Water-Mediated Promotion of Dye Sensitization of TiO₂ under Visible Light

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S *Supporting Information*

ABSTRACT: Preadsorbed water along with surrounding bulk water significantly modulates the surface electronic structure of TiO_2, switches the adsorption mode of dyes, and promotes dye sensitization of TiO_2 under visible-light irradiation. This opens a door toward facile improvement in the efficiency of photodegradation of dyes and dye-sensitized solar cells under visible-light irradiation without any complicated and expensive surface modulation.

TiO_2 has been intensively studied for solar energy harvesting and conversion for decades. Tremendous works have been conducted to pursue highly efficient sensitization methods.[1] Dye sensitization is one of the most promising pathways for utilizing visible light for solar cells, environmental remediation, and so on.[1] The function of sensitization mostly arises from the fast electron transfer (ET) from visible-light-excited chromophores of the dye to the conduction band of TiO_2, in which coupling between the dye and TiO_2 is indispensable. Nevertheless, the surface properties of TiO_2, which are prone to be modulated by the surrounding environment,[2] affect the coupling mode and thus the ET efficiency. Here we report that preadsorbed water on TiO_2 along with the bulk water surroundings can significantly modulate the surface electronic structure, switch the adsorption mode of dyes, and improve the dye sensitization process, which opens a door toward facile improvement in the efficiency of dye-sensitized solar cells and photodegradation of dyes under visible-light irradiation.

Photodegradation of a color dye [e.g., rhodamine B (RhB); Scheme S1 in the Supporting Information (SI)] in a TiO_2 suspension under visible-light irradiation is a typical dye self-sensitized process in which the reaction rate is closely related to the efficiency of ET between the adsorbed chromophores and TiO_2 (Scheme S2).[1,3] In the presence of commercial TiO_2 (P-25, Degussa, 80% anatase/20% rutile), RhB underwent pronounced degradation under visible-light irradiation. However, over P-25 calcined at a temperature above 300 °C, the reaction was dramatically suppressed (Figure S1a in the SI). The influence of textural structure changes in TiO_2 was excluded (Table S1 in the SI). In-situ FT-IR characterization (Figure S2) showed that calcination removed the water bonded to surface bridging hydroxyls (HO_{br}) through $H_2O \cdots HO_{br}$ interactions. We deduced that the loss of $H_2O \cdots HO_{br}$ structures retards the ET and lowers the photodegradation rate and that the process should be renewed if water is rebonded to HO_{br}. Actually, after exposure to atmosphere for several weeks, the calcined P-25

showed increasing photoactivity. Since the water bonding in atmosphere is extremely slow, we stirred the powders in water to accelerate the process. As expected, the photodegradation rate increased considerably upon water treatment (Figure S1a).

The above findings hint that water bonded to HO_{br} plays a crucial role in dye sensitization of TiO_2. Even TiO_2 that is carefully prepared (e.g., by annealing under O_2) still possesses many HO_{br} sites,[4] so introducing water on HO_{br} may be a versatile method for improving the dye sensitization of Ti-based photocatalysts. Inspired by this idea, we treated the original P-25 with water by simple stirring for different times and then added RhB to the suspension for photodegradation. To our surprise, this treatment significantly promoted both N-deethylation (blue shift in the wavelength of maximum absorption λ_{max}) and cycloreversion (decrease in the maximum absorption A/A_0), as shown in Figure 1a,c,d. When P-25 was treated for 84 h, the pseudo-first-order kinetic rate increased 5-fold (Figure 1b). Meanwhile, the presence of dye or gas (oxygen, nitrogen, or air) in the water during the treatment weakened this effect to some degree (Figure S1b,c).

To explain the inherent effect of water bonding, some characterizations were conducted. Water treatment decreased the isoelectric point of P-25 (Figure 2a), so the Brønsted acidity of HO_{br} was increased.[5,6] The increase in ζ potential (Figure 2b) provided evidence for the formation of positively charged species on the TiO_2 surface.[7a] Water bonding has been reported to increase the polarization and acidity of HO_{br}.[4,5] It is very likely that the water surroundings (i.e., H-bonded and physically adsorbed water layers) impose very strong solvation and polarization effects on the HO_{br} of $H_2O \cdots HO_{br}$. As a result, HO_{br} donates its proton to H_2O, forming $H_3O^+ \cdots O_{br}^-$ structures in which the hydronium is anchored by electrostatic interaction. Water bonding or/and solvation is a slow process, since a long treatment period was needed to obtain high photoactivity. Meanwhile, some TiO_2 aggregates were formed in the suspension after treatment for prolonged time (Figure S3) as a result of water-mediated interactions between acidic HO_{br} and basic terminal hydroxyl groups (HO_t) on adjacent particles.[5] However, serious agglomeration inevitably decreased the surface area of the photocatalyst and counteracted the positive effect of water treatment, as was quite obvious when the treatment time reached 168 h (Figure S4).

Adsorption of the dye on the TiO_2 surface is the prerequisite for ET from excited dye molecules to TiO_2.[1,3] The adsorption
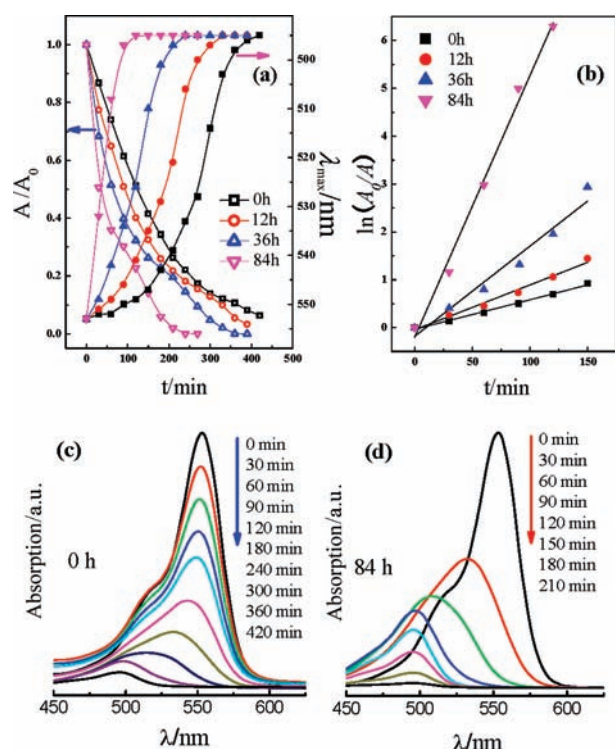
Figure 1. Photodegradation of RhB under visible-light irradiation (>420 nm) over P-25 pretreated in water for different times (0, 12, 36, and 84 h). (a) Plots of intensity of maximum absorption A/A_0 (open symbols) and wavelength of maximum absorption λ_{max} (solid symbols) vs irradiation time. (b) Pseudo-first-order kinetic fits based on absorption intensity at 553 nm. (c, d) Absorption spectra (450−600 nm) of RhB solutions at various irradiation times in the presence of P-25 pretreated in water for (c) 0 and (d) 84 h.
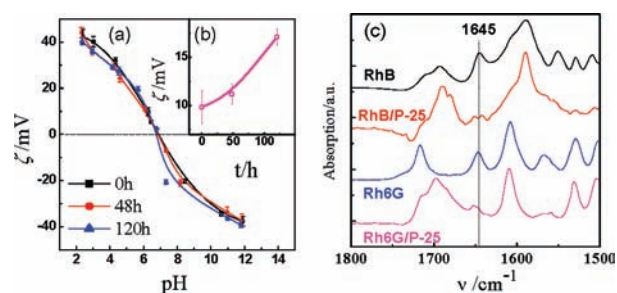

Figure 2. (a) Electrophoretic mobility of P-25 aqueous suspension (0.5 g L^{-1}, 25 °C) treated with water for different times (0, 48, and 120 h). (b) ζ potential of P-25 treated with water for different times (0, 48, and 120 h). (c) FT-IR absorption spectra of RhB, RhB/P-25, Rh6G, and Rh6G/P-25. P-25 wafers were partially hydrated, and the spectra of dye/P-25 were recorded with P-25 as a blank.

mode of RhB on P-25 was analyzed using FT-IR spectra in atmosphere. The common adsorption mode, namely, monodentate linkage via −COOH, was detected according to the splitting of the vibration band at 1693 cm^{-1} (Figure S5).[3c,d] Interestingly, the C=N vibration at 1645 cm^{-1} was split into two bands, and another cationic dye, rhodamine 6G (Rh6G), which contains R$_n$=N$^+$Et$_2$ but no −COOH, also showed similar splitting when adsorbed on P-25 (Figure 2c). Thus, there must

Table 1. Photodegradation of Dyes over P-25 with and without Water Treatment under Visible-Light Irradiation

dye[a]	irradiation time/min	dye degradation/%		treatment time/h
		original P-25	treated P-25	
Rh6G[b]	420	17.8	27.1	60
CV[b]	540	42.7	46.5	36
MB[b]	300	87.2	88.3	12
AR[c]	10	86.6	78.2	24
CR[c]	140	59.6	59.5	12
MO[c]	300	11.9	7.2	48

[a] Abbreviations: Rh6G, rhodamine 6G; CV, crystal violet; MB, methylene blue; AR, alizarin red; CR, Congo red; MO, methyl orange. [b] Cationic dye. [c] Anionic dye.

Scheme 1. Water-Mediated Modulation of the Surface of TiO$_2$ and Switching of the Adsorption Mode of RhB[a]
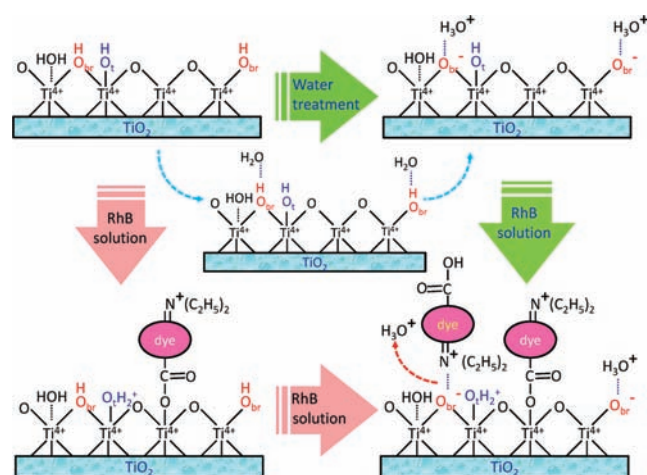
[a] Abbreviations and colors: O$_{br}$, bridging oxygen (red); O$_t$, terminal oxygen (blue).

be a new adsorption mode involving the =N$^+$Et$_2$ group. It has been reported that over a fluorinated TiO$_2$ whose surface hydroxyls have been replaced by F$^-$, the adsorption mode is switched to electrostatic interactions between the cationic moiety and F$^-$ (R$_n$=N$^+$Et$_2$···F$^-$).[3d] Preadsorption of an anionic surfactant such as dodecylbenzenesulfonate (DBS$^-$) on TiO$_2$ also induces this adsorption mode (R$_n$=N$^+$Et$_2$···DBS$^-$).[7] Similarly, we believe that the new adsorption mode over water-treated TiO$_2$ is a electrostatic interaction between =N$^+$Et$_2$ and O$_{br}^-$ (R$_n$=N$^+$Et$_2$···O$_{br}^-$). Moreover, the new linkage should be responsible for the water-mediated promotion effect. With this consideration, the effect should be valid for any cationic dye but not for anionic dyes, which was supported by the degradation of the cationic dyes Rh6G, crystal violet, and methylene blue as well as the anionic dyes alizarin red, Congo red, and methyl orange (Table 1; for dye structures, see Scheme S1).

Now we can describe the water-mediated promotion of the dye sensitization of TiO$_2$ (Scheme 1). Water can be bonded to HO$_{br}$ through strong hydrogen-bonding interactions (H$_2$O···HO$_{br}$). The solvation effect of adsorbed and surrounding bulk water enhances the polarization and acidity of HO$_{br}$ greatly;

as a result, hydronium structures $(H_3O^+ \cdots O_{br}^-)$ are formed. This process is very slow in atmosphere but significantly accelerated in bulk water. When dye cations are added to the system, they displace H_3O^+ and form the electrostatic adsorption mode $(R_n\!=\!N^+Et_2 \cdots O_{br}^-)$. The electrostatic adsorption induces ultrafast ET from the aromatic adsorbate to the semiconductor, thus significantly promoting the sensitization under visible-light irradiation. The analogy among fluorination, anionic surfactant treatment, and water treatment of TiO_2 is worthy of note. $Ti-F^-$ and adsorbed anionic surfactants serve as the adsorptive sites for dye cations in the former two cases, whereas bridging O_{br}^- species $(O_{br}^- - Ti)$ derived from HO_{br} are the adsorptive sites on water-treated TiO_2. Water bonding and solvation of bulk water surroundings are the keys for the electronic structural rearrangement of HO_{br} and the switch of adsorption mode. When other molecules such as dye or gas are present in water during the treatment, their competitive adsorption on the TiO_2 surface hinders water bonding and suppresses the water-mediated promotion effect.

In summary, simple water treatment can significantly modulate the surface electronic structure of TiO_2, switch the adsorption mode of cationic dyes, and promote the dye sensitization of TiO_2 under visible-light irradiation. It provides a cheap and green way to improve the efficiency of dye-sensitized solar cells and environmental photocatalysis. Specifically, the combination of the present work with TiO_2 exposed with highly reactive facets[8] is expected to produce very promising results. In addition, the present work reminds us of some important but often ignored issues. The exposure environment and/or reaction surroundings may have a huge effect on photocatalysis, which explains why the literature often gives controversial results on the activity of one photocatalyst in similar reactions. Thus, care must be taken when evaluating the inherent performance of a photocatalyst.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Detailed experimental procedures and results of characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Chen, X.; Mao, S. S. *Chem. Rev.* **2007**, *107*, 2891–2959. (b) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663. (c) Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. *Acc. Chem. Res.* **2008**, *41*, 339–348. (d) Schnadt, J.; Brühwiler, P. A.; Patthey, L.; O'Shea, J. N.; Södergren, S.; Odelius, M.; Ahuja, R.; Karis, O.; Bässler, M.; Persson, P.; Siegbahn, H.; Lunell, S.; Mårtensson, N. *Nature* **2002**, *418*, 620–623. (e) Zhang, M.; Chen, C.; Ma, W.; Zhao, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 9730–9733.

(2) (a) Zhao, J.; Li, B.; Onda, K.; Feng, M.; Petek, H. *Chem. Rev.* **2006**, *106*, 4402–4427. (b) Fujishima, A.; Zhang, X.; Tryk, D. A. *Surf. Sci.* *Rep.* **2008**, *63*, 515–582. (c) Diebold, U. *Surf. Sci. Rep.* **2003**, *48*, 53–229. (d) Henderson, M. A. *Surf. Sci. Rep.* **2002**, *46*, 1–308. (e) Miller, K. L.; Falconer, J. L.; Medlin, J. W. *J. Catal.* **2011**, *278*, 321–328. (f) Miller, K. L.; Lee, C. W.; Falconer, J. L.; Medlin, J. W. *J. Catal.* **2010**, *275*, 294–299.

(3) (a) Chen, C.; Ma, W.; Zhao, J. *Chem. Soc. Rev.* **2010**, *39*, 4206–4219. (b) Zhuang, J.; Dai, W.; Tian, Q.; Li, Z.; Xie, L.; Wang, J.; Liu, P.; Shi, X.; Wang, D. *Langmuir* **2010**, *26*, 9686–9694. (c) Zhao, D.; Chen, C.; Wang, Y.; Ma, W.; Zhao, J.; Rajh, T.; Zang, L. *Environ. Sci. Technol.* **2008**, *42*, 308–314. (d) Wang, Q.; Chen, C.; Zhao, D.; Ma, W.; Zhao, J. *Langmuir* **2008**, *24*, 7338–7345. (e) Wu, T.; Liu, G.; Zhao, J.; Hidaka, H.; Serpone, N. *J. Phys. Chem. B* **1998**, *102*, 5845–5851.

(4) Ketteler, G.; Yamamoto, S.; Bluhm, H.; Andersson, K.; Starr, D. E.; Ogletree, D. F.; Ogasawara, H.; Nilsson, A.; Salmeron, M. *J. Phys. Chem. C* **2007**, *111*, 8278–8282.

(5) Soria, J.; Sanz, J.; Sobrados, I.; Coronado, J. M.; Hernández-Alonso, M. D.; Fresno, F. *J. Phys. Chem. C* **2010**, *114*, 16534–16540.

(6) Fu, X.; Clark, L. A.; Yang, Q.; Anderson, M. A. *Environ. Sci. Technol.* **1996**, *30*, 647–653.

(7) (a) Zhao, J.; Wu, T.; Wu, K.; Oikawa, K.; Hidaka, H.; Serpone, N. *Environ. Sci. Technol.* **1998**, *32*, 2394–2400. (b) Liu, G.; Li, X.; Zhao, J.; Hidaka, H.; Serpone, N. *Environ. Sci. Technol.* **2000**, *34*, 3982–3990.

(8) (a) Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. *Nature* **2008**, *453*, 638–641. (b) Yang, H. G.; Liu, G.; Qiao, S. Z.; Sun, C. H.; Jin, Y. G.; Smith, S. C.; Zou, J.; Cheng, H. M.; Lu, G. Q. *J. Am. Chem. Soc.* **2009**, *131*, 4078–4083. (c) Wen, C. Z.; Jiang, H. B.; Qiao, S. Z.; Yang, H. G.; Lu, G. Q. *J. Mater. Chem.* **2011**, *21*, 7052–7061. (d) Wen, C. Z.; Zhou, J. Z.; Jiang, H. B.; Hu, Q. H.; Qiao, S. Z.; Yang, H. G. *Chem. Commun.* **2011**, *47*, 4400–4402.