Supporting Information
Enhanced Photocatalytic Activity of Hydroxylated and N-doped Anatase Derived from Amorphous Hydrate
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Contents
1. Preparation of TiO$_2$ samples S2
2. Characterization methods of structure and properties S2
3. Figures S4
4. Tables S7
References S7
1. Preparation of TiO$_2$ samples

The sample of original amorphous TiO$_2$ was prepared through titanium sulfate (Ti(SO$_4$)$_2$) and ammonia water reacting in aqueous phase at ice-water bath. Every 100mL of the Ti(SO$_4$)$_2$ solution contained 8.0g solute and the concentration of the ammonia water was 4mol/L. 12mL of the prepared Ti(SO$_4$)$_2$ solution and 20mL of the prepared ammonia water were added into 100mL of deionized water. Then the system would react at ice-water bath for 2h under magnetic stirring to control the synthetic rate. After the reaction finished, the sol was centrifuged (5500rpm, 8min) and ultrasonic washed (100W, 20min) by deionized water, and the sol after ultrasonic washing was the amorphous hydrate, which would be dried at a low temperature (60~80°C) to get the powder of original amorphous TiO$_2$. The heating treatment was conducted in a muffle to keep amorphous TiO$_2$ at a station temperature for 3h, and the heating rate was about 20°C per minute. Heating at a series of temperatures would produce hydroxylating anatase with different degrees of disorder.

In the contrast experiments, KOH, NaHCO$_3$ and NH$_4$HCO$_3$ were used to take place of the ammonia water, each alkali compound would be added into the prepared Ti(SO$_4$)$_2$ solution at ice-water bath gradually until the pH of synthetic system reach 10, the other steps were exactly the same as mentioned above. The amorphous TiO$_2$ synthesized in the contrast experiments was heated at 200°C and 400°C to conclude the effects of hydroxylation and N-doping.

2. Characterization methods of structure and properties

**X-ray diffraction (XRD):** XRD patterns were performed on all the samples of TiO$_2$ using an X`Pert PRO diffractometer operating at 3kW and a Cu K$_\alpha$ radiation source. The scan range was 10°~90° and the step size was 0.02deg/min.

**High resolution transmission electron microscopy (HRTEM):** The samples of TiO$_2$ were finely ground using an agate mortar and then dispersed in ethanol at an ultrasonic bath. A drop of the suspension was deposited on a holey-carbon film supported on a copper 300 mesh grid. The specimen was taken micrographs by a Hitachi H-9500 HRTEM operating at 300kV.

**X-ray photoelectron spectroscopy (XPS):** All the Ti 2p, O 1s, N 1s and VB XPS spectra were performed by an Escalab 250Xi spectrometer operating at an Al K$_\alpha$ radiation source. The binding energy was corrected for specimen charging by referencing the C 1s peak to 284.6eV. And the accuracy of the binding energy was 0.02eV.

**Diffuse reflectance UV-Vis absorbance:** The powders of samples were pressed in a round glass model and a BaSO$_4$ disk was used as reference material for background measurement. All samples were measured by a Shimazu UV-4100 spectrophotometer, scanned from 300nm to 1000nm and the scanning speed was 300nm/s.

**Thermogravity (TG):** Each sample would be dried in a vacuum oven at 100°C for 24h to remove the physical water on surface as clearly as possible before the measurement. The weight after drying was noted as the original weight of each sample. Then each sample would be sent into a muffle and heated at 800°C for 3h to remove the hydroxyls, making the phase totally crystalline, and we weighed each sample again to calculate the moisture content, from which we judged the
degree of disorder of hydroxylating anatase.

*BET surface area analysis:* The surface area of TiO$_2$ was measured by a Tristar 3020 BET surface area and porosity analyzer, and all the samples should be preprocessed at 100°C to clean the surface.

*Photocatalysis:* The photocatalytic activity of each sample was measured by monitoring the change in optical absorption of acid fuchsin (AF) solution during the process of its decomposing under illumination of a xenon lamp (the illumination current was 20A). The original concentration of the AF dyestuff solution was 0.0134g/L, and each photocatalytic system contained 150mL of the AF solution and 0.05g powder of TiO$_2$ as photocatalyst. Every 10min, the UV-Vis absorbance of AF solution would be measured by a Shimazu UV-4100 spectrophotometer (scanned from 300nm to 800nm; scanning speed was 300nm/s), each photocatalytic decomposition process under illumination of a xenon lamp sustained for 90min.
3. Figures

*Figure S1.* XRD patterns of original amorphous TiO$_2$ and rutile that heated at 1000°C.
Figure S2. (a) A photo of TiO$_2$ heated at 200°C that synthesized from NaHCO$_3$ and KOH respectively; (b) A photo of TiO$_2$ heated at 400°C that synthesized from NaHCO$_3$, KOH and NH$_4$HCO$_3$ respectively. The contrast experiments confirmed that the hydroxylation induced the brown colour and the N-doping induced the yellow colour.
Figure S3. The decomposing rates of AF solution with (a) original amorphous TiO$_2$ and (b) amorphous TiO$_2$ heated at 200°C under solar-driven, visible-light-driven and in darkness.
4. Tables

**Table S1.** The surface area of original amorphous TiO\textsubscript{2} and treated TiO\textsubscript{2} heated at 200°C, 400°C and 800°C.

<table>
<thead>
<tr>
<th>Heating temperature/°C</th>
<th>original</th>
<th>200°C</th>
<th>400°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface area/m\textsuperscript{2}g\textsuperscript{-1}</td>
<td>328.55</td>
<td>281.88</td>
<td>161.18</td>
<td>19.35</td>
</tr>
</tbody>
</table>

References