Light induced activity switch in interfacial hydrogen-bond catalysis with photo sensitive metal oxides†

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UV light switches on the catalytic activities of several metal oxides in hydrogen bond catalyzed reactions because of the changes in the concentration of the surface hydroxyl groups.

Photo sensitive metal oxides, in particular titanium oxide (TiO_2), have been very important materials in various applications. As a semi-conductor, TiO_2 can be used to help the electron-hole separation in photovoltaic devices.[1] TiO_2 is also widely used in photo-catalysts[2] and self-cleaning coatings.[3] In these applications, such as the photolysis of organic pollutants,[4–6] and the splitting of water,[7,8] TiO_2 has been used to break the chemical bonds. TiO_2 as a catalyst to form chemical bonds, *e.g.* partial oxidation of organic compounds,[9] is less studied.

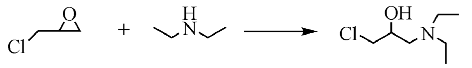
Another important application of TiO_2 is due to its photo induced reversible wettability. Super hydrophilicity and normal hydrophilicity on TiO_2 surface can be switched by UV irradiation and dark storage. The switch mechanism under ambient conditions is believed to be surface hydroxyl group related. When TiO_2 is irradiated by UV light, the water molecules in the air may coordinate with the titanium atoms on the surface, forming more surface hydroxyl groups. This greatly enhances the concentration of surface hydroxyl groups and leads to super hydrophilicity.[10–12] In high vacuum and low temperatures, surface hydroxyl group and UV-induced super-hydrophilicity may not be correlated.[13]

Such changes in terms of the concentration of the surface hydroxyl groups have not been fully exploited in catalysis, particularly in hydrogen bond catalysis. Hydrogen bond catalysis plays a crucial role in C–C bond formation in many organic reactions[14–17] and biological systems.[18] Recently we extended hydrogen bond catalysis from homogeneous solutions to the liquid/solid interface in heterogeneous systems, where surface hydroxyl group rich nano-solids such as iron hydroxide, alumina and zinc hydroxides showed high activity in several organic reactions,[19] and the concentration of the surface hydroxyl group determines the apparent reaction rate.

Based on these findings, we expect that higher activity in hydrogen bond catalyzed reactions can be observed on UV-irradiated TiO_2 catalysts than dark stored ones. In this communication, we will demonstrate that several organic reactions, including aldol reactions, epoxide-opening reactions, Diels–Alder reactions and C–C coupling reactions, can be catalyzed by TiO_2 porous nanospheres. UV irradiation of the TiO_2 catalyst results in much higher activity. More importantly, we observed repeated activity switchs, *i.e.* switch on by UV irradiation and switch off by dark during the reactions. Similar results have been observed from SnO_2 and WO_3 materials.

All five reactions in this study were carried out in sets. In each set of reactions, two parallel experiments were carried out under identical conditions, except that in one experiment dark stored TiO_2 catalyst was used and in the other experiment UV irradiated TiO_2 was used.

We first tested the epoxide-opening reaction (eqn (1)) between 3-chloro-1,2-epoxypropane and diethylamine at room temperature. As shown in Table 1, the activity enhancement of TiO_2 catalyst from UV irradiation was very substantial. After 6 h of reaction, nearly no product was detected using dark stored TiO_2 catalyst, while a 33% yield was achieved from UV irradiated catalyst, suggesting possibly several orders of reaction rate increase.



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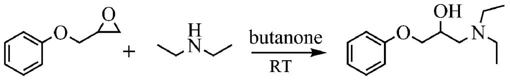

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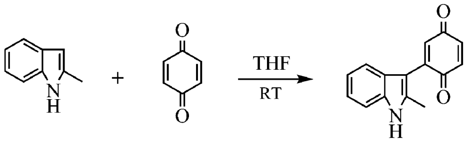

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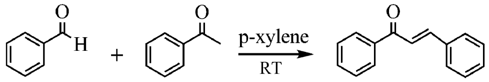

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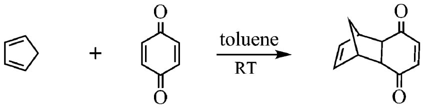

(5)

Table 1 The yield of eqn (1) catalyzed by TiO_2 nanospheres[a]

Catalyst	Yields (%) 1 h	6 h
UV irradiated TiO_2	17	33
Dark stored TiO_2	0	trace

[a] The reaction was conducted using TiO_2 catalyst (200 mg), 3-chloro-1,2-epoxypropane (0.2 mmol), diethylamine (0.4 mmol), and toluene (0.1 mmol, as internal standard for GC analysis) at room temperature in 2 ml of butanone solution.

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† Electronic supplementary information (ESI) available: The preparation of metal oxides; XRD, IR, and contact angle image of TiO_2 nanospheres; experimental details of reaction 2–5. See DOI: 10.1039/b908834b

Table 2 The yields of eqn (2)–eqn (5) catalyzed by TiO_2 nanospheres

Reaction	Catalyst	Yields (%)
2[a]	UV irradiated TiO_2	38
	Dark stored TiO_2	9
3[b]	UV irradiated TiO_2	54
	Dark stored TiO_2	30
4[c]	UV irradiated TiO_2	64
	Dark stored TiO_2	18
5[d]	UV irradiated TiO_2	76
	Dark stored TiO_2	34

[a], [b], [c], and [d] refer to 6 h, 24 h, 20 h, and 1 h of reaction, respectively. All reactions were carried out in a dark box.

Similar reaction rate enhancements were observed in the other four reactions (eqn (2)–eqn (5)). Table 2 summarizes the yields of each reactions using either UV irradiated or dark stored TiO_2 catalysts (the detailed reaction conditions of these reactions are listed in the ESI†). All reactions were carried out at room temperature to ensure moderate conversion. These apparently very different reactions have one common feature, which is they can all be catalyzed by hydrogen bonds.[14,19] Apparently, UV irradiation can significantly increase the activity of TiO_2 catalyst.

Such a substantial reaction rate increase from UV irradiated TiO_2 catalysts by itself is very useful in C–C bond formation for organic synthesis. Such a UV induced high activity catalysis system can be a promising venue in organic synthesis. TiO_2 is relatively low cost. Except for hydroxyl groups, no other functional groups are needed on the TiO_2 surface. Thus this TiO_2 catalyst is a environmentally friendly catalyst. We plan to exploit this catalysis system in more organic reactions.

The TiO_2 catalysts used in this study are nanoporous TiO_2 spheres prepared through a procedure reported earlier.[20] Fig. 1a shows the TEM image of one nanoporous TiO_2 sphere, which consists of interconnected TiO_2 nanoparticles of about 10 nm in size. The XRD pattern of the spheres shows that the obtained TiO_2 sample is pure anatase phase and the BET analysis result shows that this sample has a specific surface area of 240 $m^2\ g^{-1}$. As reported before, only high surface area metal oxides may have enough surface hydroxyl groups to be active hydrogen bond catalysts.[19] Because of such a high surface area, even dark stored TiO_2 catalysts showed moderate activity in above reactions (except eqn (1)). Extended exposure to UV light did not change the crystallinity of the TiO_2 catalyst. Identical XRD patterns (See ESI,† Fig. S1) were obtained from UV and non-UV irradiated TiO_2 catalyst.

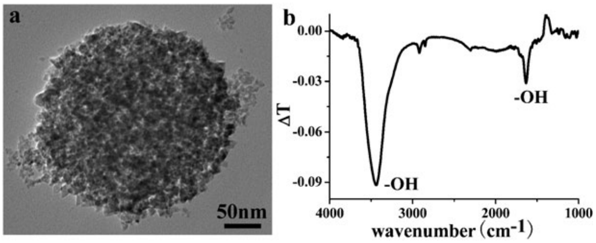


Fig. 1 (a) TEM of TiO_2 nanoporous sphere and (b) the IR difference spectrum of TiO_2 catalyst obtained from IR spectrum of UV irradiated TiO_2 spheres minus the IR spectrum of dark stored sample.

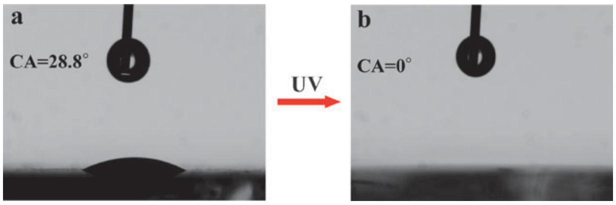


Fig. 2 Photographs of a water droplet with a contact angle of (a) 28.8°and (b) 0° before and after UV illumination at the surface of TiO_2 films deposited on a glass substrate.

In order to study the difference between UV irradiated and dark stored catalysts, the IR spectra of the same TiO_2 sample disc after UV irradiation or dark storage (See ESI,† Fig. S2) were acquired. Both spectra show strong and broad absorbance bands between 3100 and 3500 cm^{-1}, as well as sharp peaks at 1620 cm^{-1}. Broad bands near 3200 cm^{-1} are most likely due to physico-adsorpted water, while bands close to 3400 cm^{-1} and the sharp peaks at 1620 cm^{-1} are from surface hydroxyl groups on TiO_2 nanoporous spheres.

To highlight the difference between these two spectra, the difference spectrum between UV irradiated TiO_2 and dark stored TiO_2 is obtained as shown in Fig. 1b. Since the same IR TiO_2 sample disc and the same parameters were used to acquire the IR spectra, the difference spectrum is a reliable method to compare the two samples. As Fig. 1b indicates, the UV irradiated TiO_2 sample has a much stronger absorbance with sharp peaks at 3420 cm^{-1} and 1620 cm^{-1}. These two peaks are due to surface hydroxyl groups, indicating significantly enhanced surface hydroxyl group concentration on the UV irradiated TiO_2.

We also measured the wettability of TiO_2 nanoporous spheres deposited as a film on a glass substrate. As show in Fig. 2, before UV irradiation, the catalyst film is normally hydrophilic with a contact angle (CA) of 28.8° (Fig. 2a). However, the UV irradiation transformed it into a super hydrophilic material with a CA of 0° (Fig. 2b). Such a wettability change is due to the increase of the surface hydroxyl groups, agreeing very well with the IR characterization. Note that the contact angle in Fig. 2b was measured 30 min after the UV irradiation (the sample needs to be transferred from UV irradiation chamber to CA measurement chamber). This indicates that the enhancement in surface hydroxyl groups is a lasting effect.

In several experiments, after the reaction, the catalyst was collected and deposited as a film on a glass substrate to test its contact angle with water droplet again. The used catalyst has a CA of 12° (See ESI,† Fig. S3a). The contact angle of a water droplet on a solid is affected by the chemical property and the morphology of the surface.[11,13] The difference in the contact angle of water between the used catalyst and fresh catalyst does not offer much information. The fact that the used catalyst is no longer superhydrophilic implies that during the reaction, the catalyst may lose some of the surface hydroxyl groups. Super hydrophilic TiO_2 film can be slowly transformed into normal hydrophilic by dark storage. Note that all reactions in this study are carried out in dark. The reason for the TiO_2 catalyst being less hydrophilic is likely the same as reported for TiO_2 film.[10]

The used TiO_2 catalyst then underwent 1 h of UV irradiation, and it became superhydrophilic again (See ESI,† Fig. S3b),

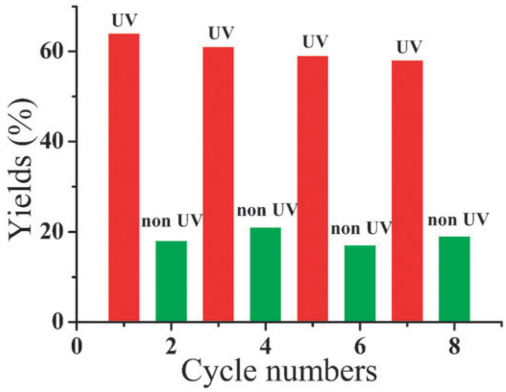
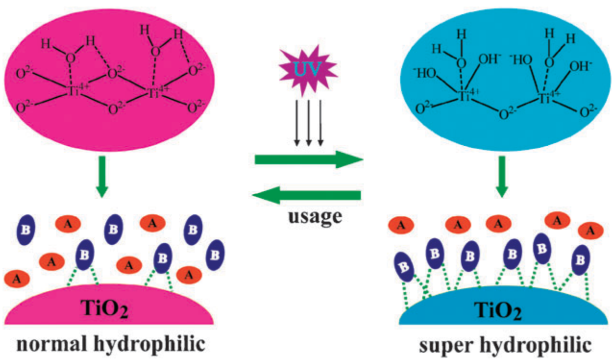


Fig. 3 The yields of eqn (4) using TiO_2 catalysts from UV irradiation or non UV irradiation in 8 batches of the reaction.

suggesting that UV irradiation will restore the super hydrophilicity and surface hydroxyl groups on TiO_2 catalyst. Therefore, the concentration of the surface hydroxyl groups can be regulated by UV irradiation or use in the dark. We believe that such changes in the concentration of surface hydroxyl groups provide a switch mechanism for the catalytic activity of the TiO_2 catalyst in the above reactions.

We tested the activity switch in the aldol reaction (eqn (4)). The experiments started with UV irradiated TiO_2 catalyst, after one batch of reaction the catalyst was collected and washed and then directly tested in another batch of the same reaction. Afterward, the catalyst was collected, UV irradiated for 1 h and tested again. Such a cycle was repeated 4 times. As shown in Fig. 3, in 8 batches of reactions, the yields of eqn (4) are constant at about 60% for the UV irradiated catalyst, and about 20% for the non UV irradiated catalyst. Apparently, the UV irradiation of the catalyst will switch on the activity; while during the reaction in dark, the activity is gradually switched off.

Such an activity switch is a new finding in hydrogen bond catalysis. We propose the following mechanism in Scheme 1 to explain the activity switch for TiO_2 catalyst: UV irradiation induces super hydrophilicity and substantially increases the concentration of surface hydroxyl groups. These hydroxyl groups act as hydrogen bond donors to catalyze the organic reactions. The hydrogen bonds between one reactant (both ellipses A and B refer to the reactants in Scheme 1) and the surface hydroxyl groups on the TiO_2 catalyst provide a venue to decrease the energy barrier of the reaction. During the reaction in the dark, somehow the UV irradiation induced surface hydroxyl groups are gradually lost, as is the catalyst's ability as the hydrogen bond donor. Repeated UV irradiations restore the surface hydroxyl groups and catalytic activity in each cycle. Later UV irradiation may also remove organic residues on the catalyst surface by photo-oxidation, thus restoring the catalyst activity. However, low catalytic ability from fresh TiO_2 catalyst calcined at 500 °C but stored in the dark suggests that coking may not be the major deactivation factor.



Scheme 1 Mechanism of photo-induced catalytic activity switch.

We observed similar results from SnO_2 and WO_3 materials in eqn (3) (See ESI†). The wettability can be switched between hydrophobic and super hydrophilic on SnO_2[21] and WO_3[22] by UV irradiation. Thus the mechanism of their catalytic activity switches can also be explained by Scheme 1. Other metal oxides, Fe_2O_3 and $Fe(OH)_3$, did not show an appreciable activity difference in hydrogen bond catalysis by dark storage or UV irradiation (See ESI†) for eqn (3). Unlike TiO_2, SnO_2 and WO_3, Fe_2O_3 and $Fe(OH)_3$ are not known for their light induced wettability changes. We are exploring other semi-conducting metal oxides for their behaviours in catalysis with UV irradiation.

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Notes and references

1. A. L. Linsebigler, G.-Q. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**, 735–758.
2. B. O'Regan and M. Gratzel, *Nature*, 1991, **353**, 737–740.
3. C. Euvananont, C. Junin, K. Inpor, P. Limthongkul and C. Thanachayanont, *Ceram. Int.*, 2008, **34**, 1067–1071.
4. A. Heller, *Acc. Chem. Res.*, 1995, **28**, 503–508.
5. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269–271.
6. J.-H. Pan, X.-W. Zhang, A. J. Du, D. D. Sun and J. O. Leckie, *J. Am. Chem. Soc.*, 2008, **130**, 11256–11257.
7. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38.
8. J.-W. Tang, J. R. Durrant and D. R. Klug, *J. Am. Chem. Soc.*, 2008, **130**, 13885–13891.
9. L.-F. Liao, C. F. Lien, M. T. Chen, Y.-F. Lin and J. L. Lin, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1912–1916.
10. R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Nature*, 1997, **388**, 431–432.
11. X.-J. Feng, J. Zhai and L. Jiang, *Angew. Chem., Int. Ed.*, 2005, **44**, 5115–5118.
12. G. Caputo, C. Nobile, T. Kipp, L. Blasi, V. Grillo, E. Carlino, L. Manna, R. Cingolani, P. D. Cozzoli and A. Athanassiou, *J. Phys. Chem. C*, 2008, **112**, 701–714.
13. T. Zubkov, D. Stahl, T. L. Thompson, D. Panayotov, O. Diwald and J. T. Yates, *J. Phys. Chem. B*, 2005, **109**, 15454–15462.
14. A. G. Doyle and E. N. Jacobsen, *Chem. Rev.*, 2007, **107**, 5713–5743.
15. T. R. Kelly, P. Meghani and V. S. Ekkundi, *Tetrahedron Lett.*, 1990, **31**, 3381–3384.
16. S. J. Connon, *Chem.–Eur. J.*, 2006, **12**, 5418–5427.
17. M. S. Taylor and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, 2006, **45**, 1520–1543.
18. A. J. White and C. W. Wharton, *Biochem. J.*, 1990, **270**, 627–637.
19. F. Niu, C.-C. Liu, Z.-M. Cui, J. Zhai, L. Jiang and W.-G. Song, *Chem. Commun.*, 2008, 2803–2805.
20. L.-S. Zhong, J.-S. Hu, L.-J. Wan and W.-G. Song, *Chem. Commun.*, 2008, 1184–1186.
21. W. Q. Zhu, X. J. Feng, L. Feng and L. Jiang, *Chem. Commun.*, 2006, 2753–2755.
22. S.-T. Wang, X.-J. Feng, J. N. Yao and L. Jiang, *Angew. Chem., Int. Ed.*, 2006, **45**, 1264–1267.