Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Enhanced catalyst selectivity in the direct synthesis of H_2O_2 through Pt incorporation into TiO_2 supported AuPd catalysts.

Xiaoxiao Gong[a][b] ǂ, Richard J. Lewis[a]ǂ, Song Zhou[c][d][e], David J. Morgan[a], Thomas E. Davies[a], Xi Liu[c][f], Christopher J. Kiely[a,g], Baoning Zong[b] * and Graham J. Hutchings[a] *

[a]Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom.

[b]Laboratory of Catalytic Materials and Chemical Engineering, Research Institute of Petroleum Processing, SINOPEC, Beijing, 100083, P.R.China

[c]SynCat@Beijing, Synfuels China Technology Co. Ltd. Beijing, 101407, P.R.China

[d]State Key Laboratory of Coal Convers, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, P.R.China

[e]School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing, 100049, P.R.China

[f]School of Chemistry and Chemical, In-situ Centre for Physical Science, Shanghai Jiao Tong University, 200240, Shanghai, P. R. China

[g] Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA

ǂ These authors contributed equally to this work

*Zongbn.ripp@sinopec.com, Hutch@cardiff.ac.uk

Supplementary Information.

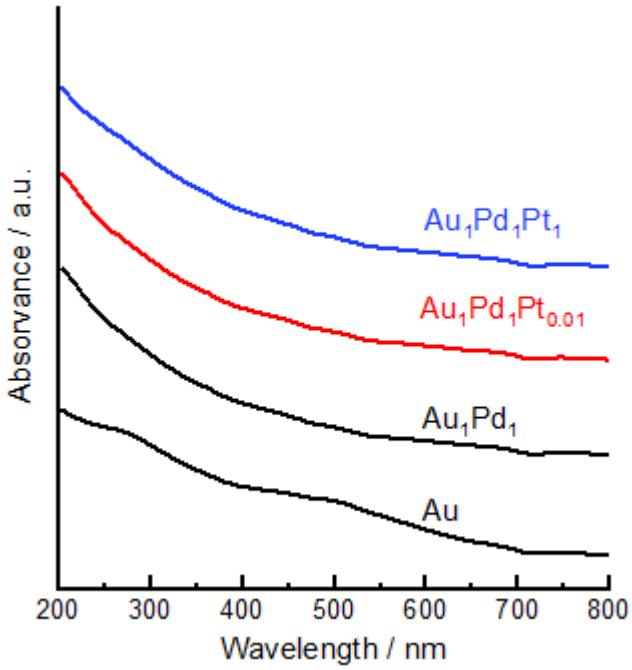

Figure S1. Representative UV-vis spectra from aqueous sol-immobilisation prepared colloidal catalysts prior to immobilisation. The absence of the Au plasmon peak (at approx. 550 nm) in the bimetallic and trimetallic colloids indicative of alloy formation.

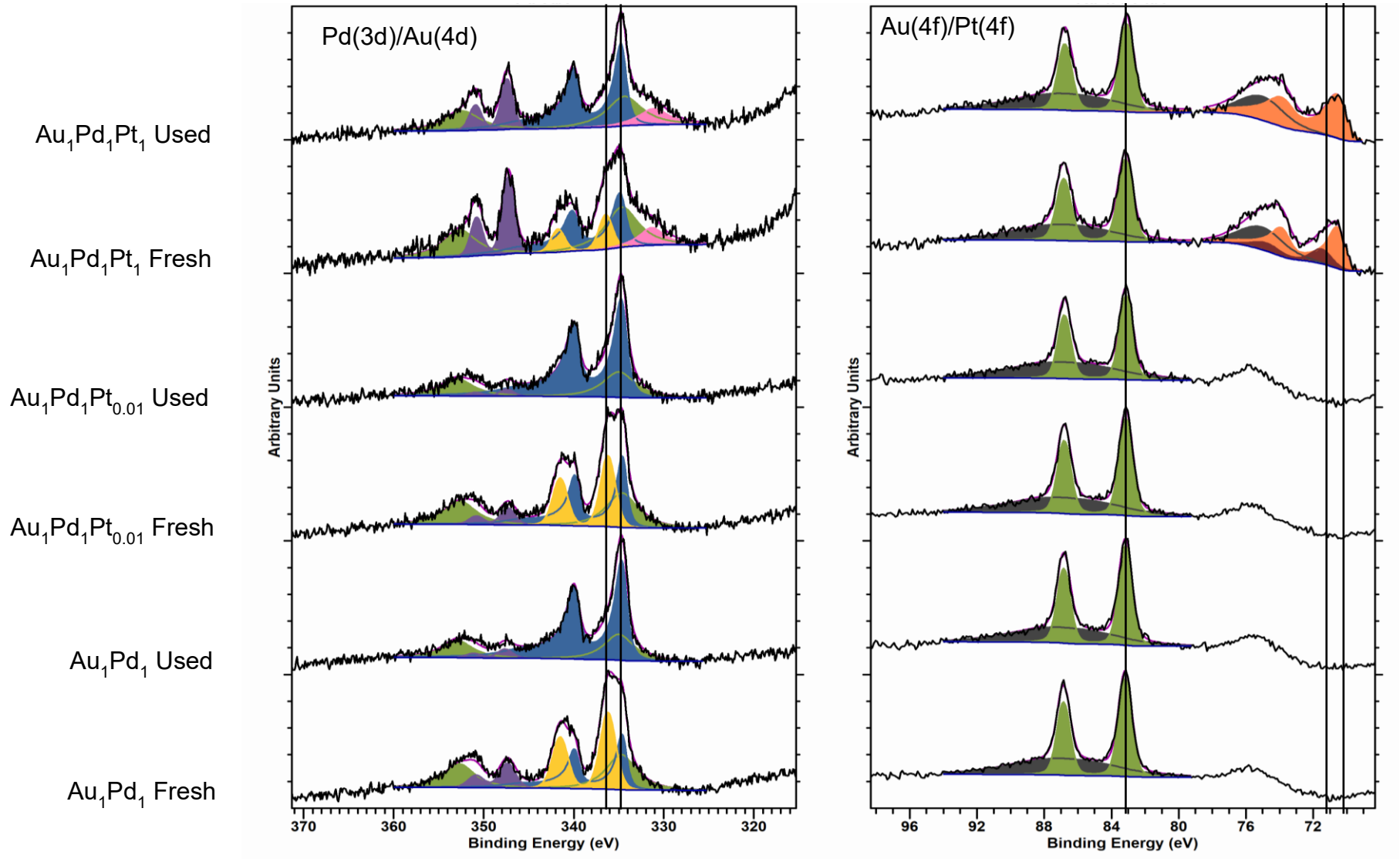

Figure S2. Corresponding XPS Pd(3d)/Au(4d) and Au(4f)/Pt(4f) spectra for fresh and used 1%Au_1Pd_1/TiO_2, 1%$Au_1Pd_1Pt_{0.01}/TiO_2$, and 1%$Au_1Pd_1Pt_1/TiO_2$ catalysts. Au^0= Green, Pd^0=Blue, Pd^{2+}= Yellow, Pt^0= Peach, Pt^{2+} = Burgundy, Ca^{2+}= Purple, Ti loss of structure = Black.

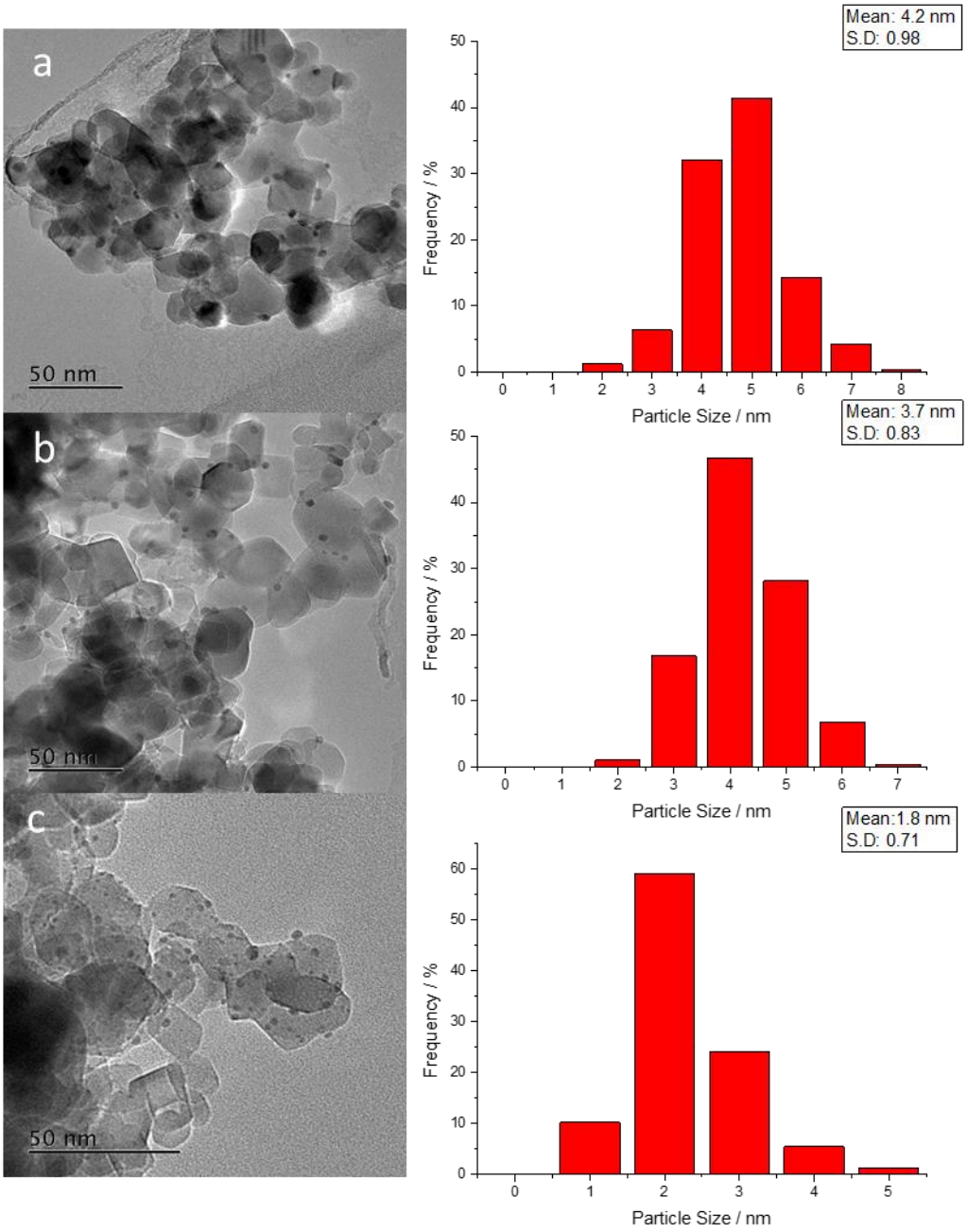

Figure S3. Representative bright field transmission electron micrographs and corresponding particle size distributions of TiO_2 supported bi- and tri-metallic catalysts prepared by a sol-immobilisation methodology, calcined 400 ^{o}C, 3h, static air, ramp rate = 10 ^{o}C min^{-1}. (a) 1%Au_1Pd_1/TiO_2, (b) 1%$Au_1Pd_1Pt_{0.01}/TiO_2$, and (c) 1%$Au_1Pd_1Pt_1/TiO_2$.

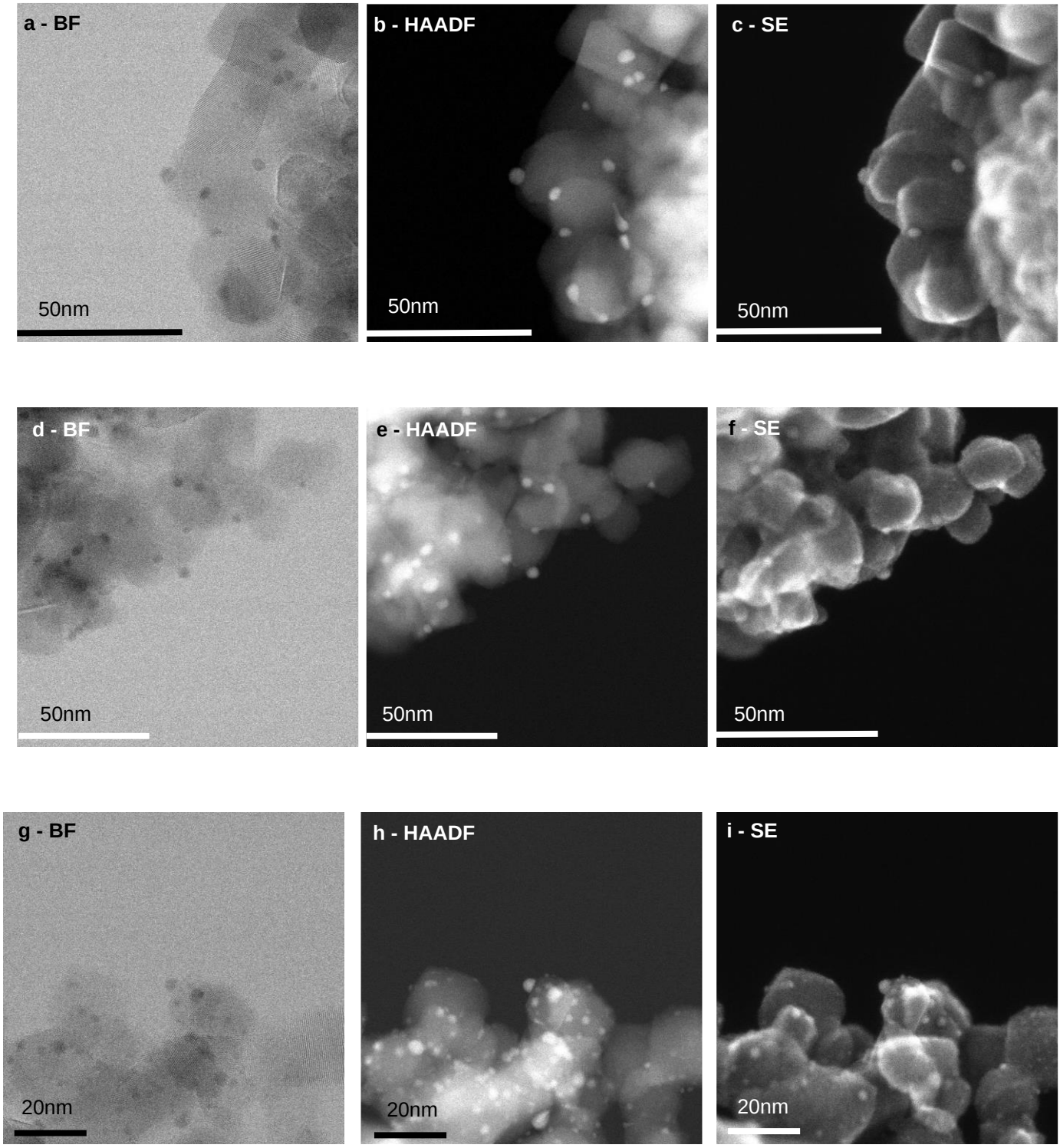

Figure S4 - Complementary bright field (BF)-STEM, high angle annular dark field (HAADF)-STEM and secondary electron (SE)-STEM images of (a, b, c) 1% Au_1Pd_1/TiO_2, (d, e, f) 1% $Au_1Pd_1Pt_{0.01}/TiO_2$ and (g, h, i) 1% $Au_1Pd_1Pt_1/TiO_2$ catalyst samples prepared by sol-immobilisation.

Table S1. Elemental composition of 1%AuPdPt/TiO_2 catalysts before and after use in the direct synthesis of H_2O_2, as determined by EDX.

Catalyst	Au (At%)	Pd (At%)	Pt (At%)
1%Au_1Pd_1/TiO_2	0.19	0.15	-
1%$Au_1Pd_1Pt_{0.01}/TiO_2$	0.17	0.18	BDL*
1%$Au_1Pd_1Pt_1/TiO_2$	0.17	0.11	0.11

Table S2. Comparison of initial H_2O_2 synthesis rates over various TiO_2 supported AuPdPt catalysts.

Catalyst	**Rate of reaction** / $mmol_{H2O2}min^{-1}$	
	Use 1	**Use 2***
1%Au_1Pd_1/TiO_2	0.034	0.042
1%$Au_1Pd_1Pt_{0.01}/TiO_2$	0.049	0.056
1%$Au_1Pd_1Pt_1/TiO_2$	0.023	0.027

*Catalyst used for 30 min under standard reaction conditions prior to determination of reaction rate over 0.083 h.
H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.083 h, 2 ˚C 1200 rpm

Table S3. Elemental surface composition of 1%AuPdPt/TiO_2 catalysts after use in the direct synthesis of H_2O_2, as determined by XPS analysis.

Catalyst		Au : Pt	Pd : Au	Pd^{2+} : Pd^0
1%Au_1Pd_1/TiO_2	Fresh	-	1.92	1.30
	Used	-	2.27	0.00
1%$Au_1Pd_1Pt_{0.01}/TiO_2$	Fresh	n.d	1.92	0.92
	Used	n.d	2.78	0.00
1%$Au_1Pd_1Pt_1/TiO_2$	Fresh	0.78	1.86	0.63
	Used	0.50	1.78	0.00

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 2 ˚C 1200 rpm.
n.d: not able to determine

Table S4. Total metal leaching from various TiO_2 supported AuPdPt catalysts during H_2O_2 synthesis reaction, as determined by ICP-MS analysis.

Catalyst	**Productivity (Fresh)** / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	**Au Leaching** / μgL^{-1}	**Pd Leaching** / μgL^{-1}	**Pt Leaching** / μgL^{-1}
1%Au_1Pd_1/TiO_2	81	-	0.21	-
1%$Au_1Pd_1Pt_{0.01}/TiO_2$	112	-	1.56	-
1%$Au_1Pd_1Pt_1/TiO_2$	30	-	-	-

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 2 ˚C 1200 rpm.

Table S5. Mean metal particle size of various TiO_2 supported AuPdPt catalysts, as prepared and after use in the H_2O_2 synthesis reaction, as determined by analysis of bright field TEM micrographs.

Catalyst	**Mean Particle size** / nm (Standard deviation)	
	Fresh *	Used**
$1\%Au_1Pd_1/TiO_2$	4.2 (0.98)	4.3 (0.91)
$1\%Au_1Pd_1Pt_{0.01}/TiO_2$	3.7 (0.55)	4.6 (1.2)
$1\%Au_1Pd_1Pt_1/TiO_2$	1.8 (0.56)	2.2 (0.84)

* Catalysts calcined, 400 °C, 3h, static air. ** Catalysts dried under vacuum (17h, 30 °C) after first use in H_2O_2 synthesis reaction.

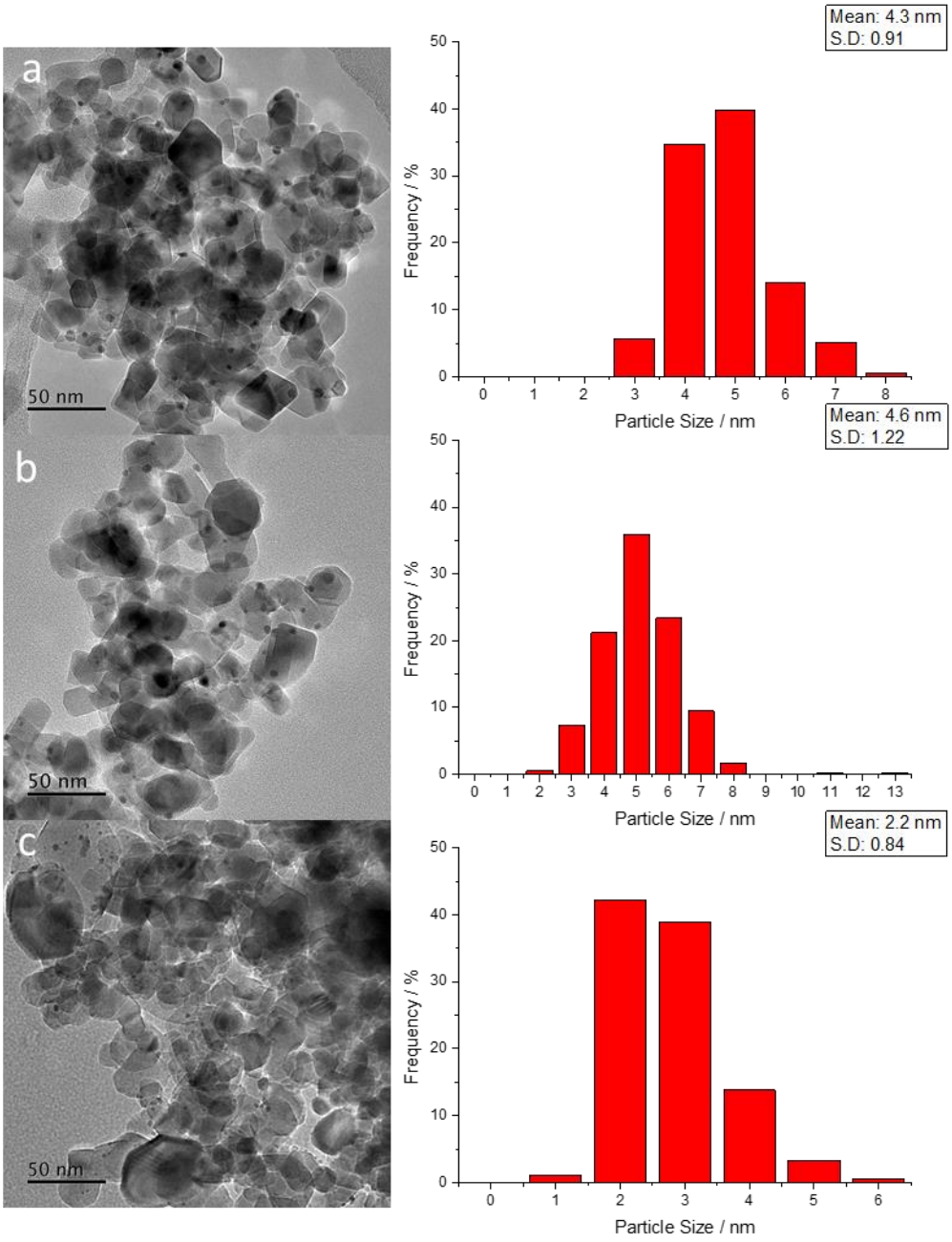

Figure S5. Representative bright field transmission electron micrographs and corresponding particle size distributions of 1% AuPdPt/TiO_2 catalysts after use in the direct synthesis of H_2O_2. Catalysts prepared by a sol-immobilisation methodology, calcined 400 ^{o}C, 3h, static air, ramp rate = 10 ^{o}C min^{-1}. (a) 1%Au_1Pd_1/TiO_2, (b) 1%$Au_1Pd_1Pt_{0.01}/TiO_2$ and (c) 1%$Au_1Pd_1Pt_1/TiO_2$.