

Electronic Supplementary Material

**The role of adsorbed oxygen in formic acid oxidation by Pt/TiO₂
facilitated by light pre-treatment**

Wibawa H. Saputera^a, Jason Scott^{a*}, Nathania Ganda^a, Gary K-C. Low^a, Rose Amal^{a*}

^a Particles and Catalysis Research Group, School of Chemical Engineering, Faculty of Engineering, University of New South Wales, Australia

* Correspondence should be addressed to Jason Scott and Rose Amal

Address: Tyree Energy Technology Building 348, University of New South Wales, Kensington, NSW 2052, Australia

E-mail: jason.scott@unsw.edu.au

E-mail: r.amal@unsw.edu.au

Fax.: +61293855966

Fax.: +61293855966

Tel.: +61293857361

Tel.: +61293854361

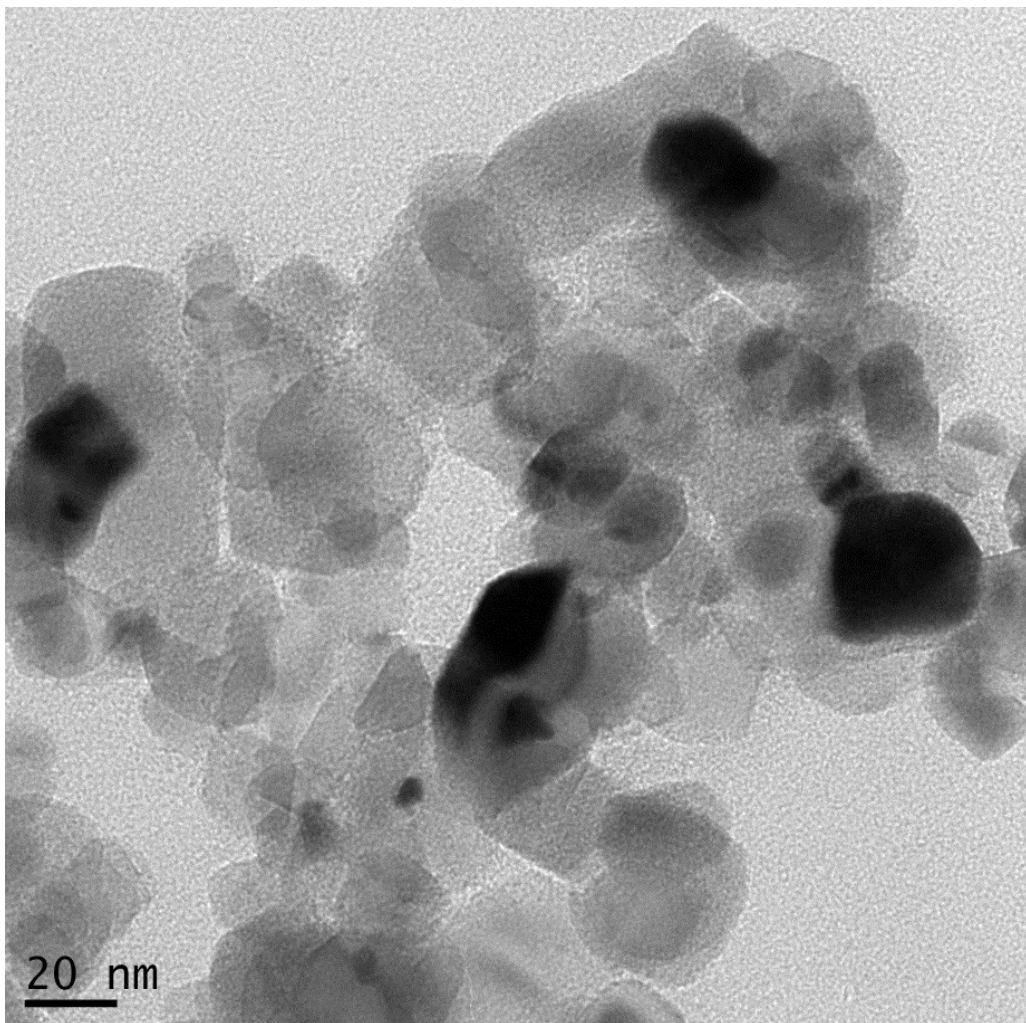


Fig. S1 TEM image of Pt_{ox}/TiO₂. No visible Pt_{ox} deposits are observable.

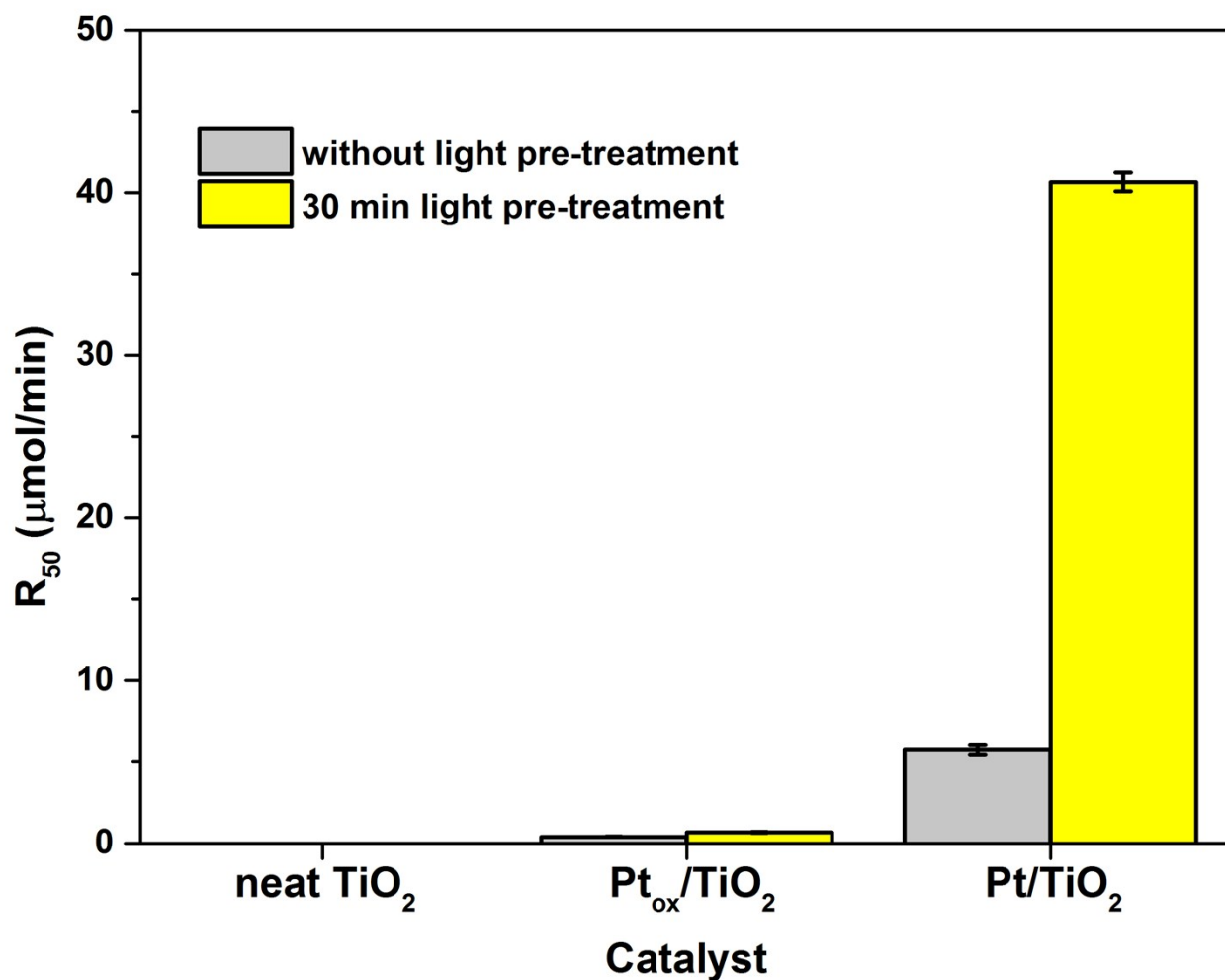


Fig. S2 Effect of Pt oxidation states on the formic acid oxidation rate (R_{50}) by Pt/TiO_2 prior to and following light pre-treatment. $\text{Pt}_{\text{ox}}/\text{TiO}_2$ represents Pt/TiO_2 which has been calcined at 300°C . Pt/TiO_2 represents Pt/TiO_2 which has been hydrogenated at 500°C . Neat TiO_2 is included as a control. Formic acid oxidation conditions: catalyst loading = 1 g/L; initial formic acid loading = 100 μmole ; suspension pH = 3 ± 0.05 ; air equilibration time = 10 minutes; relaxation time = 10 minutes; no illumination was performed during reaction.

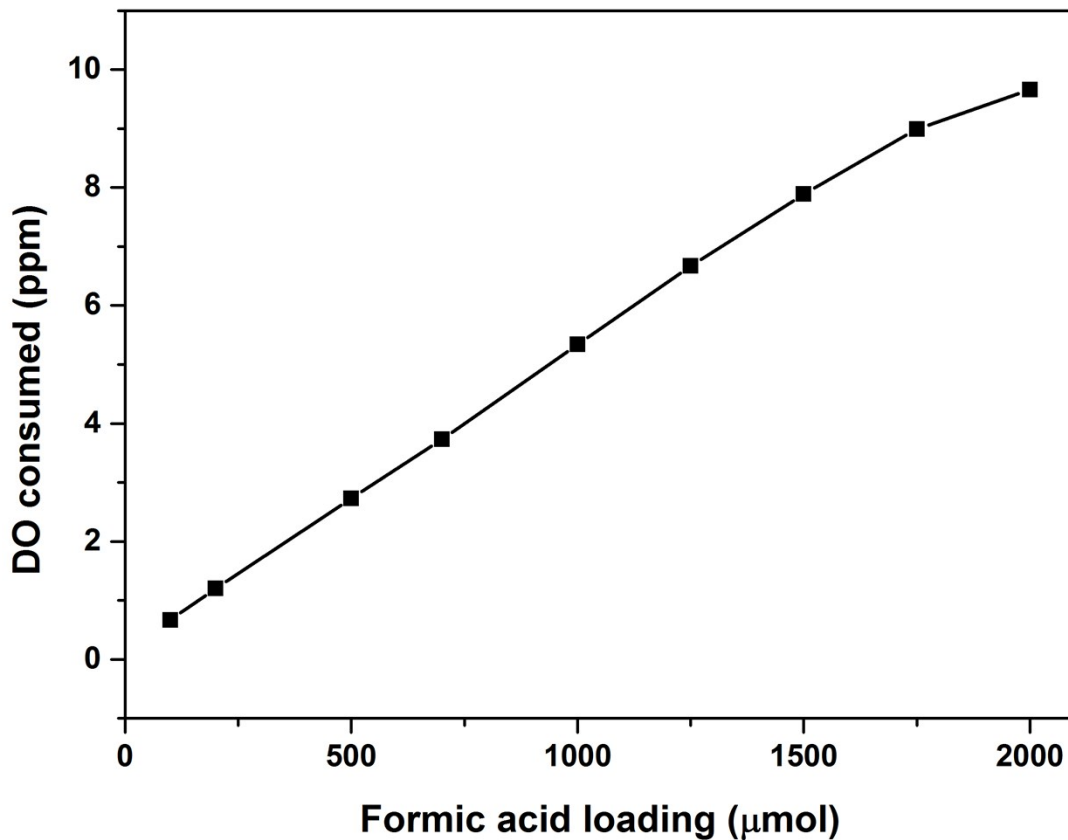


Fig. S3 Effect of initial formic acid loading on dissolved oxygen consumed during formic acid oxidation by Pt/TiO₂ following UV light pre-treatment. Formic acid oxidation conditions: catalyst loading = 1 g/L; suspension pH = 3 ± 0.05; air equilibration time = 10 minutes; relaxation time = 10 minutes; no illumination was performed during reaction.

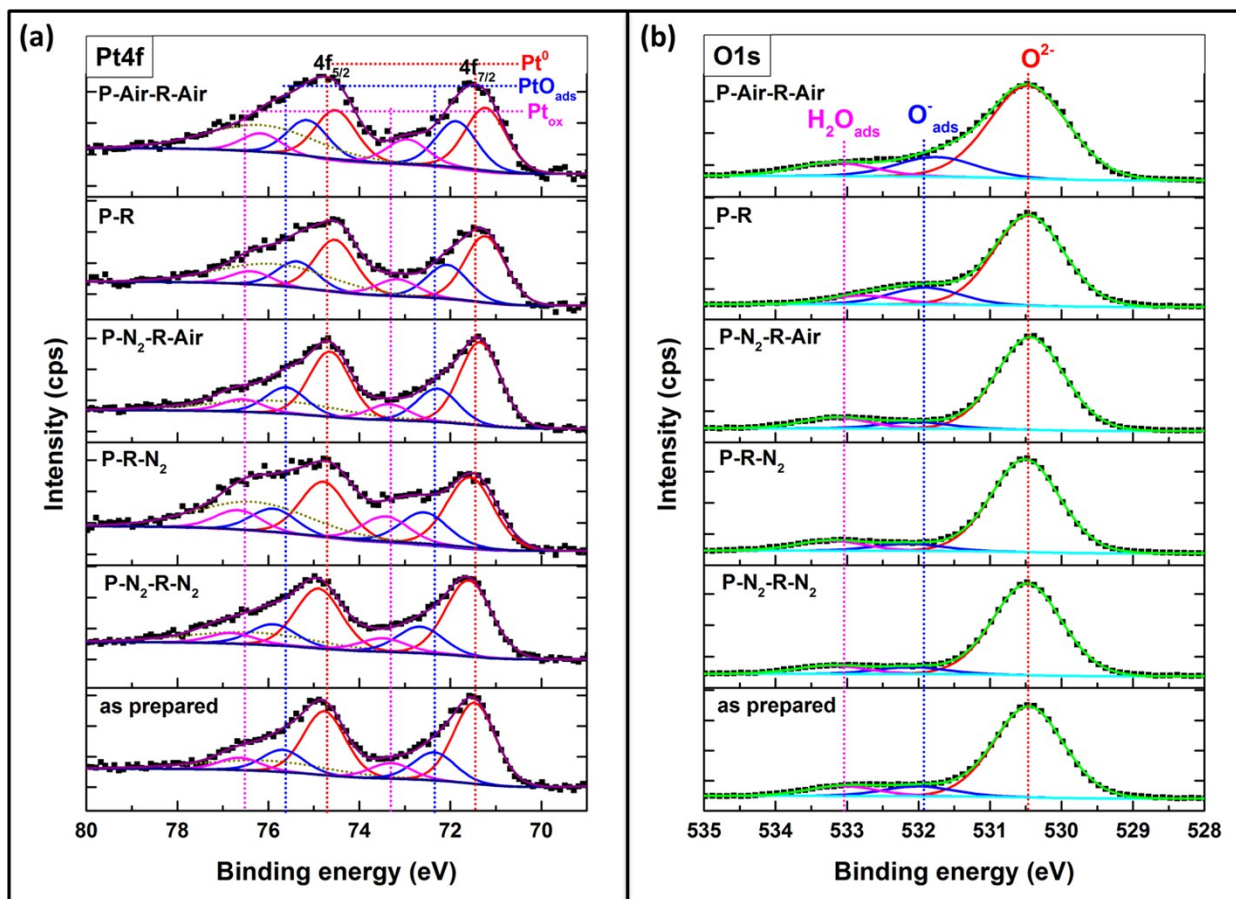


Fig. S4 Deconvolution of (a) Pt4f and (b) O1s core levels for Pt/TiO₂ with different dissolved oxygen concentrations prior to formic acid injection. Peak shifts to a lower binding energy were observed for the oxygen rich condition while peak shifts to a higher binding energy were observed for the nitrogen rich condition (when compared to the as-prepared Pt/TiO₂).

Table S1 Effect of air or N₂ purging at various stages of the light pre-treatment-relaxation process on Pt and O speciation for Pt/TiO₂.

Pt/TiO ₂ treatment	Pt4f core level (%)			O1s core level (%)		
	Pt ⁰	PtO _{ads}	Pt _{ox}	O ²⁻	O ⁻ _{ads}	H ₂ O _{ads}
No light pre-treatment	65.2	21.7	13.1	82.2	8.9	8.9
30 min light pre-treatment (P-R)	61.7	28.6	9.7	77.9	14.6	7.5
30 min light pre-treatment with N ₂ bubbling during light pre-treatment and relaxation stages (P-N₂-R-N₂)	54.2	25	20.8	83.4	6.8	9.8
30 min light pre-treatment with N ₂ bubbling during relaxation stage (P-R-N₂)	56.7	27.3	16	82.5	8.5	9
30 min light pre-treatment with N ₂ bubbling during light pre-treatment stage and air bubbling during relaxation stage (P-N₂-R-Air)	58.4	28	13.6	79.6	9.7	10.7
30 min light pre-treatment with air bubbling during light pre-treatment and relaxation stages (P-Air-R-Air)	52.2	34.8	13	75.8	16	8.2