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Switchable Pickering Emulsions Stabilized by Awakened TiO_2 Nanoparticle Emulsifiers Using UV/Dark Actuation

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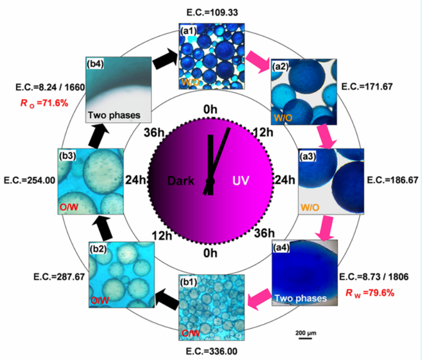
S *Supporting Information*

ABSTRACT: In this work, switchable Pickering emulsions that utilize UV/dark manipulation employ a type of smart TiO_2 nanoparticle as emulsifiers. The emulsifiers can be awakened when needed via UV-induced degradation of grafted silanes on TiO_2 nanoparticles. By tuning the surface wettability of TiO_2 nanoparticles *in situ* via UV/dark actuation, emulsions stabilized by the nanoparticles can be reversibly switched between the water-in-oil (W/O) type and oil-in-water (O/W) type for several cycles. Due to the convertible wettability, the smart nanoparticle emulsifiers can be settled in either the oil phase or the water phase as desired during phase separation, making it convenient for recycling. The present work provides a facile and noninvasive method to freely manipulate the formation, breakage, and switching of the emulsion; this method has promising potential as a powerful technique for use in energy-efficient and environmentally friendly industries.



KEYWORDS: *pickering emulsions, inversion, nanoparticles, wettability, UV/dark actuation*

1. INTRODUCTION

Many industrial applications that rely on emulsions would benefit from an efficient method of forming/breaking emulsions at a specific desired stage,[1] including emulsion polymerization,[2] bioreaction and bioseparation in microemulsions,[3,4] functional polymer microspheres fabrication,[5] cleaning of oily stains,[6] viscous oil transportation through pipelines,[7] oil recovery,[8] and removal of oily makeup cosmetics.[9] In these applications, emulsions can typically assist certain processes, while they are undesired in others; e.g., they may hinder the separation of components.[1] Accordingly, in the past two decades, temporary emulsions stabilized by convertible emulsifiers have attracted much attention due to their numerous industrial applications,[10,11] for which the emulsions must only temporarily be stabilized and subsequently demulsified. A key challenge in such applications is the development of recyclable and green emulsifiers for which the type of emulsions can be switched and the emulsions can be formed and broken with fine control as desired.

Recently, the so-called Pickering emulsion, which refers to an emulsion that is stabilized solely by solid particles, has aroused great interest. The adsorption of densely packed particles at the oil−water interface is driven by the total interfacial energy decrease,[12] offering the robust and reproducible characteristics of Pickering emulsions.[13] Compared with classical molecular surfactants, particle emulsifiers are recyclable and require lower consumption. More importantly, by using different types of solid particles that are responsive to different environmental stimuli, on-demand switchable emulsions can be prepared. In previous literature reports, many stimuli-responsive Pickering emulsions were proposed, such as those that respond to changes in pH,[14] temperature,[15] CO_2/N_2,[13] magnetic-field intensity,[16] or a specific ion concentration[17] as well as to dual stimuli, including pH−temperature,[18] magnetic-field intensity−temperature,[19] and pH−ionic strength.[20] However, most of the available approaches are actuated using an invasive method, usually by changing the environment of the systems, which can have a direct effect on the sensitive components, thereby restricting their use in certain practical applications. In contrast, a neat and contactless external stimulus, such as a light-driven approach, would be preferred.[21] To the best of our knowledge, only Chen et al. have used photochromic spiropyrans conjugated upconversion nanophosphors[22] to achieve the reversible inversion of a light-triggered Pickering emulsion; nevertheless, multistep synthesis is inevitable.

The type and stability of a Pickering emulsion is believed to be determined in some way by the wettability of its particle emulsifiers.[23] Generally speaking, hydrophilic particles with an oil−water interface contact angle (CA, measured through the aqueous phase) smaller than 90° result in oil-in-water (O/W) emulsions, whereas hydrophobic particles with CA greater than 90° form water-in-oil (W/O) emulsions.[24] TiO_2 nanoparticle is a stable, low toxicity, and environmentally friendly material that is widely used in industrial applications. The surface wettability of TiO_2 nanoparticles can be reversibly converted by light actuation due to the adsorption and desorption of hydroxyl groups on their surfaces.[25−27] Interestingly, we found that such light-induced wettability conversion behavior of TiO_2 nano-

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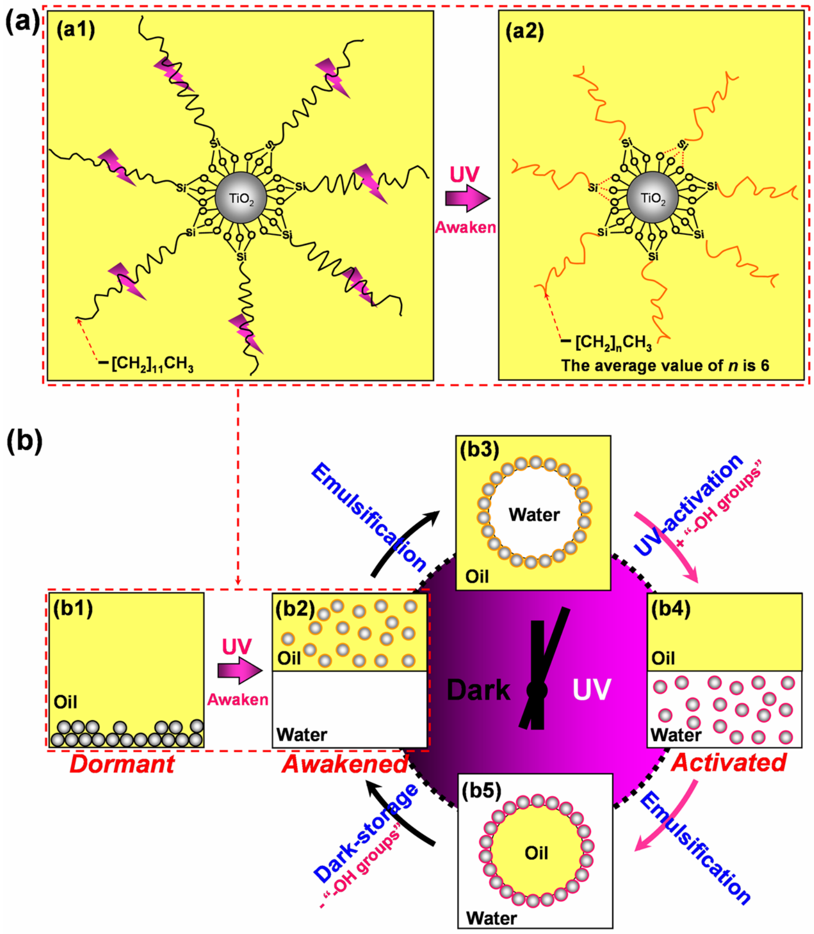

Figure 1. (a) Schematic representation of nanoparticle emulsifiers consisting of a TiO_2 core and a shell in which long-chain silanes (a1) are degraded to short-chain silanes (a2) via UV irradiation in hexane. (b) Schematic of the switchable Pickering emulsions using TiO_2 nanoparticle emulsifiers under UV/dark actuation: (b1) the dormant emulsifiers; (b2) the emulsifiers awakened via UV irradiation; (b3) the stabilized W/O type emulsions; (b4) coalescence and phase separation of the W/O emulsions in response to UV-activation; (b5) the stabilized O/W type emulsions and (b2) coalescence and phase separation of the W/O emulsions induced by dark storage. The oil is hexane.

particles can also be observed in a water−hexane solution system and anticipate that it could be used as an alternative stimuli-responsive pattern for the switch of emulsions.

In practical applications, the raw materials, including emulsifiers are usually fed in one batch for continuous production. Here, we report a novel type of smart-particle emulsifier that can be awakened on demand and the usage of such emulsifiers to control the formation, breakage, and conversion of Pickering emulsions *in situ* via UV/dark actuation. As shown in Figure 1, by applying UV-irradiation to a hexane solution, the long-chain silanes grafted onto the surface of TiO_2 particles (Figure 1a1) are degraded to short-chain silanes (Figure 1a2). Correspondingly, the wettability of TiO_2 nanoparticle emulsifier is converted from amphiphobicity (Figure 1b1: dormant form) to oleophilicity (Figure 1b2: awakened form), thereby enabling them to be able to stabilize W/O emulsions after homogenization (Figure 1b3). Once exposed to UV light, the TiO_2 nanoparticle surface becomes hydrophilic due to the adsorption of hydroxyl groups, leading to the coalescence of droplets and demulsification of the W/O emulsions until complete phase separation is achieved (Figure 1b4: activated form). Subsequently, the rehomogenization results in O/W emulsions (Figure 1b5). Storing the O/W emulsions in the dark, they become unstable and undergo a complete phase separation (Figure 1b2) as a result of the recovery of the hydrophobicity of the TiO_2 nanoparticle surface, where the hydroxyl groups are desorbed. By tuning the surface wettability of TiO_2 nanoparticles *in situ* with an alternation of UV irradiation and dark storage, the emulsions stabilized by the nanoparticles can be reversibly switched. Furthermore, these smart-particle emulsifiers can be settled in either the oil or water phase as desired, during phase separation, making them convenient for recycling.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercially available tetrabutyl titanate (TBOT) was used as the hydrolysis precursor. Glacial acetic acid, hexane, hydrogen peroxide (30 wt %), methylene blue, and anhydrous ethanol were purchased from the Chengdu Kelong Chemical Reagents Co., Ltd. Trichlorododecylsilane (($C_{12}H_{25}SiCl_3$), Tokyo KaSei Industry Co., Ltd., Japan) was used for amphiphobic modification. Deionized water was utilized in the experiments. All of the chemical agents were of analytical grade and used directly without further purification.

2.2. Preparation of TiO_2 Nanoparticles. TiO_2 nanoparticles were prepared using the hydrothermal synthesis method. Nine mL of TBOT, which was dissolved in 36 mL of ethanol, was reacted with 52 mL of an aqueous 0.013 M acetic acid solution at room temperature. Vigorous stirring was required during the entire process until the reaction solution became transparent. The reaction solution was placed into a Teflon-lined autoclave of 150 mL capacity. Next, the autoclave was sealed in a stainless steel tank and maintained at 150 °C for 2 h without shaking or stirring during heating. After the autoclave was naturally cooled to room temperature, the resulting suspension was centrifuged, and then, the precipitate was thoroughly washed three times with ethanol. The solvent was removed by centrifugation after each washing step. The collected products were dried at 60 °C for 12 h. Finally, the products were calcinated at 500 °C for 30 min to convert to uniform anatase TiO_2 nanoparticles with diameters of ∼30 nm.

2.3. Preparation of Dormant/Awakened TiO_2 Emulsifiers. The prepared TiO_2 nanoparticles were mixed with 20 mL of a 30 wt % hydrogen peroxide solution that resulted in a homogeneous and transparent yellow suspended mass. The mixture was stirred for 4 h in the dark and finally dried in air at 45 °C to gain hydroxylated TiO_2 nanoparticles. The long-chain silane grafted TiO_2 nanoparticles were prepared by treating the above fabricated hydroxylated TiO_2 nanoparticles with a trichlorododecylsilane solution (1 mL of trichlorododecylsilane in 20 mL of hexane). The mixture was stirred for 12 h at room temperature and then dried in air at 50 °C to produce dormant TiO_2 nanoparticle emulsifiers. Next, the emulsifiers immersed in hexane were stirred and irradiated using a UV lamp (λ = 254 nm, WFH-203 three-function ultraviolet analyzer, 12 W, China) at a vertical distance of 10−15 cm. The awakened TiO_2 emulsifiers were obtained after a UV illumination period of 24 h.

2.4. Reversible Phase Inversion of the Pickering Emulsions. In the oil phase, the awakened TiO_2 emulsifiers (3 wt %) were immersed in 10 mL of hexane with ultrasonic treatment to obtain a solution with good dispersion. In the water phase, deionized water or methylene blue solution (pH = 3, 5 wt ‰) was used. Next, the oil phase was added to the water phase; following homogenization for approximately 1 min, W/O emulsions were obtained. The W/O emulsions were exposed to UV light (λ = 254 nm) for 36 h until complete phase separation occurred, and then, the mixture was homogenized to achieve inversed O/W emulsions. Storage of the O/W emulsions in the dark for 36 h resulted in phase separation again, and then, the mixture was rehomogenized back to W/O emulsions. By repeating this sequence several times, stable emulsions were readily obtained.

2.5. Recycling of TiO_2 Nanoparticle Emulsifiers. When the emulsions were broken and completely separated, the two phases were dried, and then, their respective residues were weighed. In this way, the TiO_2 nanoparticle emulsifiers were recycled and used to evaluate the recycling rate according to the following eqs 1 and 2:

$$R_W = \frac{B_{Water}}{A} \times 100\% \tag{1}$$

$$R_O = \frac{B_{Oil}}{A} \times 100\% \tag{2}$$

where R_W and R_O are the percent recovery (%) of TiO_2 nanoparticle emulsifiers in the water and oil phases, A is the initial mass of the emulsifiers (g), and B_{Water} and B_{Oil} are the masses of the emulsifiers collected in the recycling process in the water and oil phases, respectively.

2.6. Evaluation of the Surface Wettability of the Emulsifiers during the Cycles of UV-Activation and Dark-Storage. The reversible and reproducible wettability of the prepared TiO_2 nanoparticle emulsifiers was determined by recording their water CA values using a CA instrument (DSA100, Krüss, Germany) using a standard video camera. A slide glass was dipped into the hexane solution of the awakened emulsifiers (3 wt %), blown with a stream of nitrogen, and then dried under atmosphere. Three μL of water droplets was utilized to measure the CA value of the coated surface. By treating the coated slide glass with UV irradiation and dark storage in turn, as described above, the CA values of different emulsifier forms were measured. For each sample, the average CA value was obtained from a minimum of five measurements.

2.7. Characterization Techniques. X-ray photoelectron spectroscopy (XPS, XSAM800, KRATOS, UK) and Fourier transform infrared (FTIR, IR Prestige-21, Shimadzu, Japan) spectroscopy were used to verify the surface chemistry of TiO_2 nanoparticle emulsifiers during the preparation process. The FTIR specimens were prepared using the KBr disc technique. Conductivity measurement (Mettler-Toledo Instruments Co., Switzerland) was used to determine the emulsion type and stability during the reversible phase inversion processes. The emulsion droplet size distributions were examined by optical microscopy after the emulsions had been equilibrated at 25 °C for 1 h. All of the droplets were viewed using an XSP-24 (Phoenix Co., Ltd., China) research microscope fitted with a Moticam 2000 camera. The images were captured using Motic Images Plus 2.0 software and then processed and analyzed using Image Pro Plus software.

3. RESULTS AND DISCUSSION

FTIR spectral analysis is performed to determine the surface functional groups of TiO_2 nanoparticle emulsifiers during the preparation process. The spectrum of hydroxylated TiO_2 nanoparticles (Figure 2a) shows the typical absorption bands of the hydroxyl group at 3395 cm^{-1} and of the Ti−OH group at 1650 cm^{-1}. In contrast, the spectrum of long-chain silane grafted TiO_2 nanoparticles (Figure 2b) shows a remarkable reduction of the peaks at 3395 and 1650 cm^{-1}, which indicates that most of the hydroxyl groups have reacted with trichlorododecylsilane. In addition, the appearance of the peaks at 2921−2853 and 1035−1125 cm^{-1} are attributed to aliphatic $-CH_3$ and $-CH_2$ and Si−O−Ti stretching vibrations, respectively, suggesting the grafting of long-chain silane onto the TiO_2 nanoparticle surface. After UV-irradiation, the intensity of the peaks at 2921−2853 cm^{-1} decreases (Figure 2c), suggesting that the grafted long-chain silanes are degraded to shorter silanes at the surface of the TiO_2 nanoparticles.

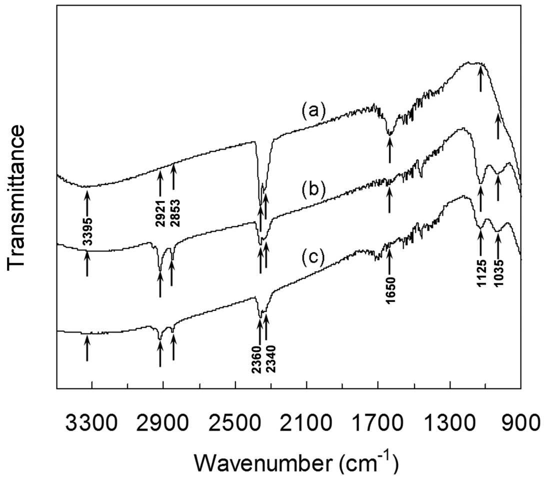

Figure 2. FT-IR spectra of hydroxylated (a), long-chain silane grafted (b), and short-chain silane grafted (c) TiO_2 nanoparticles.

XPS measurements are performed to investigate the surface chemical composition on both the long-chain (a, c, and e) and short-chain (b, d, and f) silane grafted onto TiO_2 nanoparticles. As shown in Figure 3a,b, the obvious decrease of the Si 2p peak (102.4 eV) suggests the UV-induced breakage of certain Si−O bonds. Comparing Figure 3c,d, the C 1s peak at 284.7 eV becomes weaker, revealing the decrease of the amount of the carbon element. Estimated from the XPS studies, the number of carbon atoms per silane at the degraded TiO_2 nanoparticles is approximately 7. In contrast, in Figure 3e, the decrease of Si−O O 1s (532.2 eV) and the increase of Ti−O O 1s (530.2 eV) are clearly observed in Figure 3f, which can be attributed to the UV-induced breakage of some Si−O bonds and hence to the

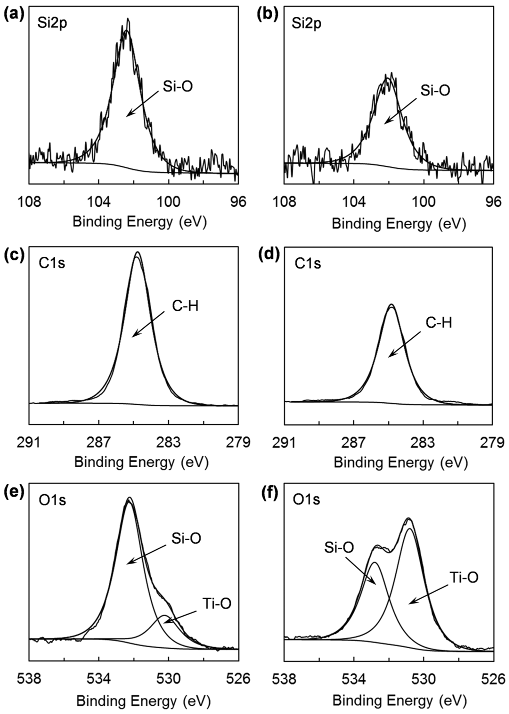

Figure 3. XPS spectra of long-chain silane grafted (a, c, and e) and short-chain silane grafted (b, d, and f) TiO_2 nanoparticles.

exposure of Ti—O bonds. Considering both the FTIR and XPS results, we speculate that a UV-induced degradation of grafted silanes occurs, resulting in shorter silanes with approximately 7 carbons.

In the photocatalytic degradation process of silanes grafted TiO_2 nanoparticles, when the adsorption of a photon with energy is equal to or larger than TiO_2 band gap, it will lead to the generation of holes and electrons.[25] Most of these holes and electrons self-recombine immediately, but some of them can separate and migrate to the TiO_2 surface. The trapped holes then react with hydroxyl groups or water dissolved with a minor mount in hexane to generate hydroxyl radicals; at the same time, the photogenerated electrons react with dissolved molecular oxygen in hexane to produce superoxide radical anion and other further reactive oxygen species. Both the highly active hydroxyl radicals and oxygen species contribute to the photocatalytic degradation of organic long-chain silanes grafted on TiO_2 surfaces.

Figure 4 shows the effect of the surface chemistry of the TiO_2 nanoparticles on emulsifier form and Pickering emulsion inversion. Initially, the long-chain silane grafted TiO_2 nanoparticles (Figure 4a) are dispersed in hexane with vigorous stirring. Due to their amphiphobic characteristics, the nanoparticles are unable to be wetted by hexane or water (Figure 4b) and thus are unable to stabilize emulsions; such nanoparticle emulsifiers are denoted as the "dormant" form. UV irradiation is used to awaken dormant emulsifiers *in situ*, on the basis of the degradation of the grafted long-chain silanes, into short ones (Figure 4c); such nanoparticle emulsifiers are denoted as the "awakened" form. These awakened emulsifiers show good dispersion in hexane (Figure 4d) due to their structural similarity (silane-grafted with approximately 7 carbons) with the solvent. After homogenization for only 1 min, W/O emulsions stabilized by the awakened emulsifiers are obtained with a mean droplet diameter of ~200 μm (Figure 4e,f), and they exhibited no evidence of phase separation for several weeks. Interestingly, if the emulsions are treated with UV irradiation, they gradually coalesce and separate into two layers, presumably as a result of the UV-induced adsorption of hydroxyl groups on the surface of TiO_2 emulsifiers ("activated" form). After rehomogenization in the presence of the activated emulsifiers, O/W emulsions are formed with a similar droplet diameter (Figure 4g,h). Subsequently, storage of the O/W emulsions in the dark leads to emulsion inversion back to W/O emulsions due to the loss of the surface hydroxyl groups of the TiO_2 emulsifiers. More importantly, this reversible switching between the W/O and O/W emulsions is reproducible over 4 cycles. These results indicate that the surface chemistry tuning of TiO_2 nanoparticles plays a critical role in the entire process.

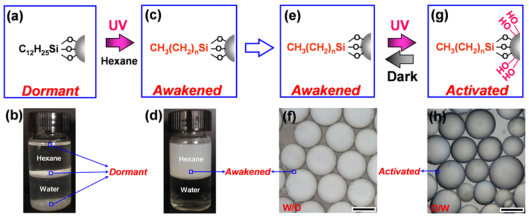

Figure 4. Schematic diagrams and images of emulsifier awaken and emulsion inversion based on surface chemistry tuning of TiO_2 nanoparticles. (a, b) The long-chain silane grafted TiO_2 nanoparticles are dormant and located at the hexane/water interface; (c, d) short-chain silane grafted TiO_2 nanoparticles as awakened emulsifiers disperse in hexane; (e, f) W/O emulsions stabilized by the awakened emulsifiers; (g, h) O/W emulsions stabilized by the activated emulsifiers. The scale bar is 200 μm, and the average value of n is 6.

It is well-known that TiO_2 possesses two inherent photo-induced properties, photocatalytic degradation and photo-induced wettability switch.[25] On the one hand, in the "awaken" process of TiO_2 emulsifiers, the trichlorododecylsilane grafted on TiO_2 nanoparticles are degraded into short-chain silanes by UV irradiation. On the other hand, in the UV/dark process, phase inversion of emulsions is a result of wettability switch of TiO_2 nanoparticles due to the adsorption/desorption of hydroxyl groups.[27] In addition, to determine whether the short-chain silanes continue to degrade to the shorter ones in the later UV/dark process, additional XPS tests are employed to detect the element composition of the TiO_2 nanoparticle surface before (Figure S1a), after one (Figure S1b), and after two (Figure S1c) UV/dark cycles, as well as the corresponding element contents (Figure S1d). The results indicate a slight degradation of the short-chain silanes on the surface of TiO_2 nanoparticle after two cycles. Theoretically, the shorter the alkyl chain, the higher is the required UV energy for it's degradation.

To better demonstrate the capabilities of the switchable Pickering emulsions, methylene blue, a cationic dye, is used (pH = 3 and 5 wt ‰) to distinguish the water and hexane phases in the micrographs. As shown in Figure 5a, the blue water phase is observed in the droplets and the W/O type emulsions can be clearly identified, with a mean droplet diameter of ~200 μm. Significantly, the W/O emulsions with high internal ionic strength remain stable for at least 4 weeks. Upon UV irritation, reversed O/W type emulsions are formed, where the outer phase is blue (Figure 5b); after storage in the dark, the emulsions become W/O again. Figure 5c,d shows the corresponding interface schematics of the W/O and O/W type emulsions, respectively. It is difficult to directly test CA value at

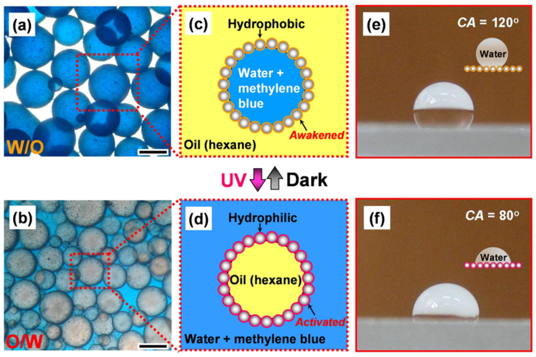

Figure 5. Optical micrographs (a, b) and interface schematics (c, d) of a UV/dark actuated emulsion inversion based on the wettability conversion (e, f) of the emulsifier surface; the scale bar is 200 μm.

the oil–water interface of the emulsifiers in our study because they are nanoparticles and absorbed at the interface of the emulsion. The wettability of particle emulsifiers was quantified in terms of water CA. Figure 5e,f show two CA images of coated surfaces with different forms of emulsifiers. The awakened emulsifiers are hydrophobic, with a CA value of 120°, acting as emulsifiers for W/O emulsions. In contrast, the CA value of the activated emulsifiers decreases to 80°, which is relatively hydrophilic, thereby stabilizing the O/W emulsions.[28] Although TiO_2 nanoparticles are known for their UV-induced reversible wettability conversion, utilizing this property in an emulsion system is, to our knowledge, unprecedented. In addition, the experimental results of the hydrophobic/hydrophilic transition on TiO_2 nanoparticles are well consistent with our speculation that surface chemistry tuning (adsorption or desorption of hydroxyl groups) dominates the change of emulsifier form via UV/dark actuation.

To illustrate the process of a reversible emulsions switch, a diagram exhibiting a 72 h-cycle is shown in Figure 6 in detail. Microscopy images are utilized to reveal the morphology of the emulsions, and the electrical conductivity (E.C.) measurement is used to determine the emulsion type[29] during phase inversion. In addition, the nanoparticle emulsifiers are recycled and their recycling rate is assessed. During 36 h of UV activation, a remarkable size increase of W/O droplets is observed, with mean diameters changing from 200 to 1000 μm which is the result of the coalescence of emulsions due to the hydrophilic transition of the emulsifiers.[30,31] This result is further supported by the E.C. measurement of Pickering emulsions: as the values of the continuous oil phase rise from 109.33 to 186.67 $\mu S \cdot cm^{-1}$, an increasing instability of the W/O emulsions is revealed (Figure 6a1–a3). After UV treatment for 36 h, the emulsions rupture and separate into two layers. The E.C. values of the oil and water phases are 8.73 and 1806 $\mu S \cdot cm^{-1}$, respectively. As expected, most of the emulsifiers are dissolved in water due to their hydrophilicity, and the percent recovery from water (R_W) is 79.6% (Figure 6a4). During the dark treatment, the size of the O/W droplets also increases, whereas the E.C. values of the continuous aqueous phase of the Pickering emulsions decrease from 336.00 to 254.00 $\mu S \cdot cm^{-1}$, both indicating the occurrence of the demulsification process (Figure 6b1–b3). After 36 h, two clear layers are observed, with the E.C. values of oil and water phases being 8.24 and 1660 $\mu S \cdot cm^{-1}$, respectively. At this time, the emulsifiers can be recycled from hexane with a R_O value of 71.6% (Figure 6b4). Even after 4 cycles, the R_W and R_O values remain close to their initial values, suggesting the effective recycling of the emulsifier in either the oil phase or the water phase, as desired, via UV/dark alternation.

TiO_2 is well-known as a UV photocatalyst, whether and to what extent it can degrade the components in solution mainly depends on the UV wavelength, intensity, and exposure time applied. According to the Langmuir–Hinshelwood mechanism,[32] the catalyst always prefers to react with the compounds grafted/absorbed at a catalyst surface to the components in solution. In our study, the energy of UV irradiation is utilized to degrade preferentially the long-chain silanes grafted on the surface of TiO_2 nanoparticles rather than the inert solvent hexane. In the subsequent UV/dark experiments, the emulsions can be reversibly switched between W/O and O/W type. This was ascribed to the photoreduction of surface Ti^{4+} to Ti^{3+} at definite sites,[27] leading to preferential adsorption of dissociative water (hydroxyl groups), and the dark storage resulted in the reversion of the surface wettability due to the desorption of the hydroxyl groups. What makes more sense is such a nonintrusive way to control the phase inversion of the emulsions under the designed UV condition.

The influence of the TiO_2 nanoparticle concentration ($C_{(NP)}$) on the mean diameters of droplets is shown in Figure 7. When $C_{(NP)}$ is below 1 wt %, no stable emulsion is formed (Figure 7a). Increasing the $C_{(NP)}$ from 1% to 5 wt % leads to

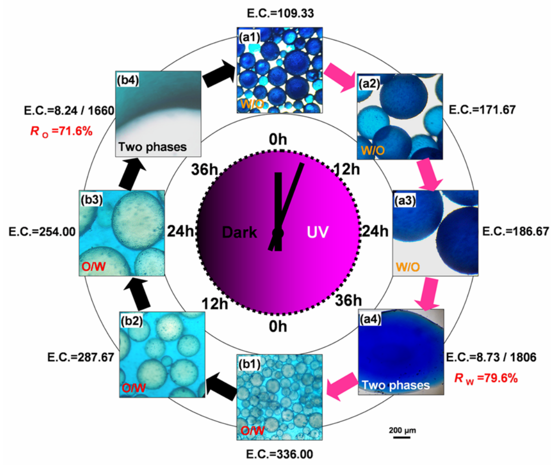

Figure 6. Optical micrographs of UV/dark alternation induced formation, breakage, and switching of Pickering emulsion cycles and the corresponding E.C. values ($\mu S \cdot cm^{-1}$): (a1–a4) treated with UV activation; (b1–b4) treated with dark storage.

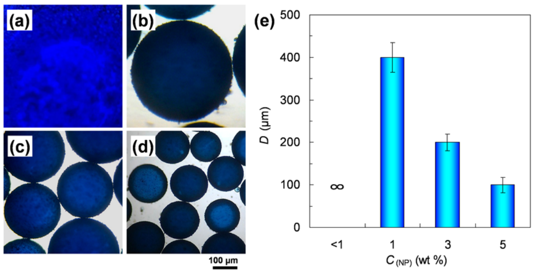

Figure 7. Optical microscopy images of emulsion droplets with varied TiO_2 nanoparticle concentrations; $C_{(NP)}$: (a) < 1%, (b) = 1%, (c) = 3%, and (d) = 5%. (e) Effect of $C_{(NP)}$ on the mean diameters of the emulsion droplets.

the formation of stable emulsions (Figure 7b–d) with decreasing diameters as illustrated in Figure 7e, which can be explained by the classical theory of limited coalescence.[31,33]

4. CONCLUSIONS

In summary, we presented a novel stimulus-responsive method that manipulates switchable Pickering emulsions in a facile manner using neat UV/dark as a trigger and smart TiO_2 nanoparticles as emulsifiers. By using *in situ* UV/dark treatment, the surface chemistry of the TiO_2 nanoparticles is tuned, resulting in the degradation of the grafted molecules to awaken the emulsifiers and enable the conversion of the wettability to guide the formation, breakage, and switching of emulsions as well as to enable the recycling of emulsifiers. As found in the experimental results, a high percent recovery of emulsifiers is obtained, even after 4 cycles of emulsions inversion. In addition, when varying the concentration of the emulsifiers, stable emulsion droplets with different diameters are easily obtained. In view of these characteristics, we expect that this UV/dark actuated switchable Pickering emulsion system will provide unique opportunities for energy-efficient and environmentally friendly industrial applications. Moreover, instead of UV light, visible light may be used as a trigger by means of element doping (e.g., doping with nitrogen or iron) in the TiO_2 nanoparticle emulsifiers; such visible light activation will benefit applications in life sciences and biology. Our group has been performing studies on such visible-light activated systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06808.

> The XPS results of the surface of the short-chain-grafted TiO_2 nanoparticles, after one UV/dark cycle, two UV/dark cycles, and the element contents of the TiO_2 nanoparticle surface (PDF)

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Notes

The authors declare no competing financial interest.

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