Supplementary Information for

Light-Triggered Reversible Sorption of Azo Dyes on Titanium Xerogels with Photo-Switchable Acetylacetonato Anchors

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This file contains the following supplementary information:

1 Chart
1 Table
5 Figures

Text S1

Materials and Methods

***Materials*:** Tetra-n-butyl titanate (TNBT), acetylacetone (AcAc), ethanol, nitric acid and ultrapure water were used for preparation of the TiO_2 xerogel. Two anionic azo dyes, Acid Orange 7 (AO7) and Methyl Orange (MO), and one cationic xanthene dye, Rhodamine B (RhB), were used as probing adsorbates. The molecular structures of the three dyes are shown in Chart S1. AO7 has two pKa of 8.2 and 11.4 with color change from amber (pH 7.2) to orange (pH 8.6) and orange (pH 10.2) to red (pH 11.8). MO has a pKa of 3.76 with color change from red (pH 3.0) to yellow (pH 4.4). All chemicals are analytical purity grade and were used as received.

***Preparation of TiO_2 Xerogel*:** The TiO_2 xerogel was prepared by the sol-gel method.[1] In the prepartion of the sol, the contents of TNBT, ethanol and water were constant while the volumes of HNO_3 and AcAc were adjusted for preparation of xerogels with variant components. Firstly, 10 mL TNBT was dropwise added to a mixture of ethanol (10 mL) and AcAc (0.75-3.0 mL) under magnetic stirring. Nitric acid diluted with ultrapure water (6-35%) of 0.5 mL was added to 20 mL ethanol. The nitric-containing ethanol was then dropwise added to the TNBT-ethanol-AcAc solution and was stirred for 30 min. A yellowish sol was obtained and aged at room temperature for a week and was slowly turned to gel. The gel was vacuum dried in an oven at 80°C until a constant weight was obtained. Detailed parameters used in the sol-gel process are listed in Table S1.

***Photo-Irradiation Experiments*:** TiO_2 xerogel of 0.01-0.05 g was dosed to 40-100 mL dye solutions (20-100 mg/L of AO7, 20 mg/L of MO, and 20 mg/L RhB). The mixtures were irradiated with a low-pressure mercury lamp with an incident irradiance of 3.0 mW/cm^2 at 254 nm, unless otherwise stated. The UV incident irradiance was determined by the KI/KIO_3 method[2] and a UV-A radiometer (Photoelectric Instrument Factory of Beijing Normal University, China) with a calibrated sensor of peak sensitivity at 365 nm. It should be noted that the photo-induced adsorption is highly dependent on the incident irradiance. In the studied range (10-46 $\mu W/cm^2$ at 365 nm), a higher incident irradiance led to a higher photo-induced AO7 uptake. If the light was too weak (below 10 $\mu W/cm^2$ at 365 nm), no photo-induced adsorption could be observed. On the other hand, if the light was too strong, for example, if a medium pressure mercury lamp was used (2.7-7.4 mW/cm^2 at 365 nm), the photo-induced adsorption could not occur either. Blank control experiments were conducted to detect the direct photo-oxidation of dyes. The concentration changes of dyes were used to calculate adsorption/desorption capacities. To exclude the interference of spontaneous adsorption from the photo-controlled process, 0.01 g TiO_2 xerogel was firstly soaked in 50 mL of 100 mg/L AO7 solution (pH 4) for 3 days before UV irradiation. The equilibrated concentration of the AO7 solution was around 60 mg/L. The spontaneous AO7 uptake by the TiO_2 xerogel in Table S1 under the given conditions was 210 mg/g. The AO7-saturated TiO_2 xerogel was separated from the solution through centrifugation and was added to another AO7 solution. The photo-induced uptake was 108 mg/g, about half of the spontaneous uptake. Figure 1 shows exclusively the sorption induced by UV irradiation and the dark recovery. For clarity, in the text and figures, UV off or dark was used to describe the condition without UV irradiation. Unless otherwise stated, the UV on-off cycle is composed of a 2-h UV irradiation followed a 24-h dark standing.

***Characterization of Dyes and the TiO_2 Xerogel*:** The dye solutions prior to and after irradiation were analyzed with a double beam spectrophotometer (UV-2550, Shimadzu Co., Japan). The point of zero charge of the TiO_2 xerogel was determined by conducting potentiometric titration experiments with $NaNO_3$ as the background electrolyte at ionic strengths of 0.001, 0.01, and 0.1 M with a computer controlled automatic titration system (T50, Mettler Toledo Co., Swiss) equipped with a combined glass electrode (DGi115-SC). The solution pH in the UV on-off cycle was also determined with this titration system. Atomic force microscopy (AFM) images were recorded with a Bruker microscope (Scanasyst-Air, Germany) equipped with a silicon tip on nitride lever. The water contact angle of the xerogel was determined with a sessile drop-tangent method by using a drop shape analysis system (DSA100, Krüss Co., Germany). Prior to analysis, the TiO_2 xerogel was ground to fine particles and attached to a double-sided tape on a glass slide. The ^{1}H Hanh-echo and ^{13}C CP/MAS solid-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III wide-bore spectrometer at a proton frequency of 400 M Hz. Fourier transform infrared (FTIR) spectra were recorded with a Thermo

NEXUS870 spectrometer (Nicolet Inc., USA) in the form of KBr tablets. X-ray photoelectron spectroscopy (XPS, Spectrometer PHI 5000 VersaProbe, UlVAC-PHI Co., Japan) with an Al K_α radiation (1486.6 eV) source was employed to record the O1s spectra.

Text S2.

In a certain molar ratio range (0.02 – 0.08), a higher HNO_3 dose was favorable for the photo-induced sorption. However, it should be noted that overdose of AcAc and HNO_3 would lead to an unreasonably long gelation time, or even worse, failure in formation of gel. Moreover, not all the AcAc dosed in the sol could be composed into xerogel. At an initial AcAc molar ratio over 0.25, free AcAc was detected in the soaking dye solution and the solution underwent some non-reversible bleaching upon UV irradiation, because free AcAc could act as an activator in the photo-decoloration of azo dyes.[3]

Text S3.

Due to the interference of water, the broken intramolecular hydrogen bond could not reform in the dark standing. As a result, in the ^{1}H NMR, the peak at 5.3 ppm was enhanced upon UV irradiation but could not reduce back (Fig. 2a). However, the ^{13}C NMR clearly shows the reversible change of the AcAc moiety (Fig. 2a).

References

1. L. L. Hench, J. K. West, *Chem. Rev.*, 1990, **90**, 33-72.

2. (a) R. O. Rahn, *Photochem. Photobiol.*, 1997, **66**, 450-455; (b) S. Goldstein, J. Rabani, *J. Photochem. Photobiol. A*, 2008, **193**, 50-55.

3. S. J. Zhang, X. T. Liu, M. S. Wang, B. D. Wu, B. C. Pan, H. Yang, H. Q. Yu, *Environ. Sci. Technol. Lett.*, DOI: 10.1021/ez400024b

Figure and table captions

Table S1. Parameters for the sol-gel preparation of TiO_2 xerogel.

Chart S1. Molecular structures of AO7, MO, and RhB.

Fig. S1 Potentiometric titration of the TiO_2 xerogel in solutions of three ionic strengths: 0.001, 0.01, and 0.1 M.

Fig. S2 UV-Vis spectra of (a) AO7 and (b) MO solutions in a UV on-off cycle.

Fig. S3 SDBS ^{13}C NMR spectrum of AcAc in a $CDCl_3$ solution (0.5 mL : 1.5 mL) (SDBS No. 1030CDS-04-041).

Fig. S4 FTIR spectra of the TiO_2 xerogel in a UV on-off cycle: (a) the full spectra, (b) the spectra in the range of 2100-2400 cm^{-1}.

Fig. S5 (a) AFM and (b) water contact angle images of the TiO_2 xerogel in a UV on-off cycle.

Table S1 Parameters for the sol-gel preparation of TiO_2 xerogel.

Parameter	Component in the sol[a]					Xerogel[b]
	TNBT	ethanol	H_2O	HNO_3	AcAc	
Volume (mL)	10	30	3.3	0.15 (0.15 ~ 0.03)[c]	0.75 (0.75 ~ 3.0)	
Density ($g\ mL^{-1}$)	1	0.79	1	1.51	0.98	
Molecular weight ($g\ mol^{-1}$)	340.36	46.07	18.01	63.01	100.11	548.11
Molar ratio	**1**	17.51	6.24	0.12	0.25	**1.02**
Yield (%)						11.0
Q_{AO7}[d]						0.24

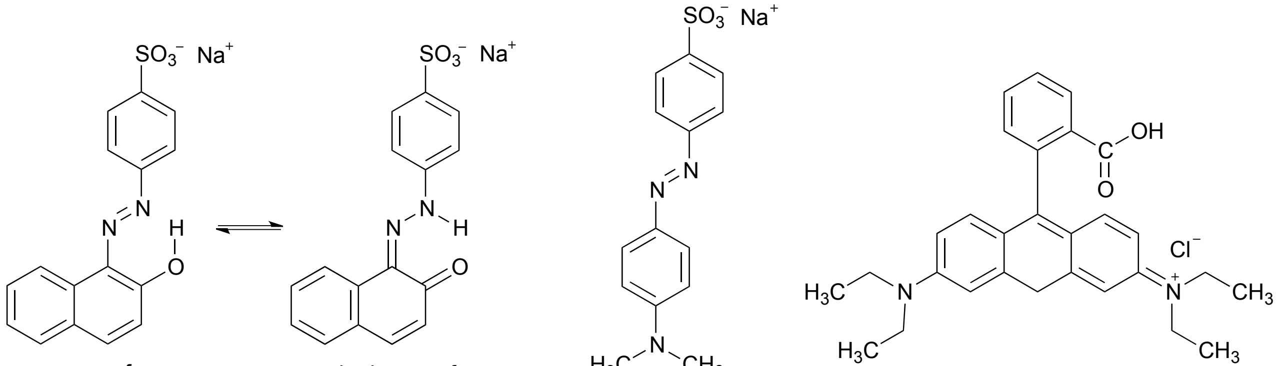
[a] The data in brackets are the volume ranges of HNO_3 and AcAc used in the preparation of xerogels.

[b] A sample TiO_2 xerogel with a yield of 11.0% and a proposed formula as $Ti_4O_{12}(OH)_2AcAc(-H)\cdot(HNO_3)_{0.5}$.

[c] The volume of HNO_3 was normalized to that of 100% HNO_3.

[d] The molar ratio of the adsorbed AO7 (photo-induced uptake) scaled with AcAc.

Chart S1 Molecular structures of AO7, MO, and RhB.



azo form

hydrazone form

Acid Orange 7 (AO7)

Methyl Orange (MO)

Rhodamine B (RhB)

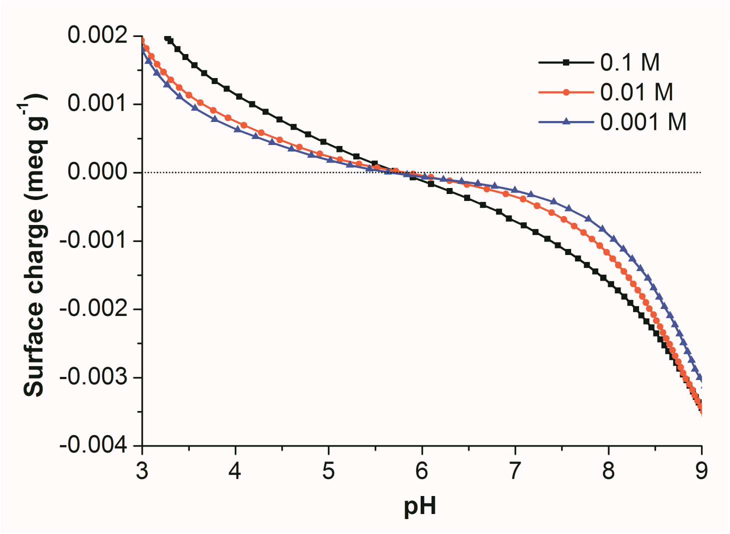
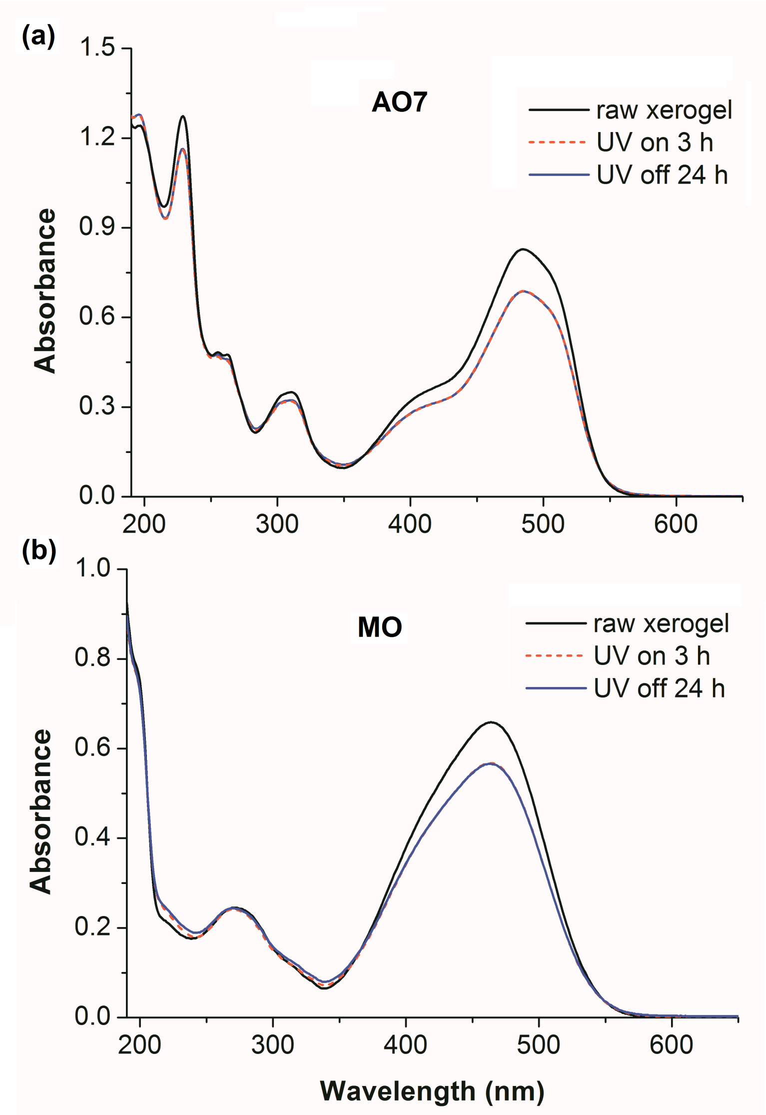


Fig. S1 Potentiometric titration of the TiO_2 xerogel in solutions of three ionic strengths: 0.001, 0.01, and 0.1 M.*

*: The intersection was the point of zero charge.



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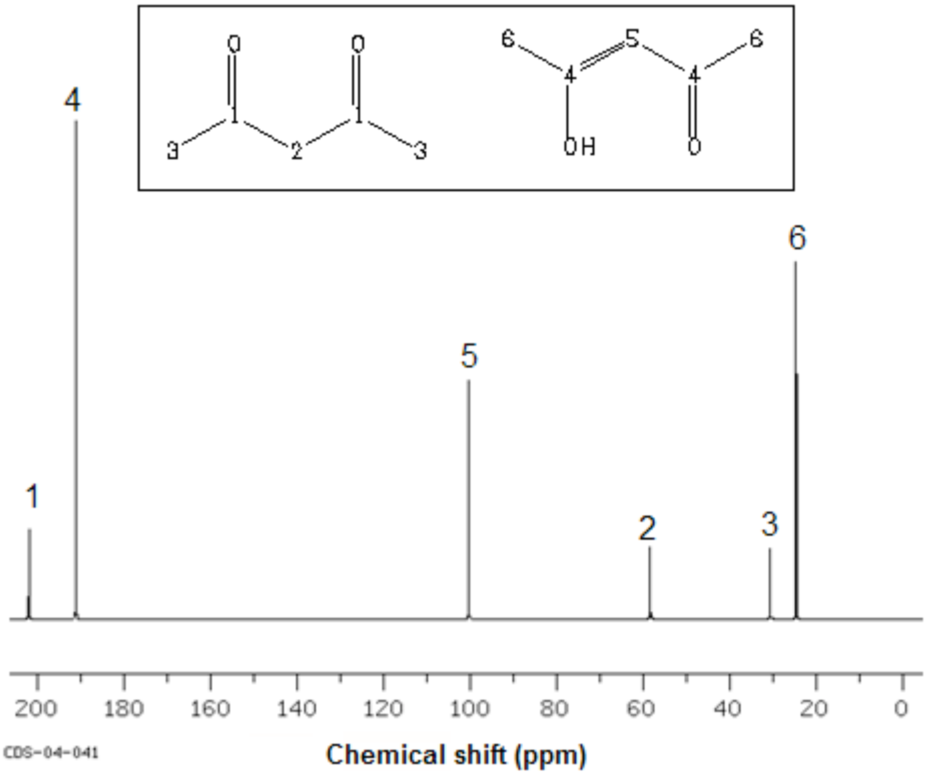

Fig. S3 SDBS ^{13}C NMR spectrum of AcAc in a $CDCl_3$ solution (0.5 mL: 1.5 mL) (SDBS No. 1030CDS-04-041).

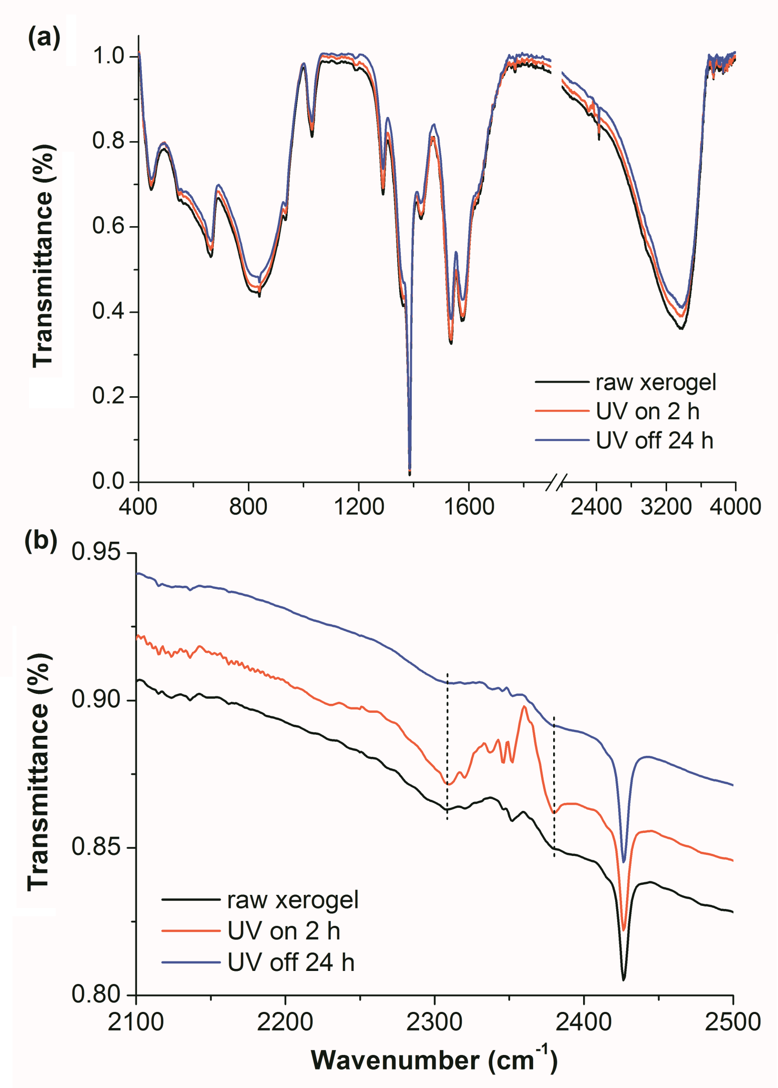

Fig. S4 FTIR spectra of the TiO_2 xerogel in a UV on-off cycle: (a) the full spectra, (b) the spectra in the range of 2100-2400 cm^{-1}.*

*: The peaks between the two dashed lines were responsive to UV irradiation.

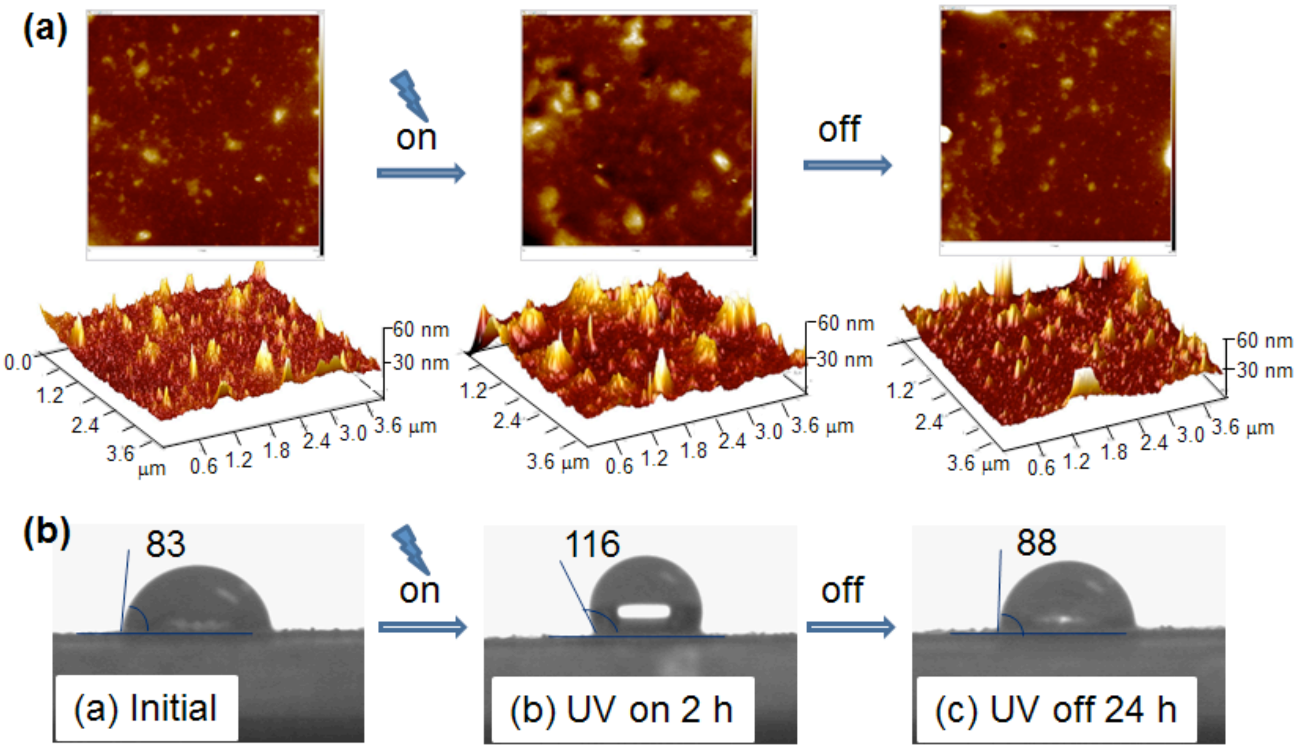

Fig. S5 (a) AFM and (b) water contact angle images of the TiO_2 xerogel in a UV on-off cycle.