Supporting Information

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Photocatalytic Oxidation of CO in the Presence of H₂ Over Pre-vacuumed TiO₂: The chemisorptions of O₂, CO and H₂ at TiO₂ Surface and Their Influences on the Photocatalytic Performances of TiO₂

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Supporting Information (SI) 1

Testing methods. Transmission electron microscopy (TEM) investigations were carried out on a JEOL JEM-2010 EX with field emission gun at 200 kV. The textural data of catalysts were measured by N₂ adsorption at liquid N₂ temperature with a micromeritics ASAP 2020 BET analyzer. Before the analysis the samples were outgassed at 250 °C under vacuum for 4 h. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer using Cu Ka radiation (λ = 0.15418 nm) operated at 40 kV and 40 mA. The ultraviolet-visible diffuse reflection spectra (UV-vis DRS) were recorded using a Varian Cary 500 UV-Vis-NIR spectrophotometer.

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**Supporting Information (SI) 2**

Fig. 1 TEM images of TiO$_2$ powder catalyst

TiO$_2$ nanoparticles with sizes of *ca.* 10 nm present a typical (101) surface plane (the width of the surface unit cell is 0.34 nm). This indicates that the TiO$_2$ is mainly composed of anatase structure.
Fig. 2 The N₂ adsorption isotherm of TiO₂

Table 1 BET analysis results of TiO₂

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pore Volume, ml/g</th>
<th>Surface Area, m²/g</th>
<th>Pore Radius, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0.18</td>
<td>158.30</td>
<td>2.46</td>
</tr>
</tbody>
</table>

The N₂ sorption isotherm of the TiO₂ catalyst is of type II, indicating that it is a porous material. This prepared TiO₂ powder catalyst presents a large surface area and pore volume.
Fig. 3 XRD pattern of TiO$_2$. Symbols *, +, and - denote anatase, rutile, and brookite, respectively.

This prepared TiO$_2$ powder is mainly composed of anatase phase, but with a small amount of rutile and brookite phases.
Fig. 4 UV-vis diffuse reflection spectra of TiO$_2$

This TiO$_2$ shows a light absorption of semiconductor, which the light absorption onset was *ca.* 376 nm (corresponding to a band gap of 3.30 eV).
Fig. 5 XPS spectra of Ti2p (A) and O1s (B) on TiO₂ treated in (a) non-pretreatment, (b) a vacuum at 200 °C for 2h, and (c) O₂ atmosphere at 120 °C for 2h after (b).

For a careful XPS analysis, the relatively quantitative analysis is performed according to the following equation:

\[
\frac{N_i}{N_j} = \frac{A_i}{A_j} \frac{S_j}{S_i} \]

Where \(N\) is the atomic number, \(A\) is the XPS peak area of a kind of element, \(S\) is the elemental sensitivity factor. Thus, according to the elemental sensitivity factor of Ti2p and O1s as well as their corresponding XPS areas, the ratio of atomic number among Ti and O can be evaluated. And, utilizing the evaluated atomic number ratio, the percentage of surface oxygen vacancy content can be calculated by the following formula:

\[
x = 100(1 - \frac{N_{O_x}}{N_{Ti} \times 2}) \]

Where \(x\) is the percentage of surface oxygen vacancy content, \(N\) is the atomic number.
Adsorbing CO can promote the color change of TiO₂ from light to dark, and the introduction of H₂ can further strengthen the change of color. However, the subsequent introduction of O₂ can weaken the change of color, and pre-introduction of O₂ can further weaken the change of color. This result indicates that the adsorption of CO can benefit to the formation of surface oxygen vacancy sites (SOVs) at TiO₂ surface, which can be further promoted in the presence of H₂. On the contrary, the adsorbed O₂ can reconstruct the lattice oxygen.