Plasmon enhanced visible light photocatalysis for TiO$_2$ supported Pd nanoparticles

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Supporting Information

Materials

The reagents for the synthesis and photo-decolourisation reactions were used as purchased, with no further purification. TiO$_2$ powder (Evonik P25) was the precursor for the preparation of the photocatalyst. Manufacturer data reports mean particle diameter of 21 nm and a surface area of $(50 \pm 15)$ m$^2$/g with an average anatase to rutile crystal phase ratio of 80:20. Palladium(II) chloride (PdCl$_2$) powder was purchased from Alfa Aesar and RhB from Sigma Aldrich. Reagent grade acetic acid purchased from Sigma Aldrich was used as the target molecule in experiments.

Preparation of Pd:TiO$_2$

A 0.02 M PdCl$_2$ solution was prepared by dissolving 354.65 mg of PdCl$_2$ powder in a 100 mL, 0.01 M aqueous HCl solution by vigorous stirring with a magnetic stir bar at 80 °C for 24 hrs. In a typical synthesis 10 mL of the prepared PdCl$_2$ solution and 1 g of P25 powder were mixed in a glass reaction vessel sealed with a quartz lid and magnetically stirred under UV irradiation (100 W Hg arc lamp) for a maximum of 30 min at an irradiance value of 9.5 mW/cm$^2$. After irradiation the catalyst was separated from the solution by centrifuge at 4000 rpm for 30 minutes then washed several times with deionised water by centrifugation at the same rpm and time, and finally dried in air. Once the Pd:TiO$_2$ catalyst was dry it was crushed with a mortar and pestle to de-aggregate the particles, ready to use.

Photocatalytic degradation of RhB

The photocatalytic degradation reactions for dye degradation experiments were carried out under atmospheric conditions at room temperature in a borosilicate glass vessel containing 50 mL of RhB solution at a concentration of 10 mg/L and catalyst loading of 100 mg/L. Prior to irradiation the solution was magnetically stirred in the dark for 30 min to allow for the adsorption/ desorption equilibrium of dye on catalyst surface. Aliquots were taken during the reaction at predetermined time intervals to measure the decrease in dye concentration. The solution was separated from the powder through repeated centrifugation and extraction at 4000 rpm for 30 minutes until the solution was powder free.
The characterisation techniques used for analysis were UV-VIS (PerkinElmer Lambda 950) fitted with an integrating sphere accessory for diffuse reflectance measurements; TEM imaging using a Jeol 2010 at the Nanovision Centre at Queen Mary, University of London, XPS surface analysis conducted at the NEXUS facility at Newcastle University and ICP atomic absorption spectrometry (Varian SpectrAA 220FS).

Photodecolourisation rate calculation

The reaction mechanism is generally accepted to follow Langmuir-Hinshelwood (L-H) kinetics which is the most common kinetics model used in heterogeneous catalysis for the degradation of organic compounds in aqueous solutions:

\[
    r = \frac{-dC}{dt} = \frac{k_r K_a C}{1 + K_a C}
\]

Where \( r \) is the reaction rate, \( C \) is the concentration of RhB, \( k_r \) is the reaction rate constant and \( K_a \) is the adsorption/ desorption equilibrium constant. Typically, the concentrations used in photocatalytic experiments are considered to be low where the value \( K_a C << 1 \) and \( k_r K_a \) can be taken as an apparent rate constant, \( k_{app} \) (min\(^{-1}\)). Equation 1 can therefore be simplified to:

\[
    \frac{dC}{dt} = k_{app} C
\]

The analysis of the degradation of RhB is assumed to follow pseudo-first order kinetics and the apparent rate constant for all experiments were calculated using equation 3:

\[
    \ln \frac{C_0}{C} = k_{app} t
\]

Where \( C_0 \) is the initial concentration of RhB and \( C \) is the concentration at \( t \). In this case the half-life of decolourisation (\( t_{1/2} \)) values have been used as the main indicator for photocatalytic activity.

Characterisation

XPS measurements analysed the chemical state of Pd on the Pd:TiO\(_2\) catalyst. Results show the spin-orbit doublet of the 3d\(_{3/2}\) and the 3d\(_{5/2}\) electron orbitals in a ratio of 2:3 with binding energies of 340 eV and 335 eV respectively, as shown in figure 1. This is consistent with the expected values of relative binding energies and intensities of the 3d electron subshell for Pd\(^0\).
Figure 1 Binding energy values correspond to that of metallic Pd, confirming the photo-reduced nanoparticles are metallic Pd.

ICP analysis was carried to quantitatively determine the amount of Pd photo-deposited onto the TiO$_2$ substrate. The amount of Pd detected was 0.5 wt%.

BET Surface Area

$\text{TiO}_2 = 50.9815 \pm 0.2120 \text{ m}^2/\text{g}; \text{Pd:TiO}_2 = 51.9970 \pm 0.1839 \text{ m}^2/\text{g}$

XRD analysis of P25 and Pd:TiO$_2$

Figure 2 XRD analysis shows that there that no crystallographic changes were detected after the photodeposition procedure. Pd at this loading level was not detected. The peaks corresponding to the anatase phase of TiO$_2$ (A) have been highlighted indicating that the P25 is composed almost entirely of TiO$_2$ in the anatase structure.
UV-VIS

Raw data

Figure 3 Raw UV-VIS results of the absorption spectra of TiO$_2$ and Pd:TiO$_2$ from DR measurements.

Calculation of the increase in absorption of light by catalyst

Increase in absorption was measured by calculating the area under the curves for the absorption spectra obtained for TiO$_2$ and Pd:TiO$_2$. The spectra were normalised before integration using the integrate function in Origin8 to return the area for each sample. The area under the curve for each catalyst is shown in table 1.

Table 1 Values of the area under the absorption spectra curves calculated by Origin8 for TiO$_2$ and Pd:TiO$_2$ obtained via diffuse reflectance measurements

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TiO$_2$</th>
<th>Pd:TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area under curve</td>
<td>55.05</td>
<td>59.83</td>
</tr>
</tbody>
</table>

The increase in absorption of the catalyst compared to TiO$_2$ was then calculated as the percentage increase of the area of Pd:TiO$_2$ compared to TiO$_2$. This worked out to be 8%. This value was associated with the visible region since the only difference in absorption detected was in this region of the spectrum as shown in figure 4.
Figure 4 The UV-VIS spectra obtained for TiO$_2$ and the Pd:TiO$_2$ catalyst. The increase in absorption is detected only in the visible region and this was calculated to be an 8% increase in absorption in the visible region for the Pd:TiO$_2$ catalyst compared with TiO$_2$.

Control experiment results

Figure 5 Results of control experiment carried out in the absence of catalyst and in the presence of TiO$_2$ under UV blocking conditions preventing the absorption of super band gap photons and deactivating the catalyst.
Figure 6 Cut-off points of optical filters with respect to the solar spectrum. Figure a) no filter b) UV blocking filter c) VIS blocking filter d) Tauc plot

Figure 6c shows the cut-off point of the VIS blocking filter. There is a region between the onset of absorption for both catalysts and the onset of UV irradiation where the filter is blocking some proportion of super band gap photons. The lack of photons in this region is thought to be the reason for the reduction in reaction rate under UV irradiation for P25 and Pd:TiO$_2$.

The plasmon fit was obtained via calculation of a Gaussian function of the form:

$$ f(x) = a \exp \left( -\frac{(x-b)^2}{2c^2} \right) $$

(4)

Where $a$, $b$ and $c$ are variables.

Comparison of Pd:TiO$_2$ catalyst with other work

A comparison of the new Pd:TiO$_2$ catalyst was made with other research in the literature using supported Pd on TiO$_2$ photocatalysts in the degradation of various target molecules. The activity was measured in terms of µmols of target compound per gram of catalyst per hour. It was not possible to
control for the irradiance value of the light source since vessel geometries, distance of source from reactor and estimated losses could not be obtained. The light source data given is in terms of the region of the spectrum used for irradiation.

Table 2 Comparison of catalytic activity of new Pd:TiO$_2$ with previous work

<table>
<thead>
<tr>
<th>Compound</th>
<th>Activity/ µmol/ g/ hr</th>
<th>Light region</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhB</td>
<td>4.64</td>
<td>Solar</td>
<td>[1]</td>
</tr>
<tr>
<td>AMX</td>
<td>2.74</td>
<td>Visible</td>
<td>[2]</td>
</tr>
<tr>
<td>MO</td>
<td>39.72</td>
<td>Solar</td>
<td>[3]</td>
</tr>
<tr>
<td>EY</td>
<td>7.23</td>
<td>Visible</td>
<td>[4]</td>
</tr>
<tr>
<td>RhB</td>
<td>4.00</td>
<td>Visible</td>
<td>[5]</td>
</tr>
<tr>
<td>AG</td>
<td>100.00</td>
<td>UV</td>
<td>[6]</td>
</tr>
<tr>
<td>4-ClP</td>
<td>2.08</td>
<td>Visible</td>
<td>[7]</td>
</tr>
<tr>
<td>MB</td>
<td>104.22</td>
<td>Visible</td>
<td>[8]</td>
</tr>
<tr>
<td><strong>RhB</strong></td>
<td><strong>208.76</strong></td>
<td><strong>Solar</strong></td>
<td></td>
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References


