

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

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Supporting Information

Experimental Details:

Preparation of TiO₂ porous nanospheres: In a typical synthesis procedure, 2 ml of Tetrabutyl titanate (Beijing Chemicals Co.) was added to 50 ml of ethylene glycol (Beijing Chemicals Co.) with magnetic stirring at room temperature for 8h, then the solution was mixed with a solution of 170 ml of acetone and 2.7 ml of water, and was stirred for one hour. The white precipitate (Titanium glycolate nanospheres) was collected via centrifugation, followed by washing with ethanol for five times. Then the obtained Titanium glycolate nanospheres was mixed with 150 ml of water and refluxed for 1 h. The obtained white precipitate (TiO₂ porous nanospheres) was collected by a centrifugation, followed by washing with water for five times and was dried at 60 °C for further usage.

Preparation of SnO₂ materials: The SnO₂ catalyst was self-prepared via adding 2 ml of ammonia solution (25%, Beijing Chemicals Co.) into 30 ml of Tin tetrachloride (Beijing Chemicals Co., 0.5 mol/L) aqueous solution quickly with a vigorous stir at room temperature. Then the white deposition was gathered by centrifugation and dried in a 110 °C oven for further usage.

WO₃ materials: The commercial WO₃ powder (Beijing Chemicals Co.) was used to test reaction 3.

Preparation of Fe₂O₃ and Fe(OH)₃ materials: The iron hydroxide nanoparticles were prepared via adding ammonia solution (25%) to iron nitrate solution (0.5 M, 20 ml) with a vigorous stir. Then the brown precipitate was gathered by centrifugation

and dried in a 110 °C oven. Fe₂O₃ was prepared by calcinations of iron hydroxide nanoparticles at 600 °C for 3h.

Preparation of TiO₂ film: For testing the wettability of TiO₂ catalyst, the sample was deposited as a film on a glass substrate using the following process. 50mg of TiO₂ catalyst was dispersed in 2ml of alcohol to form a suspension, then a clean glass substrate was dipped in this suspension quickly and dried at 60 °C for directly CA testing or UV irradiation. The film of the reused TiO₂ catalyst was prepared using the same procedure.

For UV irradiation, the metal oxides catalysts are dispersed onto a glass substrate and are irradiated with an 80 mw/cm² of UV light (obtained from a 400 W high-pressure Hg lamp and the wavelength range between 350 nm to 450 nm) in a dark room under 25 °C and a controlled humidity of about 40%. After 1h of UV-irradiation, the catalyst was collected and added into the reaction flasks immediately. Dark stored catalyst was directly added into the reaction mixture and the reactions were carried out in the dark box.

Reaction 1-5 are all carried out at room temperature and the results of reaction 1, 4, and 5 were determined by GC (Agilent, 6890N), while results of reaction 2 and 3 were determined by HPLC (Shimadzu, LC-10Avp plus) analysis. All of the products were confirmed by GC-MS (Shimadzu, GC-MS QP2010) analysis.

The detailed reaction conditions of reaction 2-5:

Reaction 2 was conducted by using TiO₂ catalyst (200 mg), glycidyl phenyl ether (0.2 mmol), diethylamine (0.4 mmol), and toluene (0.1 mmol, as internal standard compound for HPLC analysis) in 2 ml of butanone solution at room temperature.

Reaction 3 was conducted by using TiO₂ catalyst (200 mg), 2-methylindole (0.4 mmol), 1,4-benzoquinone (0.8 mmol), and diphenyl (0.2 mmol, as internal standard compound for HPLC analysis) in 2 ml of THF solution at room temperature.

Reaction 4 was conducted by using TiO₂ catalyst (200 mg), benzaldehyde (0.5 mmol), phenyl methyl ketone (1 mmol), and diphenyl (0.2 mmol, as internal standard compound for GC analysis) in 2 ml of p-xylene solution at room temperature.

Reaction 5 was conducted by using TiO_2 catalyst (100 mg), cyclopentadiene (0.4 mmol), 1,4-benzoquinone (0.2 mmol), and p-xylene (0.05 mmol, as internal standard compound for GC analysis) in 2 ml of toluene solution at room temperature.

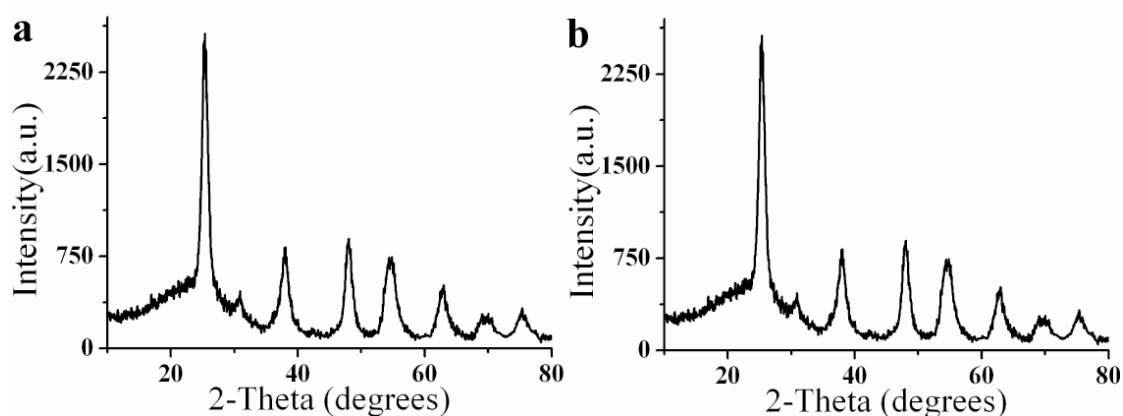


Figure S1. The XRD patterns of (a) non-UV and (b) UV irradiated TiO_2 porous nanospheres shows that the obtained sample are pure anatase phase, the identical XRD patterns show stability of the TiO_2 catalyst exposed to UV light.

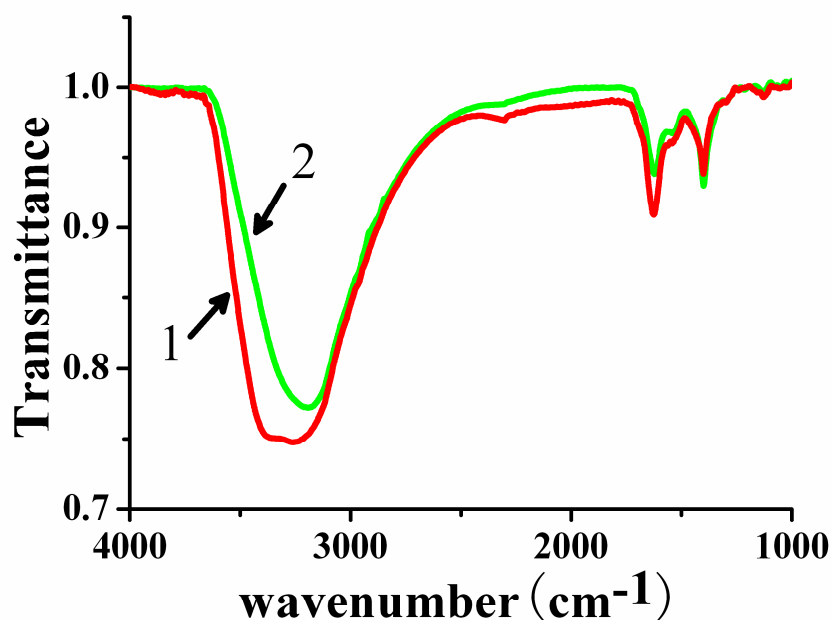


Figure S2. IR spectra of TiO_2 nanoporous sphere from (1) 1h of UV irradiation and (2) dark storage sample

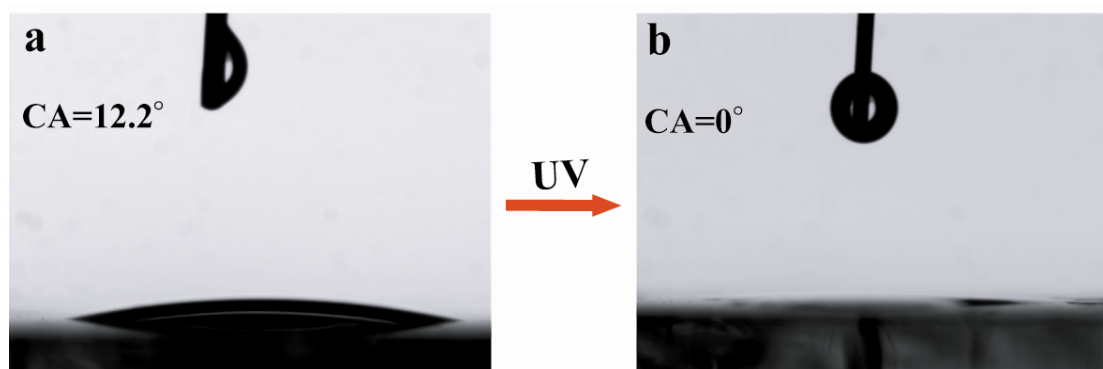


Figure S3. After the reaction in reaction 4, the film of the used TiO_2 catalyst deposited on a glass substrate has a contact angle of (a) 12.2° and (b) 0° before and after UV illumination

Table S1. Yields of reaction 3 catalyzed by WO_3 and SnO_2 materials

Catalyst	Reaction time (h)	Yields (%)
UV irradiated WO_3	24	15
Dark stored WO_3	24	6
UV irradiated SnO_2	24	6
Dark stored SnO_2	24	trace

We use reaction 3 as a model reaction to test the photo induced activity switch of SnO_2 and WO_3 materials. In a typical experiment, 200 mg of SnO_2 and WO_3 catalysts were mixed with 2 ml of THF solution containing 0.4 mmol of 2-methylindole, 0.8 mmol of 1,4-benzoquinone, and 0.2 mmol of diphenyl (as internal standard compound for HPLC analysis) with vigorous stir. After 1h of UV irradiation, WO_3 achieved a yield of 15% in 24h; while WO_3 which was stored in dark only produced 6% yield in 24h. The similar result was observed from SnO_2 materials, the UV irradiated SnO_2 for 1h proceeded reaction 3 to 3 times faster than SnO_2 stored in dark. These results confirm that UV irradiation is the crucial factor for the activity enhances of these materials.

Table S2. Yields of reaction 3 catalyzed by Fe_2O_3 and $\text{Fe}(\text{OH})_3$ catalysts

Catalyst	Reaction time (h)	Yields (%)
UV irradiated Fe_2O_3	24	trace

Dark stored Fe_2O_3	24	trace
UV irradiated $\text{Fe}(\text{OH})_3$	24	61
Dark stored $\text{Fe}(\text{OH})_3$	24	63

The reaction was conducted by using self-prepared Fe_2O_3 or $\text{Fe}(\text{OH})_3$ catalyst (200 mg), 2-methylindole (0.4 mmol), 1,4-benzoquinone (0.8 mmol), and diphenyl (0.2 mmol, as internal standard compound for HPLC analysis) in 2 ml of THF solution at room temperature. As shown in Table S2, the UV irradiated and dark stored Fe_2O_3 catalysts were used and there was no significant activity difference between them, so did the $\text{Fe}(\text{OH})_3$ catalysts. Both Fe_2O_3 and $\text{Fe}(\text{OH})_3$ catalysts were UV-irradiated for 1h, and were mixed with reaction mixture afterwards. Dark stored catalysts were directly added into the reaction flasks.