Supporting Information

Introducing Ti$^{3+}$ Defects Based on Lattice Distortion for Enhanced Visible Light Photoreactivity in TiO$_2$ Microspheres

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Figure S1. SEM images of as-prepared TiO$_2$ samples. The morphology of as-prepared TiO$_2$ samples greatly change when chloride ions are added.

Figure S2. SEM images of as-prepared TiO$_2$ samples of different chloride ion content (noted on the images). It can be inferred that the chloride ions acts as surface surfactant.

Figure S3. FFT of the lattice distorted TiO$_2$ sample. Great lattice distortions can be observed.
Figure S4. (a) XPS survey spectrum of lattice distorted TiO$_2$; (b) Cl 2p XPS spectrum of TiO$_2$ with lattice distortion.

No chlorine signal was present in the high resolution Cl 2p scan.

Figure S5. Kinetic fit for the degradation of RhB under visible light irradiation. The TiO$_2$ hollow microspheres with both lattice distortion and Ti$^{3+}$ defects achieved the highest degradation rate of RhB under visible light irradiation.
Figure S6. \((\alpha h\nu)^{1/2}\) vs \(E_{\text{photon}}\) curves of TiO\(_2\) microspheres. The band gap of Original, Defects, Distortion, and Distortion & Defects are 3.06 eV, 2.98 eV, 3.06 eV, and 2.98 eV, respectively.

Figure S7. TG and DTG curves of (a) Defects and (b) Distortion & Defects. It can be seen from the TGA curves that no organic matter remains after EG reduction.
Figure S8. The degradation of phenol using the different TiO$_2$ samples under visible light irradiation. The degradation tendency of phenol is almost the same as the degradation of RhB; therefore, the dye sensitization was not found to be that significant.

Table S1. BET Surface area of as-prepared TiO$_2$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original</th>
<th>Distortion</th>
<th>Defects</th>
<th>Distortion &amp; Defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>185</td>
<td>188</td>
<td>114</td>
<td>143</td>
</tr>
</tbody>
</table>

Theoretical Calculation

Density functional theory (DFT) calculations are carried out with a VASP package (the Vienna ab initio Simulation Package) using plane wave basis sets with a cutoff of 340 eV. The generalized gradient approximation with the function of Perdew-Burke-Ernzerhof (PBE) is utilized for all geometric optimization and energy calculation. A $2\times 2\times 1$ supercell containing 24 Titanium atoms and 48 Oxygen atoms was employed, where a vacuum of 10 Å is used to simulate the surface in periodic boundary condition. The effect of chlorine is simulated by adding 4 Chlorine atoms above the (101) surface of TiO$_2$ within vacuum layer. The bond length change was calculated through geometry optimization and the energy change was calculated through energy calculations.
It was found that the length of the Ti-O bond increases from 1.780 Å to 1.802 Å with the existence of Cl atoms due to its higher electronegativity than O ion, resulting in the lattice expanding on the surface of TiO$_2$. Surface oxygen ions in these distorted TiO$_2$ lattices are easier to be removed and oxygen vacancies are easier to be generated on the basis that less energy (~0.032 eV less) are required in lattice-distorted areas (6.08 eV) than in perfect lattice areas (6.11 eV).