superhydrophobicity for efficient oil–water separation Environmental Science & Technology 50 906–14
[34] Li X et al 2014 Facile immobilization of Ag nanocluster on nanofibrous membrane for oil/water separation ACS Applied Materials & Interfaces 6 15272–82
[35] Gui X et al 2010 Carbon nanotube sponges Adv. Mater. 22 617–21
[36] Li J-J, Zhou Y-N and Luo Z-H 2015 Smart fiber membrane for pH-induced oil/water separation ACS Applied Materials & Interfaces 7 19643–50
[37] Zhang Y et al 2009 Superhydrophobic nanoporous polymers as efficient adsorbents for organic compounds Nano Today 4 135–42
[38] Xue Z et al 2011 A novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for oil/water separation Adv. Mater. 23 4270–3
[39] Wang L et al 2017 Controllable cyanation of carbon–hydrogen bonds by zeolite crystals over manganese oxide catalyst Nat. Commun. 8 15240
[40] Yang S et al 2018 Vapor–liquid deposition strategy to prepare superhydrophobic and superoleophilic graphene aerogel for oil–water separation ACS Applied Nano Materials 1 531–40
[41] Delley B 1990 An all-electron numerical method for solving the local density functional for polyatomic molecules J. Chem. Phys. 92 508–17
[42] Delley B 2000 From molecules to solids with the DMol 3 approach J. Chem. Phys. 113 7756–64
[43] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865
[44] Grimme S 2004 Accurate description of van der Waals complexes by density functional theory including empirical corrections J. Comput. Chem. 25 1463–73
[45] Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction J. Comput. Chem. 27 1787–99
[46] Delley B 2002 Hardness conserving semilocal pseudopotentials Phys. Rev. B 66 155125
[47] Skholdov V and et al 1997 Structure of nanocrystalline TiO2 powders and precursor to their highly efficient photosensitizer Chem. Mater. 9 430–9
[48] Kusama H, Orita H and Sugihara H 2008 TiO2; band shift by nitrogen-containing heterocycles in dye-sensitized solar cells: a periodic density functional theory study Langmuir 24 4411–9
[49] Prajapati P et al 2017 Density functional theory study of adsorption geometries and electronic structures of azo-dye-based molecules on anatase TiO2 surface for dye-sensitized solar cell applications J. Mol. Graphics Modell. 76 551–61
[50] Khammohammadi K, Sohrabi B and Meyman M Z 2018 Effect of electron-donating and-withdrawing substitutions in naphthoquinone sensitizers: the structure engineering of dyes for DSSCs J. Mol. Struct. 1167 274–9
[51] Khammohammadi Chenab K et al 2019 Naphthoquinone derivative-based dye for dye-sensitized solar cells: experimental and computational aspects Mater. Res. Express 6 085537
[52] Bawa R A, Alazraide E M and Ben N N 2013 Synthesis and electric conductivity study of the new azo dye 4-(9-anthrylazo) phenol Int. J. Journal of Engineering Research and Application 3 1–5
[53] Cao Y et al 2014 Thermo and pH dual-responsive materials for controllable oil/water separation ACS Applied Materials & Interfaces 6 2026–30
[54] Guo F and Guo Z 2016 Inspired smart materials with external stimuli responsive wettability: a review RSC Adv. 6 36623–41