Photodeposition as a facile route to tunable Pt photocatalysts for hydrogen production: on the role of methanol

Zhi Jiang, ZheYu Zhang, Wenfeng Shangguan, Mark A. Isaacs, Lee J. Durndell, Christopher M.A. Parlett, and Adam F. Lee

Fig. S1. UV-vis absorption spectra of 1 wt% Pt/TiO$_2$ catalysts as a function of methanol concentration during PD.
Fig. S2. (a) Particle size distributions, and (b) mean Pt particle size determined by HRTEM and H$_2$ chemisorption of 1 wt% Pt/TiO$_2$ as a function of methanol concentration during PD.

Fig. S3. Dark-field STEM images of 1 wt% Pt/TiO$_2$ as a function of methanol concentration during PD, and bright-field TEM highlighting (110) rutile titania lattice fringes for 50% MeOH photodeposited sample.
Fig. S4. Cl 2p XPS spectrum of 1 wt% Pt/TiO$_2$ catalysts as a function of methanol concentration during PD.
Fig. S5. O 1s XP spectra of 1 wt% Pt/TiO$_2$ catalysts as a function of methanol concentration during PD.
Fig. S6. Pt-L_{III} fluorescence XAS spectra of 1 wt% Pt/TiO_{2} catalysts as a function of methanol concentration during PD.

<table>
<thead>
<tr>
<th>%MeOH</th>
<th>% Pt</th>
<th>% PtO_{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.4</td>
<td>66.6</td>
</tr>
<tr>
<td>20</td>
<td>96.4</td>
<td>3.6</td>
</tr>
<tr>
<td>100</td>
<td>94.4</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Fig. S7. Transmission Pt L_{III}-edge $k^3$-weighted chi data. Pt foil and oxide references shown for comparison.
**Fig. S8.** Dark-field STEM images of 1 wt% Pt/TiO$_2$ prepared via (a-b) 0% MeOH and (c-d) 100% MeOH PD before and after photocatalytic hydrogen production evidencing significant sintering occurs when reduction is induced via evolved hydrogen versus electron transfer during PD.
Fig. S9. High resolution XRD patterns of 0.5 and 1 wt% Pt/TiO$_2$ catalysts as a function of methanol concentration during PD. No platinum reflections are observable for the 0.5 wt% catalyst.

Fig. S10. High resolution XRD patterns of 1 wt% Pt/TiO$_2$ catalysts post-photocatalytic hydrogen production as a function of methanol concentration during PD. No sintering occurs for the 100 % MeOH Pd catalyst, in contrast to that photodeposited in the absence of methanol for which large metallic nanoparticles are apparent.