

Supporting Information

Synthesis of hydrophobic and hydrophilic TiO₂ nanofluids for transformable surface wettability and photoactive coating

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Author Contributions

J. H., Y. Z. L., Y. Q. T. and X. F. Z. did the experiments of synthesis and photocatalytic performance. X. Y. Y. conceived the project, provided the idea, and designed the experiments. X. F. Z., J. W. L. and L. Y. W. helped with the NMR measurements and corresponding analysis. B. L. S. conceived the project, and supported scientific and technological platform. C. J. and Y. L. revised the paper. J. H., T. Z., W. G. and X. Y. Y. wrote and revised the paper. All the authors discussed results and analyzed the data.

1. Experimental Section

1.1. Synthesis

1.1.1. Materials

Dimethyloctadecyl-[3-(trimethoxysilyl)propyl]ammonium chloride (DTSACl, 42 wt% in methyl alcohol, Sigma), poly(ethylene glycol) 4-nonylphenyl-3-sulfopropyl ether potassium salt (PEG-modified sulfonate salt, Aldrich), urea (>99%, Shanghai Test), $\text{Ti}(\text{SO}_4)_2$ (>96%, Shanghai Test), anhydrous ethanol (99.7%, Shanghai Test), methanol (99.7%, Shanghai Test), sodium hydroxide (99%, Shanghai Test), commercial titania (98%, Shanghai Test). All chemicals were used as obtained from commercial sources without further purification.

1.1.2. Synthesis and purification of nano TiO_2

In a typical synthesis,^{1,2} a mixture of 4.8 g urea and 9.6 g $\text{Ti}(\text{SO}_4)_2$ were dissolved in 80 mL of deionized H_2O , then transferred to a PTFE/Teflon lined autoclave. The autoclave was sealed and heated for 6 h at 180 °C. The obtained products were washed with deionized H_2O until the filtrate turned to neutral, and then dried in an oven at 60 °C for 12 h.

1.1.3. Synthesis and purification of $\text{TiO}_2\text{-C}_{18}$

3 g of nano- TiO_2 was dispersed in 25 mL of deionized H_2O and sonicated in a water-filled ultrasonic bath for 30 min. Then several drops of aqueous NaOH (10 wt %) were added to the solution with continuous stirring for 7 d. A mixture of 10 mL of dimethyloctadecyl-[3-(trimethoxysilyl)propyl]ammonium chloride in methanol (DTSACl) was added to the system. The resulting precipitate was aged for 12 h at ambient temperature, then centrifuged, washed three times with water and methanol in turns and dried at 70 °C for 24 h under vacuum. This sample was denoted as $\text{TiO}_2\text{-C}_{18}$.

1.1.4. Synthesis and purification of $\text{TiO}_2\text{-C}_{18}\text{-PEG}$

The obtained $\text{TiO}_2\text{-C}_{18}$ was reacted with 50mL of a 10.5% (w/v) aqueous PEG-modified sulfonate salt solution at 70 °C for 24 h. The product was isolated by

centrifugation, washed three times with water and ethanol in turns, dried at 70 °C for 2 d and subsequently placed under vacuum condition at ambient temperature for an additional day. TiO₂-C₁₈-PEG were obtained.

1.1.5. Preparation of TiO₂, TiO₂-C₁₈ and TiO₂-C₁₈-PEG glass coating

A glass slide (2*2 cm²) was washed three times with deionized water and ethanol, and dried at 50°C. The TiO₂, TiO₂-C₁₈ and TiO₂-C₁₈-PEG materials were coated on the surface of glass sheet by a drop coating method with their aqueous solutions (0.1 wt%). The coating was deposited at 50 °C for 12 h.

2. Characterization

2.1. General instruments and characterization

Transmission electron microscopy (TEM) were performed on a JEOLJEM-2100F with an acceleration voltage of 200 kV. X-ray diffraction (XRD) measurements were conducted on a Bruker D8-Advance X-ray diffractometer operating with Cu K α radiation ($\lambda=1.54056 \text{ \AA}$) over the 2θ range of 20-80°. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 80 V using KBr pellet technique in the range of 400-4000 cm⁻¹. Thermogravimetric analysis (TGA) of the as-fabricated materials was performed using a Labsys EvoS60/58458 thermal analysis instrument at a temperature ramping rate of 5 °C/min in air. Dynamic light scattering (DLS) data used to evaluate the agglomeration state of nanoparticles were recorded on a Malvern Nano-ZSZEN3600 zeta sizer. 1.5 mL freshly prepared solution (<0.1 wt%) was added into a high-quality quartz glass cuvette for DLS measurement at 37 °C. Zeta potential was measured using the electrophoretic light scattering (ELS) function in dilute (<0.1 wt%) water, ensuring conductivity of about 400 μS . The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of samples were recorded over the range of 280-650 nm using a UV-2550, Shimadzu (UV-vis spectrophotometer) equipped with an integrating sphere, and BaSO₄ was used as a reference. Scanning electron microscopy were performed on a Hitachi S-4800 with an acceleration voltage of 5 kV. The nanofluid's thermal conductivity was measured using a thermal property analyzer

based on the transient plane source method (Hot Disk (TPS 2500)) with conductivities between 0.005 and 20 W/mK. The modulus G' and G'' were measured at an angular frequency of $\omega = 1\text{s}^{-1}$ and with a strain amplitude of 50% in the temperature range from 32 to 100 °C. The water contact angle (CA) was measured using the sessile-drop method at ambient temperature by an optical contact angle meter (OCA 35, Dataphysics, Germany, water droplet is 2 μL). ^1H MAS NMR spectra were carried out in a 4.0 mm MAS probe on a Bruker AVANCE-III 500 spectrometer with a sample spinning rate of 12 kHz, a ^1H $\pi/2$ pulse length of 1.8 μs and a recycle delay of 5 s after being dehydrated in vacuum 10^{-3} Pa at 400 °C.

2.2. Photocatalytic activity evaluation

The photocatalytic activity of samples was estimated from the degradation of rhodamine B (RhB). In a 100 mL of RhB aqueous solution (1×10^{-5} mol/L), 0.01 g of catalyst was dispersed in a beaker, and the distance between the solution and the lamp was fixed at 10 cm. The suspension was stirred in the dark for 30 min to establish the adsorption/desorption equilibrium between the dye molecules and catalysts until the concentration of RhB no longer changed. As for the irradiation source, a 300 W xenon lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used in the experiment. The absorbance of the solution was recorded on a UV-vis absorption photometer (UV-2550, Shimadzu, Japan).

2.3. Water contact angle experiment

The water contact angle (CA) was measured by an optical contact angle meter (OCA 35, Dataphysics, Germany). The automated micro-syringe system released a 2 μL of water droplet on the glass or coatings surface (TiO_2 , $\text{TiO}_2\text{-C}_{18}$ and $\text{TiO}_2\text{-C}_{18}$ -PEG glass coating). The shapes of the droplets on the different substrates and corresponding partial wetting were recorded by using a camera. All the measurements were performed under ambient conditions (i.e. around 25 °C and 1 atm) and were completed within a few seconds to eliminate the effect of evaporation on the contact

angle measurements. The average values of water contact angle were obtained by measuring five different positions on the surface of the glass slide and coating. The standard deviation in the contact angle measurement is $\pm 2^\circ$.

Supporting Figures:

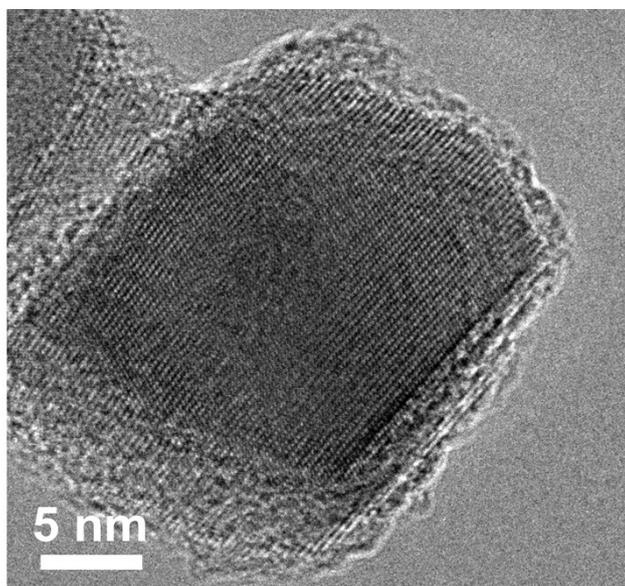


Fig. S1. TEM image of TiO₂-C₁₈.

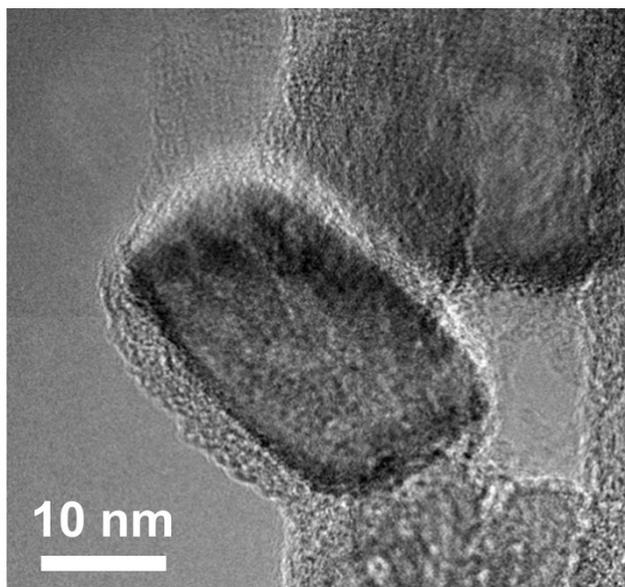


Fig. S2. TEM image of $\text{TiO}_2\text{-C}_{18}\text{-PEG}$.

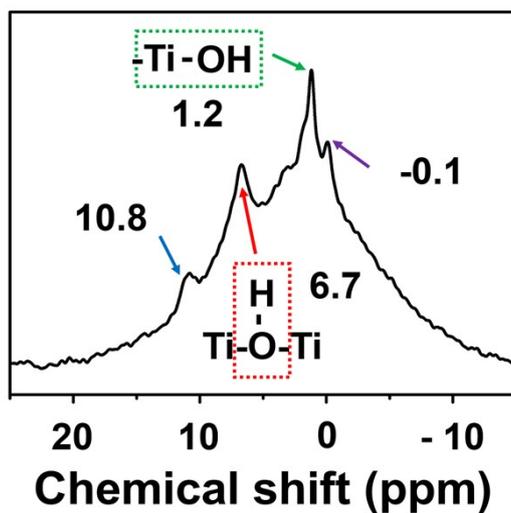


Fig. S3. ^1H MAS NMR of TiO_2 dehydrated in vacuum (10^{-3} Pa) at $400\text{ }^\circ\text{C}$. The ^1H MAS NMR spectrum of TiO_2 nanoparticles presents two strong peaks at 1.2 ppm and 6.7 ppm, which are attributed to the terminal Ti-OH and bridging Ti-O(H)-Ti , respectively.^{3,4} The signal at 10.8 ppm in the sample can be assigned to S-OH groups on the surface of the nanoparticles which contain a considerable amount of SO_4^{2-} .⁵ The bands at -0.1 ppm can be assigned to the signal of basic hydroxyls.⁶

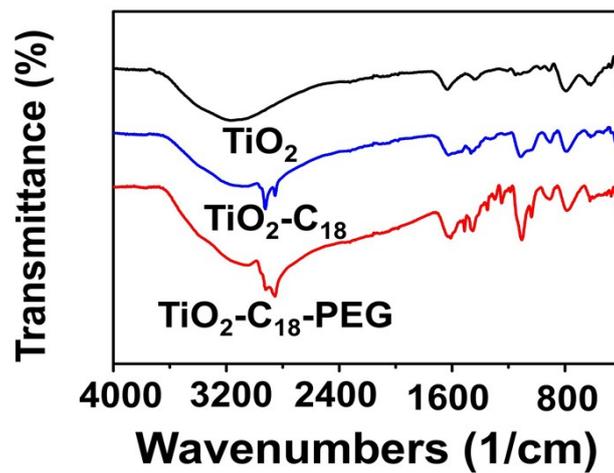


Fig. S4. FT-IR spectra of pure TiO_2 , $\text{TiO}_2\text{-C}_{18}$ and $\text{TiO}_2\text{-C}_{18}\text{-PEG}$ in the range of 4000-400 cm^{-1} .

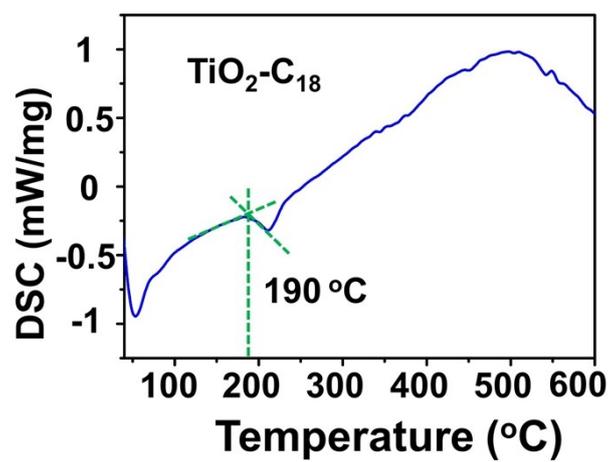


Fig. S5. DSC trace of $\text{TiO}_2\text{-C}_{18}$.

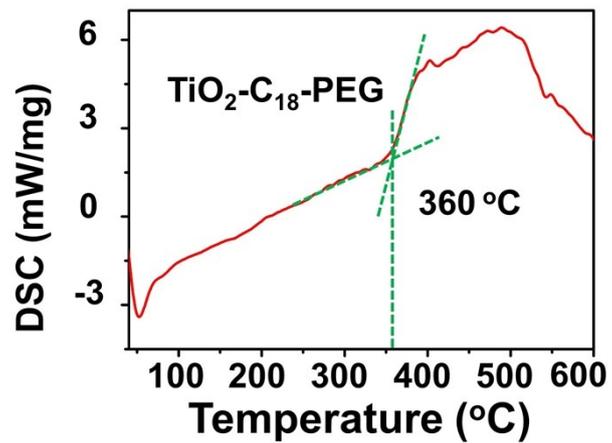


Fig. S6. DSC trace of $\text{TiO}_2\text{-C}_{18}\text{-PEG}$.

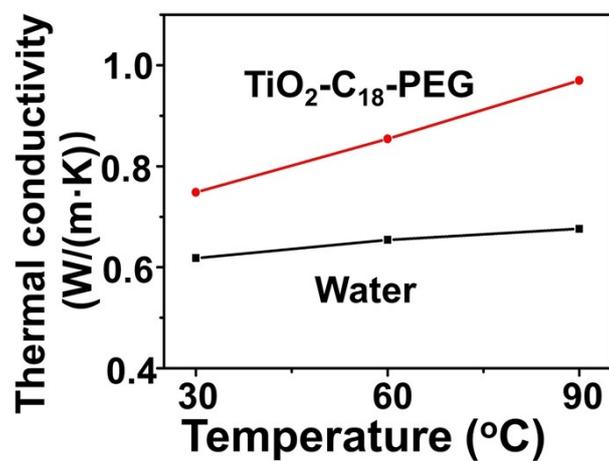


Fig. S7. The enhancement in thermal conductivity from 30 to 90 °C for the aqueous TiO₂-C₁₈-PEG solution (0.1 wt%); values for water are included for comparison.

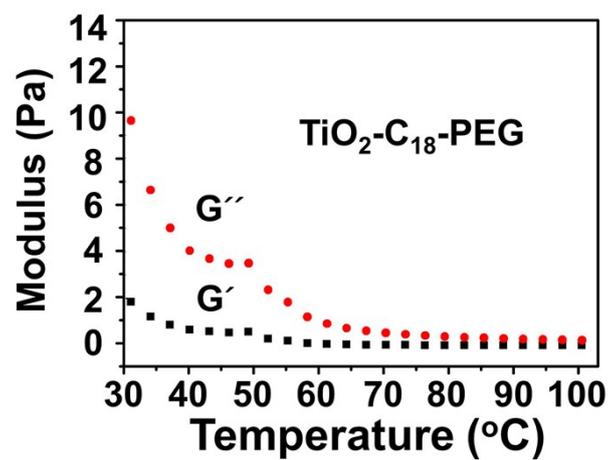


Fig. S8. The Modulus-temperature trace of $\text{TiO}_2\text{-C}_{18}\text{-PEG}$. Rheological tests demonstrate that the loss modulus G'' of TiO_2 nanofluids, which is always greater than the storage modulus G' of TiO_2 nanofluids, discloses the liquid-like behavior of the product.

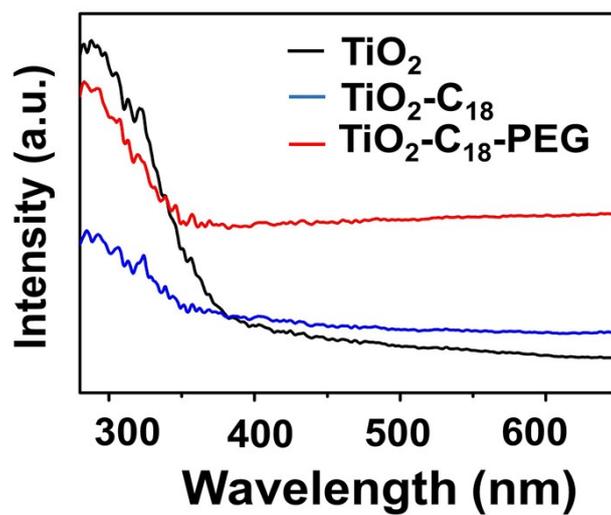


Fig. S9. Solid-state UV-vis diffuse reflection spectra of TiO₂, TiO₂-C₁₈ and TiO₂-C₁₈-PEG.



Fig. S10. Photograph of $\text{TiO}_2\text{-C}_{18}\text{-PEG}$ aqueous dispersion (30 wt%) stored for 3 years.

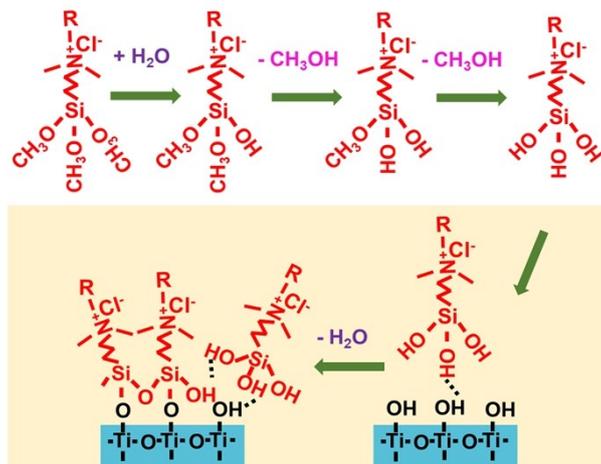


Fig. S11. Reaction process for siloxane attachment TiO_2 nanoparticles. Silane coupling agent will hydrolyze to yield the silicone hydroxide in presence of water with methanol. Notably, during the typical silane-based surface modification around inorganic nanoparticle, the silicone hydroxides partly self-condensate into silica and partly react with hydroxyl groups on TiO_2 to modify the organics on the surface of TiO_2 .⁷⁻²⁰

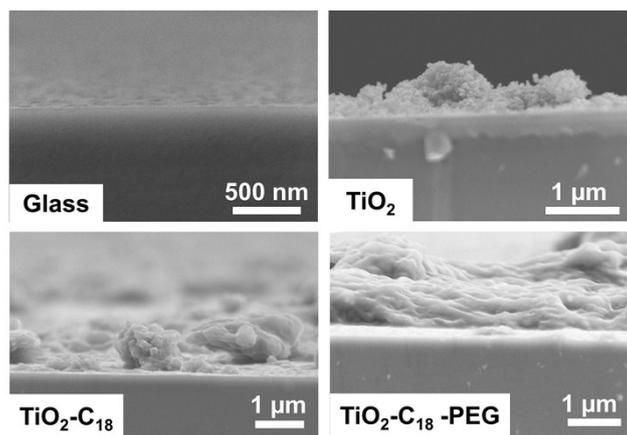


Fig. S12. SEM images of glass and glass coating of TiO₂, TiO₂-C₁₈ and TiO₂-C₁₈-PEG.

Table S1 Literature summary of modified TiO₂ nanofluids

Method	Modified chemical	Titanium source	Ref.
Surfactant micelle adsorption	Sodium dodecyl sulfate (SDS)	TiO ₂ nanoparticles	21
	Cetyltrimethylammonium bromide (CTAB)	TiO ₂ nanoparticles	22
	Polycarboxylate, trioxadecane acid	TiO ₂ nanoparticles	23
	Oleic acid	Titanium n-butoxide	24
Surface grafting	C ₃ H ₁₀ O ₆ SSi ₃ -(trihydroxysilyl)-1-propanesulfonic acid (SIT, Gelest)	Commercial TiO ₂	16
	Silane coupling agent (KH550)	TiO ₂ nanoparticles	25

Table S2 Literature summary of hydrophobic and hydrophilic nanofluids

Wettability	Materials	Application	Ref.
Hydrophobic	SiO ₂	Enhanced oil recovery	26
		Enhanced oil recovery	27
	TiO ₂	Alter solid wettability	28
	CuO	Microfluidic devices, biocompatible implants, etc (authors hypothesized)	29
Hydrophilic	SiO ₂	Alter solid wettability	30
		Enhanced oil recovery	27
	TiO ₂	Heat transfer	25
		Enhanced oil recovery	31
	CuO	Critical heat flux applications	32

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