Dual-switchable surfaces between hydrophobic and superhydrophobic fabricated by the combination of click chemistry and RAFT

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Abstract. A dual-switchable surface between hydrophobic and superhydrophobic has been fabricated successfully by combining reversible addition-fragmentation chain transfer polymerization (RAFT) polymeric technology and thiol-NCO click chemistry. Well-defined block copolymer, poly(7-(6-(acryloyloxy) hexyloxy) coumarin)-*b*-poly(N-Isopropylacryl amide), was synthesized by RAFT, and then the block copolymer was grafted onto the surface of SiO₂ modified by toluene diisocyanate (TDI) via thiol-NCO click chemistry. The results of nuclear magnetic resonance (NMR) and Fourier Transform Infrared (FTIR) spectroscopies confirmed that the block copolymer (Number average molecular weight (M_n) = 9400, polydispersity index (PDI) = 1.22) has been synthesized successfully. The static contact angle (CA) of the surface prepared by SiO₂/P (7-6-AC)-*b*-PNIPAAm switches from 98±2 to 137±2° by adjusting the temperature. Furthermore, the contact angle can also oscillate between 137±2 and 157±2° on the irradiation of UV light at 365 and 254 nm, respectively. The dual-switchable surfaces exhibit high stability between hydrophilicity and superhydrophobicity. Therefore, the method provides a new method to fabricate the dual-stimuli-responsive surface with tunable wettability, reversible switching, and also be easily extended to other dual-responsive surfaces. This ability to control the wettability by the adjustment of the temperature and UV light has applications in a broad range of fields.

Keywords: polymer composites, superhydrophobic surface, photo-sensitive, thermal-sensitive, click chemistry

1. Introduction

The wetting properties of superhydrophobic surfaces have received worldwide and tremendous attention [1] since the dual hierarchical structure of the lotus leaf was discovered [2]. Lotus-Leaf-like superhydrophobic surfaces, exhibit an amazing property for not only being wetted by water leading to a self-cleaning effect [3], but also for their great advantages in applications. In recent years, superhydrophobic surfaces are widely used in the human body implant materials [4], microfluidic tools [5], Calix azacrown [6], tunable optical lenses [7], lab-on-chip systems [8]. The wettability of the surface

is influenced by its chemical composition and morphology [9], because chemical composition determines the surface free energy, and a lower surface energy leads to higher hydrophobicity. Additionally, the hierarchical structure (micro roughness covered with nano roughness) was not only necessary for a high contact angle (CA) but essential for the stability of the water-solid and water-air interfaces [10] (the composite interface). For example, Wang *et al.* [11] prepared cauliflower-like silica nanospheres with tunable wettability through regulating chemical compositions. The chemical etching method [12] used to prepare the superhydrophobic CuO

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surfaces with tunable adhesion by controlling the etching time to control the morphology. However, these reports mainly focused on realizing controllable wettability by different means, rather than the reversibility and did not consider the transition of the reversible.

Functional surfaces with controlled wetting properties responsive to external stimuli become more attractive for both the scientific interest and the practical application due to the wide range of their potential applications. A variety of approaches including appropriate external stimuli [13], and exchange of counterions [14] can dynamically trigger the reversible wettability conversion. The external stimuli-responsive superhydrophobic materials have been intensively studied, and many positive results have also been obtained [15]. External stimuli, such as light illumination [16], temperature [17], curvature driven [18], ion pairs driven [19], pH [20], can change the surface conformation or morphology of stimuli-sensitive materials, thus resulting in the change of wettability. However, most of these wetting surfaces are responsive to only single stimulus, such as temperature, optical or electric field, and this may be the limitation in many important practical applications with complex environments, such as biological devices, which often need the surface can respond to more than one stimulus simultaneously [21]. It is, therefore, desirable to design dual- or multiresponsive surfaces to meet with the needs of double or multi-stimulation in complex environments.

Multiple functional and responsive surfaces with special wettability and reversible properties, especially thermal-sensitive and photo-sensitive surfaces, have an extensive range of application in many important fields [22–24]. Recently, several thermally, pH, or optically responsive smart interfacial materials that can switch between superhydrophilicity and superhydrophobicity or hydrophobicity and superhydrophobicity have been reported [25–27]. For the responsive superhydrophobic surfaces, it is necessary to graft some responsive groups, onto the surface of inorganic materials or organic compounds for example, a temperature-responsive polymer poly (N-isopropyl acrylamide (PNIPAAm) [28], reversible pH-responsive group [29], photosensitive materials [30], such as spiropyran [31], coumarin [32] and azobenzene [33, 34]. Therefore, grafting functional group or polymer with a responsive group onto the

inorganic sphere surface to construct multi-responsive superhydrophobic materials is a feasible method, and the most effective method to achieve the goal is the click chemistry [35] which can fabricate the core-shell structure. Additionally, it is convenient to tune the surface roughness by controlling click reaction cycles [35, 36] to obtain hierarchical structures with different sizes of SiO₂. Coumarin and its derivatives are one of the most common used to prepare for photo-sensitive materials, such as the superhydrophobic materials [32], which are potentially applied in biological and medical fields [37–39]. Reversible addition-fragmentation chain transfer polymerization (RAFT) is an effective method to synthesize living/controlled polymer and now have been applied in polymerizing PVAc [40], PHEMA [41], P4VP [42], PNIPAAm [43], PS [44] etc. The high degree of compatibility with a wide range of functional monomers and good tolerance of water and oxygen in the systems make RAFT technique has been widely used in the synthesis of functional polymers. For example, coumarin and its derivatives have been successfully grafted onto the chain of polymer by living free radical polymerization [45, 46].

In this work, we report a method for the fabrication of photo- and thermal-sensitive superhydrophobic surface by the combination of RAFT and click chemistry, resulting in that the block polymers are grafted onto the surface of silica nanosphere. The strategies in our work not only improve the grafting rate between the organic group and inorganic materials by click chemistry (thiol-NCO), but also increase the stability of the superhydrophobic materials. Moreover, the copolymers containing coumarin and N-isopropylacrylamide group can be easily synthesized by RAFT polymeric technology, and a superhydrophobic surface can be designed and constructed by using the multiple responsive block polymers which synthesized by RAFT polymeric technology. To the best of our knowledge, it is the first time to fabricate photo-sensitive and thermal-sensitive superhydrophobic surfaces by the combination of ‘click’ chemistry and RAFT polymeric technology, and graft the block polymer onto the silica surface. Therefore, it would provide a new pathway to fabricate multiple responsive superhydrophobic surfaces, and other responsive superhydrophobic surfaces can be designed and prepared by this method.

2. Experimental section

2.1. Materials

All the other chemicals were analytical grade and used as received without further purification. 7-Hydroxy coumarin (7-AC) was received from Ziyang Chemical Co. Ltd (Lianyungang, China). 1,6-dibromohexane, silica nanoparticle and N-Isopropylacrylamide (NIPAAm recrystallized twice from benzene/hexane) was purchased from Aladdin Co. Ltd. (Shanghai, China). 2-Cyanoprop-2-yl-dithiobenzoate (CPDB), N, N-dimethyl-formamide (DMF), petroleum ether and ethyl acetate were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Carbonic acid, ethanol, acrylic acid, potassium hydroxide, dibutyltin dilaurate (DBTDL), toluene di-isocyanate (TDI) and azodiisobutyronitrile (AIBN) were commercially available from Tianjin Damao Chemical Reagent Company (Tianjin, China), respectively.

2.2. Synthesis of 7-(6-bromohexyloxy) coumarin

The mixture of 7-hydroxy coumarin (10.0 g, 62 mmol) and excess 1,6-dibromohexane (45 g, 186 mmol) were dissolved in acetone (200 mL), then anhydrous K_2CO_3 (17.4 g, 124 mmol) was added into the flask. The resulted suspension was heated to reflux for 24 h. The precipitate was filtered off and extracted with acetone (3×100 mL). After the solvent was removed in reduced pressure, water was added, and used CH_2Cl_2 (3×200 mL) to extract the residue. The extract was dried with anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The product was then purified by means of column chromatography on silica oxide with mixed petroleum ether and ethyl acetate (5:1, v/v) as eluent, and resulted in a white solid after dried in vacuum drying oven (14.8 g, 74.3%). The synthesis route of 7-(6-bromohexyloxy) coumarin (7-6-BC) is shown in Figure 1a.

1H NMR($CDCl_3$): 7.65(d, 1H), 7.38(d, 1H), 6.82(d, 1H), 6.80(d, 1H), 4.02(t, 2H), 3.43(t, 2H), 1.90(m, 4H), 1.50(m, 4H).

2.3. Synthesis of 7-(6-(acryloyloxy) hexyloxy) coumarin

7-(6-bromohexyloxy) coumarin (5.8 g, 18 mmol) and excess potassium acrylate (30 g, 27 mmol) were dissolved in ethanol (150 mL). Hydroquinone (0.02 g,

1.8 mmol) was added. The solution was heated to reflux for 24 h. The precipitate was filtered off and extracted with ethanol (3×50 mL). After the solvent was removed in reduced pressure, water was added, and the residue was extracted with CH_2Cl_2 (3×100 mL). The residue was then purified by means of column chromatography on silica oxide with mixed petroleum ether and ethyl acetate (3:1, v/v) as an eluent and resulted in a white solid after dried in vacuum drying oven (4.6 g, 81.65%). The synthesis process of 7-(6-(acryloyloxy) hexyloxy) coumarin (7-6-AC) is presented in Figure 1b.

1H NMR($CDCl_3$): 7.65(d, 1H), 7.37(d, 1H), 6.80(m, 2H), 6.41(d, 1H), 6.26(d, 1H), 6.18(m, 1H), 5.82(t, 1H), 4.20(t, 2H), 4.03(t, 2H), 1.83(m, 2H), 1.65(m, 2H), 1.5(m, 4H).

2.4. Polymerization of 7-(6-(acryloyloxy) hexyloxy) coumarin by RAFT

A dry ampoule was filled with 7-(6-(acryloyloxy) hexyloxy) coumarin (0.5 g, 1.58 mmol), AIBN (1.3 mg, 0.0079 mmol), CPDB (8.75 mg, 0.0395 mmol), and N,N-dimethylformamide (DMF) (1.5 mL). The Schlenk line was used to keep the ampoule vacuum and filled with nitrogen. Then, the ampoule was placed in an oil bath at the desired temperature to polymerize. At timed intervals, the ampoule was immersed into icy water and then opened. The suspension liquid in the ampoule was dissolved in 2 mL of tetrahydrofuran (THF) and precipitated into a 200 mL of methanol. The polymer was obtained by centrifuge at the speed of 15 000 rpm and dried at room temperature. The synthesis process of poly7-(6-(acryloyloxy) hexyloxy) coumarin (P(7-6-AC)) is presented in Figure 1c.

2.5. Synthesis of P(7-6-AC)-*b*-PNIPAAm

P7-6-AC (0.1 mmol, $M_n = 8300$), AIBN (5.47 mg, 0.033 mmol), NIPAAm (1.13 g, 10 mmol) were placed in an ampoule (The volume fraction of block copolymer was 30:10), the schlenk line was used to keep the ampoule vacuum and fill with nitrogen, and the process must be repeated at least 3 times or more. Then DMF (1.5 mL) was added into the ampoule by syringe. The ampoule was placed in an oil bath at the desired temperature. At timed intervals, the suspension liquid in the ampoule was poured into 200 mL of methanol. The polymer was obtained by the centrifuge at the speed of 15 000 rpm and dried

at room temperature. The scheme and structure for the synthesis of P(7-6-AC)-*b*-PNIPAAm are described in Figure 1d.

2.6. Reduction of the end group of P(7-6-AC)-*b*-PNIPAAm

The P(7-6-AC)-*b*-PNIPAAm (0.5 g, $M_n = 9400$) was dissolved in THF (10 mL), then the NaBH_4 (114 mg, 3 mmol) was added into the solution by three times very slowly, stirring for 30 min under ice salt bath, and the exhaust system must be kept unobstructed. At last, the icy water was used to quench the activity of NaBH_4 . The solvent was extracted by CH_2Cl_2 (3×50 mL). Finally, CH_2Cl_2 was eliminated by rotating distillation, and solid samples were dried in vacuum at 35°C overnight. The synthetic route is shown in Figure 1e.

2.7. Decoration of silica with toluene diisocyanate

Silica nanosphere (14 nm) should be activated in a vacuum drying oven at 110°C overnight, then the silica (0.4 g) was dispersed evenly in ethyl acetate (120 mL) by ultrasonic cleaner, then DBTDL (0.5 mL) and TDI (2 mL) were appended in the reaction system, the flask was placed into an oil bath and heated to 60°C for 6 h under the nitrogen atmos-

phere. The final product was separated at the speed of 4000 rpm in centrifuge. Then the products were dried overnight at 60°C . Schematic representation of the modified silica nanosphere with TDI is given in Figure 2a.

2.8. The grafting of P(7-6-AC)-*b*-PNIPAAm onto the surface of SiO_2

The reduced P(7-6-AC)-*b*-PNIPAAm (0.5 g) and silica modified with TDI (0.1 g) were dissolved in THF (50 mL). DBTDL (0.25 mg) as catalyst was added. The solution was heated to 40°C for 2 h under the nitrogen atmosphere. The SiO_2 /P(7-6-AC)-*b*-PNIPAAm was obtained after being centrifuged and dried. Schematic representation of the modified silica nanosphere with TDI is given in Figure 2b.

2.9. Preparation of the film to measure the contact angles

Silicon wafers were ultrasonically cleaned in water and acetone for 10 min, respectively. Then the as-prepared SiO_2 /P(7-6-AC)-*b*-PNIPAAm dispersions were coated on the silicon wafer, and dried at room temperature for 24 h. The static water contact angles were measured with deionized water ($4 \mu\text{L}$) on a contact angle goniometer (JC2001) instrument at room

Figure 1. The scheme and structure for the synthesis of (a) 7-(6-bromohexyloxy) coumarin, (b) 7-(6-(acryloyloxy) hexyloxy) coumarin, (c) poly 7-(6-(acryloyloxy) hexyloxy) coumarin, (d) P(7-6-AC)-*b*-PNIPAAm, and (e) the reduction of the end group of P(7-6-AC)-*b*-PNIPAAm

Figure 2. Synthesis route of (a) silica nanosphere modified with TDI, and (b) SiO₂/P(7-6-AC)-*b*-PNIPAAm

temperature. The contact angles were measured at three different points for each sample surface, and the average values were reported here. The static water contact angles were further measured after the irradiation of UV light at 365 and 254 nm, respectively.

2.10. Characterization

The morphologies of functional silica particles were observed using transmission electron microscope (TEM) (JEOL JEM-2000EXII, Japan). FT-IR analysis was used to confirm the TDI functionalized SiO₂ particles and P(7-6-AC)-*b*-PNIPAAm grafted with SiO₂ particles. All FT-IR spectra were recorded at room temperature on a Magna-IR 760 (Nicolet, USA) spectrometer using 32 scans at an instrument resolution of 4 cm⁻¹. Ultraviolet spectrophotometer (Lambda 35, Perkin Elmer, Germany) was used to confirm the copolymer successfully grafted with functionalized SiO₂ and the transformation of absorbance under 365 and 254 nm UV irradiation. Thermal gravimetric analysis (TGA) (TGA 7, Perkin Elmer, Germany) was performed to analyze the weight-loss percent of the organic component. The particles were heated from 20 to 600°C at the heating rate of 10°C/min under nitrogen atmosphere with the rate of 50 mL/min. And the Attension Theta Lite (Attension, Finland) was used to measure the contact angle of the SiO₂ particles as prepared.

3. Results and discussion

3.1. Preparation of P(7-6-AC)-*b*-PNIPAAm by RAFT

The structures of 7-6-AC, P(7-6-AC) and P(7-6-AC)-*b*-PNIPAAm were characterized by ¹H NMR. The ¹H NMR spectra of the 7-6-AC, P(7-6-AC) and P(7-6-AC)-*b*-PNIPAAm are shown in Figure 3, respectively. Compared with 7-6-AC (Figure 3a), the signals (5.84, 6.23 and 6.40 ppm (CH₂=CH-)) of P(7-6-AC) disappear in Figure 3b. It clearly demonstrates that the double bond in the long chain has been polymerized. In Figure 3c, the new signal (7.95 ppm (O=C-N-H)) could be assigned to the amide group in the repeat unit of PNIPAAm structure introduced into P(7-6-AC)-*b*-PNIPAAm. The signals of ppm = 6.2, ppm = 6.6, ppm = 6.8, ppm = 7.3, ppm = 7.6 were attributed to the coumarin group in 7-6-AC, P(7-6-AC) and P(7-6-AC)-*b*-PNIPAAm. All the results indicate that the P(7-6-AC)-*b*-PNIPAAm with the end group which can easily restore to sulfhydryl has been synthesized successfully. The P(7-6-AC) (*M*_n = 8100 g/mol, PDI = 1.17) as the macro-RAFT agent, which reacted with NIPAAm to obtain the block polymer. Gel permeation chromatographic (GPC) curves (Figure 4) demonstrates that there was an increase in the molecular weights (from 8100 to 9400 g/mol) after chain extension. However, the value of PDI increases from 1.17 to 1.22 with the chain extension of the polymer. The

Figure 3. ^1H NMR spectra of (a) 7-6-AC, (b) P(7-6-AC) and (c) P(7-6-AC)-*b*-PNIPAAm

increase can be due to the increase of the block and the molecular weight of the P(7-6-AC)-*b*-PNIPAAm.

Figure 4. GPC curves of the original macro-RAFT agent P(7-6-AC) and the chain extended block copolymer P(7-6-AC)-*b*-PNIPAAm in THF solution

3.2. Fabrication of

$\text{SiO}_2/\text{P(7-6-AC)-}b\text{-PNIPAAm}$ composites

Figure 5 presents the FT-IR spectra (I), contact angles (II) and TGA profile (III) of (a) pure SiO_2 , (b) SiO_2/TDI and (c) $\text{SiO}_2/\text{P(7-6-AC)-}b\text{-PNIPAAm}$, respectively. In Figure 5(I) a, the peaks at 1105 cm^{-1} and the shoulder part between the bands of $1100\text{--}1300\text{ cm}^{-1}$ correspond to the concerted (Si–O–Si) stretches. Compared with the spectra of pure SiO_2 , the intensity of the peak at 2276 cm^{-1} (Figure 5(I)b) corresponded to the characteristic absorption peak of –NCO group, and the typical benzene ring absorption bands at $1500\text{--}1600\text{ cm}^{-1}$ are clearly found, implying that the TDI has been grafted successfully onto the surface of SiO_2 . The absorption peak of 3167 cm^{-1} in Figure 5(I)c demonstrate the existence of amide group, and the absorption appearing at 974 cm^{-1} implies that the –CH–CH₂– groups existed on the surface of SiO_2 nanosphere. These results suggest that P(7-6-AC)-*b*-PNIPAAm has been successfully grafted onto the surface of SiO_2 nanosphere by RAFT and thiol-NCO click chemistry.

Figure 5. The FT-IR spectra (I), contact angles (II) and TGA (III) profile of (a) pure SiO₂, (b) SiO₂/TDI and (c) SiO₂/P(7-6-AC)-b-PNIPAAm, respectively

Moreover, the typical absorption of the cyclic lactones group appears at 1762 cm⁻¹, which further demonstrated that the SiO₂/P(7-6-AC)-b-PNIPAAm composites were synthesized. the characteristic absorptions at 2929 and 2840 cm⁻¹ are assigned to the vibration of -CH₂- groups, the correlative peak of -CH₃ group, and the peaks at 1470, 1380, 720 cm⁻¹ can be assigned to the out-of-plane and in plane bending vibration of -CH₃ group. Additionally, the absorption peak at 2276 cm⁻¹ (Figure 5(I)c) can be attributed to the residual -NCO groups remaining on the surface of SiO₂/TDI, which did not react with -SH. The results can also be considered to the identification of the SiO₂/P(7-6-AC)-b-PNIPAAm by the TEM images, which show a core-shell structure.

In Figure 5(II), the contact angles of SiO₂, SiO₂/TDI and SiO₂/P(7-6-AC)-b-PNIPAAm were 29±2, 58±2 and 98±2°, respectively. The results imply that the wettability has been changed after the modification of TDI and P(7-6-AC)-b-PNIPAAm on the surface of SiO₂. Low contact angles (29±2°) of pure SiO₂ can be explained by the fact that many hydrophilic groups (hydroxyl groups) covered on the pure SiO₂ surface. As for SiO₂/TDI, the contact angles increases up to 58±2° for the hydrophobic group of TDI on the surface of SiO₂, which further demonstrated that PDI has been grafted on SiO₂. The sulfhydryl group on P(7-6-AC)-b-PNIPAAm as the terminal group can react with the portion of -NCO group on SiO₂/TDI surface. Therefore, the SiO₂ particles covered with -NCO group and P(7-6-AC)-b-PNIPAAm possess a higher hydrophobic surface and higher contact angles, and the high contact angle (98±2°) was primarily attributed to P(7-6-AC)-b-PNIPAAm, which own lower surface energy than inorganic molecule.

The thermal behavior of the SiO₂, SiO₂/TDI and SiO₂/P(7-6-AC)-b-PNIPAAm was investigated by TGA in N₂ for comparison, which serves to confirm the percentage of the particles surrounding by organic phase. Figure 5(III) shows the TGA analysis of the bare SiO₂, SiO₂-PDI, and SiO₂-P(7-6-AC)-b-PNIPAAm. As shown in Figure 5(III)a, the main temperature regions of weight loss appear in the interval 400–500°C, which can be assigned to the dehydration condensation reaction of the hydroxyl on the silica surface, and the chemical reaction equations can be expressed as Equation (1) [47]:

Figure 5(III)b, 5(III)c describes the thermal behavior of SiO₂/TDI and SiO₂-P(7-6-AC)-b-PNIPAAm, The results show the weight loss with 4.73% of SiO₂/TDI and SiO₂-P(7-6-AC)-b-PNIPAAm was 27.2, 41.1%, respectively, and the peak pyrolysis temperatures of SiO₂/TDI and SiO₂-P(7-6-AC)-b-PNIPAAm are 291.4 and 349.4°C. According to the reference [48], the surface grafting density of SiO₂-TDI and SiO₂-P(7-6-AC)-b-PNIPAAm was calculated to be about 1.29 mmol/g (0.222 g/g) and 0.02 mmol/g (0.188 g/g) respectively. Obviously, the graft density obtained from ‘click chemistry’ is higher than that of the traditional and classic method [49, 50], for example SiO₂ surface silanization using silane coupling agent.

3.3. The responsive switch of

SiO₂/P(7-6-AC)-b-PNIPAAm composites

It is well known that the properties of the block polymer determined by the different ratio of its two blocks. In P(7-6-AC)-b-PNIPAAm, the first block

P(7-6-AC) may cause the cross-linking because of the existence of coumarin group. If the ratio of the coumarin block too high, the PDI will out of 1.2 and the cross-linking of the coumarin will change the property of the polymer. For the second block, because of strong hydrophilicity of the amido group, the high ratio of the NIPAAm will enhance the hydrophilicity and the contact angles of the prepared nanoparticles will less than 150° . On the other hand, while the ratio is too low, the thermal-sensitive features are not obvious. In fact, a variety of block polymers with different block unit, such as 10, 15, 20, 25, 30, 50 polymerization units, have been synthesized. The thermal-sensitive characteristics and the contact angles of the $\text{SiO}_2/\text{P}(7-6\text{-AC})\text{-}b\text{-PNIPAAm}$ composites with different ratio of P(7-6-AC) and PNIPAAm is summarized in Table 1. Finally, we choose the largest molecular weight in PDI under

1.2 as the target product ($M_n = 8100$, $\text{PDI} = 1.17$, 25 units) to graft onto the surface of silica nanosphere. The photoresponse of the prepared $\text{SiO}_2/\text{P}(7-6\text{-AC})\text{-}b\text{-PNIPAAm}$ was monitored by UV-Vis spectra by the exposure of the clear dilute suspension of $\text{SiO}_2/\text{P}(7-6\text{-AC})\text{-}b\text{-PNIPAAm}$ in THF under different wavelengths (365 and 254 nm) of UV light. As illustrated in Figure 6a and the absorbed intensity of

Table 1. The thermal-sensitive characteristics and the contact angles of the $\text{SiO}_2/\text{P}(7-6\text{-AC})\text{-}b\text{-PNIPAAm}$ composites with different ratio of P(7-6-AC) and PNIPAAm

The ratio of P(7-6-AC) and PNIPAAm	The thermal-sensitive characteristics	The contact angles of the prepared nanoparticles
30:5	Not obvious	$159 \pm 2^\circ$
30:10	Obvious	$157 \pm 2^\circ$
30:20	Obvious	$148 \pm 2^\circ$
30:30	Obvious	$141 \pm 2^\circ$

Figure 6. The absorbance at 320 nm according to the exposure time under the irradiation of 356 nm (a) and the subsequent irradiation at $\lambda = 254$ nm (b); TEM images of the prepared $\text{SiO}_2/\text{P}(7-6\text{-AC})\text{-}b\text{-PNIPAAm}$ (c) and its aggregations (d) under 365 nm irradiation

coumarin at 320 nm (characteristic absorption peak) decreases continuously with the exposure time under UV irradiation at 365 nm (Figure 6b). To the contrast, the absorbance at 320 nm starts to increase for the photocleavage of coumarin after exposure under the irradiation of 254 nm UV light (Figure 6b) [51]. This interconversion between hydrophobic and superhydrophobic can attributed to the reversible photodimerization and photocleavage of the coumarin group on $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ under UV irradiation at different wavelengths.

The reversible photodimerization and photocleavage of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ are also studied by TEM. As presented in Figure 6c, a well-defined core-shell structure (20–30 nm) with SiO_2 nanospheres as core and block polymer as shell has been observed. It suggested that the SiO_2 particles were surrounded by $\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ with a thickness of about 3 nm. Moreover, the silica nanoparticles modified by $\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ is dispersive spherical particle with the size of 50 nm before the exposure of UV light. On the contrary, the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ nanoparticle aggregated after the irradiation of UV light (365 nm), and the size of the aggregations increased up to 300 nm, suggesting that $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ have been cross-linked together by the photodimerization of the coumarin under UV light at 365 nm irradiation (Figure 6d).

Figure 7 shows AFM and SEM images of the single and aggregations of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$. Compared with the results of TEM, the aggregations of the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ were also observed by AFM and SEM (Figure 7b and 7d) [52]. On Figure 7a, we can find that the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ disperse with each other, but at the irradiation of 365 nm, the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ aggregate together (Figure 7b), which can be due to the photodimerization of the coumarin groups. Therefore, we can find the same result on the SEM images (Figure 7c and Figure 7d). And a great number of cavities have also been constructed among the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ in the process of the UV irradiation at 365 nm.

The agglomeration of the prepared $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ caused by temperature and UV light are also investigated by dynamic light scattering (DLS). Figure 8b shows the size of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ based on DLS results changed with temperature and the UV irradiation at 365 nm. As shown

in Figure 8a, the radius of hydration of the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ were about 50 nm, while the temperature rises to 35°C, the radius of hydration increases up to 90 nm. The results indicate that the block polymer around the silica nanosphere is responsible for temperature, and the formation of the aggregates changed with temperature. Compared with the original $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ nanosphere, when the temperature rise to 35°C, the size of the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ nanosphere is up to 90 from 50 nm. On the other hand, the size of the $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ nanosphere after the UV irradiation at 365 nm is up to 350 nm (25°C) from 50 nm, and further increased to 530 nm after the temperature rising to 35°C (Figure 8b), which can be attributed to the crosslinking of the coumarin after photodimerization. The data of DLS are consistent with the results of TEM, and it also shows the same results with the images of atomic force microscope (AFM).

The mechanism of photo-sensitive and thermal-sensitive of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ is proposed in Figure 9. The photodimerization of the coumarins is the primary factor for photo-sensitivity, and the formation of cyclobutane rings ($[2\pi + 2\pi]$ s cycloaddition) (Figure 9a) leads to the aggregation of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$, which will be further illustrated by TEM. In general, there are two main mechanisms for the explanation of the thermal-sensitivity of PNIPAAm. One is the change of the temperature leading to the change of the polymer structure transition from linear structure to a nearly spherical structure [53]. Another one is the formation and rupture of the hydrogen bonds [54]. In $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$, we think that the thermal-sensitivity can be mostly attributed to the formation and rupture of hydrogen bonds between water and amide (Figure 9b). It is favorable for the formation of hydrogen bonds between the water molecules and amide bond under low temperature, while the hydrogen bonds are broken under high temperature.

In general, contact angle (CA) is used to estimate the wettability of a solid surface. Figure 10 describes the changes of contact angles and the reversible wettability transitions of the surface of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ on glass slide by alternating the temperature and UV irradiations at the wavelengths of 365 and 254 nm. Obviously, the SiO_2 particles grafted with block polymer exhibit the hydrophobic behavior ($\text{CA} = 98 \pm 2^\circ$ Figure 10 a) below the lower criti-

Figure 7. The AFM (a, b) and SEM (c, d) images of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ upon 254 and 365 nm UV light irradiation, respectively

Figure 8. The size distribution of $\text{SiO}_2/\text{P}(7\text{-}6\text{-AC})\text{-}b\text{-PNIPAAm}$ nanoparticles (a) UV light at 254 nm and (b) UV light at 365 nm

cal solution temperature ($\text{LCST} = 32^\circ\text{C}$). However, the CA increased evidently to $137 \pm 2^\circ$ (Figure 10b) when the temperature was up to 40°C , and the con-

tact angle can further increase once again to $157 \pm 2^\circ$ (Figure 10d) after UV irradiation at 365 nm, which shows the superhydrophobic property. On the other

Figure 9. The mechanism for photoreaction and thermal-sensitive of the SiO₂/P(7-6-AC)-b-PNIPAAm: (a) photodimerization of coumarin, (b) the thermal-sensitive mechanism of PNIPAAm, (c) the morphological characteristics of the prepared nanoparticles under different UV irradiation

Figure 10. The changes of contact angles (a)–(d) and the reversible wettability transitions (e) of the surface of SiO₂/P(7-6-AC)-b-PNIPAAm particles on glass slide by alternating the temperature and UV irradiations at the wavelengths of 365 and 254 nm. The interval time of each cycle is five days.

hand, we change the order of the stimulation, first irradiating at 365 nm and then heating to 40°C, the same result (157±2°) can be obtained. It is noted that the superhydrophobic surface can return to the orig-

inal state by changing temperature (143±2°) and using UV irradiations at the wavelengths of 254 nm. The results suggest that the surface with the reversible wettability transitions properties has been acquired

by SiO₂/P(7-6-AC)-*b*-PNIPAAm particles. To explore the thermal-sensitive and photo-sensitive behavior of the surface, cycles between hydrophobic and superhydrophobic are shown in Figure 10e. We repeatedly irradiated the particle surface with alternating UV light at 365 and 254 nm, heating and cooling, and measured the value of the CA as shown in Figure 10e. These results prove that the surface wettability can be reversibly tuned for several cycles. The results show excellent reversibility and a quick transformation between hydrophobicity and superhydrophobicity. Each cycle lasts only several minutes. It was reported that PNIPAAm [55] shows its LCST at 32°C in aqueous solution. The hydrogen bond is formed between the water and N-isopropylacrylamide group when the temperature under the LCST, and it will display the hydrophilic properties. Upon heating, the predominantly intermolecular hydrogen bonding between the PNIPAAm chains and water molecules, which contributes to the hydrophilicity and relaxed PNIPAAm chains, is replaced by intramolecular hydrogen bonding between C=O and N–H groups along the PNIPAAm chains. This results in compact and collapsed chains that interact minimally with water and thus exhibit hydrophobicity. (Figure 6b).

N-isopropylacrylamide group becomes exposed and leads to a low surface free energy and large water CAs, and the surface showed the hydrophobic property. Oppositely, the hydrogen bond is formed between water and amide, shown its hydrophilicity of as prepared SiO₂ particles at the temperature lower than 32°C. The photo-sensitive behavior of the surface can be mainly attributed to the coumarin group in the block polymer. At the irradiation of 365 nm, the coumarin groups crosslink with each other and form the disordered structure surrounding the silica.

The TEM results (Figure 6c) have demonstrated that a well-defined core-shell structure with SiO₂ as core and block polymer as shell had been constructed. Therefore, the particles convert into a series of aggregations and the air trapping forming among the aggregations at the same time after UV irradiation at 365 nm, which will result in the construction of the hierarchical structure [56].

According to the results observed from AFM and SEM images (Figure 8), the surface can be constructed a hierarchical structure for the formation of a series of branched and rugby-ball-like nanoparti-

cles, which indicates that this hierarchical structure has the largest roughness. On the other hand, 7-(6-(acryloyloxy) hexyloxy) coumarin possess a lower surface energy for the alkyl chains, which may affect the hydrophobic property of the coatings. As for the thermal-sensitivity, the oxygen groups on the prepared nanoparticles may be wrapped with alkyl chains and be trapped between particles after 365 nm UV irradiation to avoid forming hydrogen bonds with water. As a result, the CA increases with irradiation time. After photocleavage of the dimers, there is no chemical bonding between the prepared nanoparticles, and water molecules interact with oxygen groups by forming hydrogen bonds to decrease the CA.

The Wenzel and Cassie mode can explain well why the surface switches from hydrophobicity to superhydrophobicity after the irradiation of UV at 365 nm. And it also demonstrates that the mutual transformation between Wenzel model and Cassie model can be occurred via UV irradiation. The Wenzel model can also be used to explain the static contact angle. As described by Wenzel's Equation (2) [57]:

$$\cos\theta = r\cos\theta_Y \quad (2)$$

where r is the roughness coefficient and the θ_Y is the static contact angle calculated by Young's equation. After the 365 nm UV irradiation, the rough surface comes into contact with water, air trapping in the rough area may occur, which would contribute greatly to the increase of hydrophobicity. By now, because of the air trapping in the trough area, the Cassie model was used to calculate the static contact angle. The Cassie's equation can be described by Equation (3):

$$\cos\theta = f\cos\theta_Y - (1-f) \quad (3)$$

where f is the fraction of the liquid–solid interface, while $(1-f)$ is the air–liquid interface. And the air trapping would contribute greatly to the increase of hydrophobicity.

4. Conclusions

In conclusion, a stable superhydrophobic surface with thermal- and photo-sensitivity was fabricated successfully by a facile approach which combined technology of RAFT with click-chemistry. The SiO₂ particles as prepared form the air trapping by the photoisomerization of coumarin groups under 365 nm UV irradiation along with the Wenzel Cassie

transition, and the formation and rupture of hydrogen bond between amide and water were controlled by the changing of temperature, all resulting in the CA changing from 98 ± 2 to $157\pm 2^\circ$. The repeated experiments of the CA changing indicate that the surface wettability can be transformed between hydrophobicity to superhydrophobicity reversibly, indicating that the surface has good stability. This novel method using RAFT technology to synthesize multiple responsive block polymers will be widely used in fabricating multiple responsive superhydrophobic surfaces. The multiple responsive superhydrophobic surfaces have great potential application in the controlled release of drugs fields and the fabrication of responsive switches.

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