

Enhanced catalyst selectivity in the direct synthesis of H₂O₂ through Pt incorporation into TiO₂ supported AuPd catalysts.

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Supplementary Information.

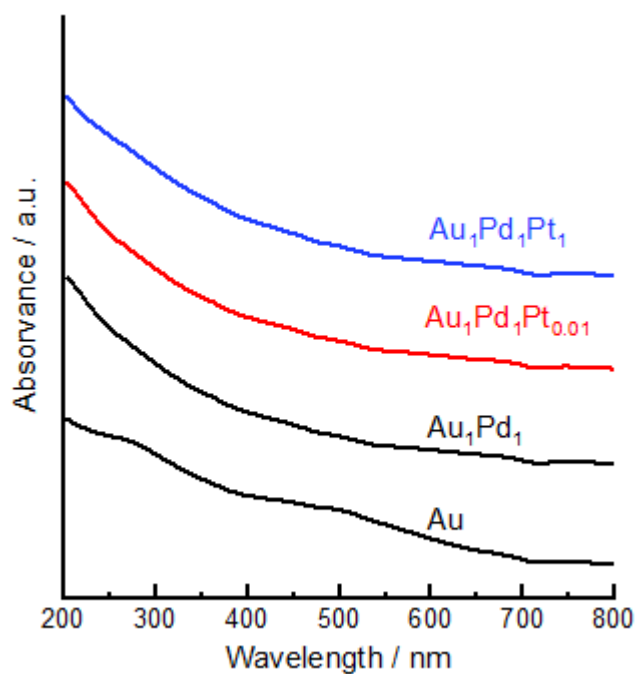


Figure S.1. Representative UV-vis spectra from aqueous sol-immobilisation prepared colloidal catalysts prior to immobilisation. The absence of the Au plasmon peak (at approx. 550 nm) in the bimetallic and trimetallic colloids indicative of alloy formation.

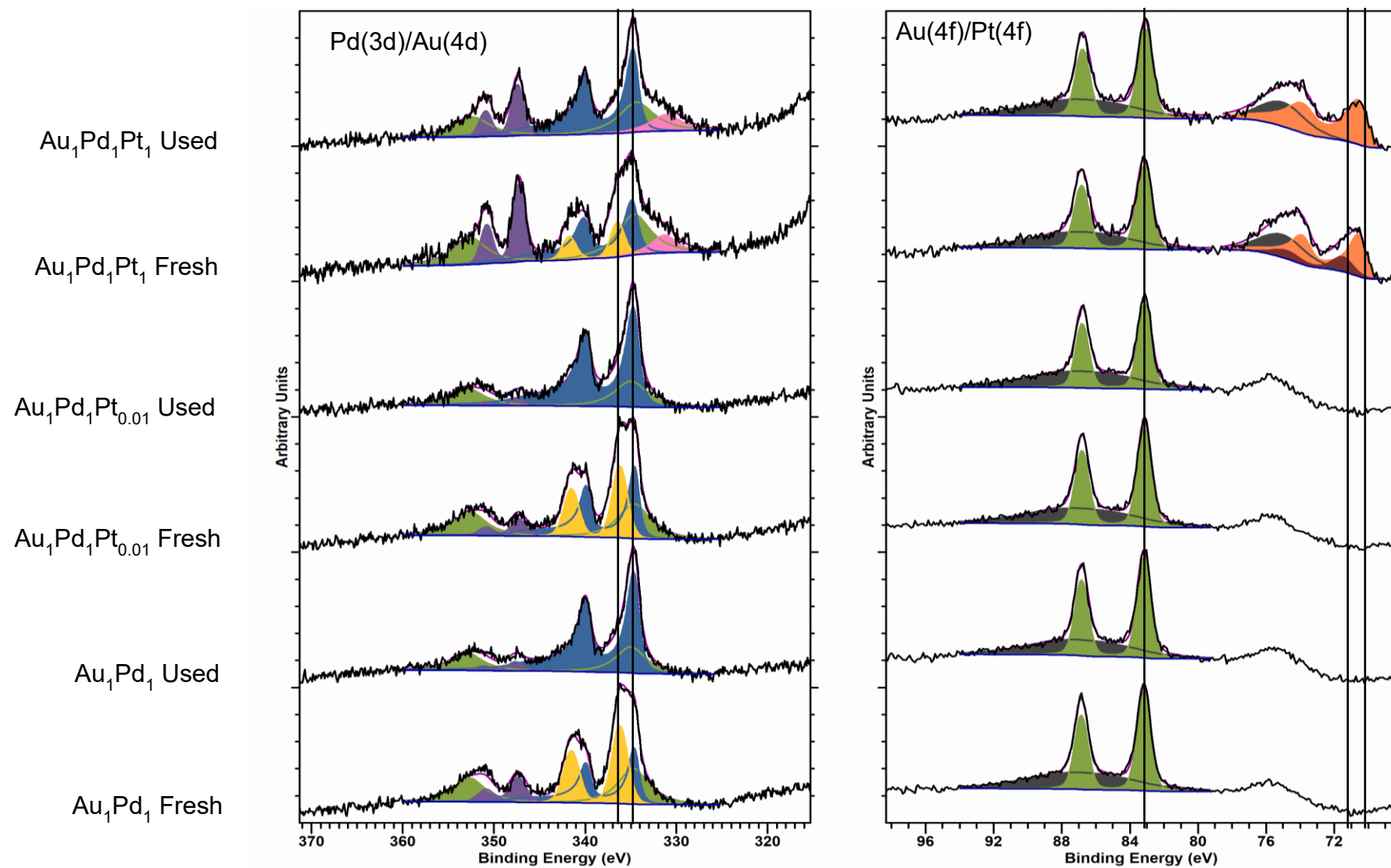


Figure S.3 Corresponding XPS Pd(3d)/Au(4d) and Au(4f)/Pt(4f) spectra for fresh and used 1%Au₁Pd₁/TiO₂, 1%Au₁Pd₁Pt_{0.01}/TiO₂, and 1%Au₁Pd₁Pt₁/TiO₂ catalysts. Au⁰= Green, Pd⁰=Blue, Pd²⁺= Yellow, Pt⁰= Peach, Pt²⁺ = Burgundy, Ca²⁺= Purple, Ti loss of structure = Black.

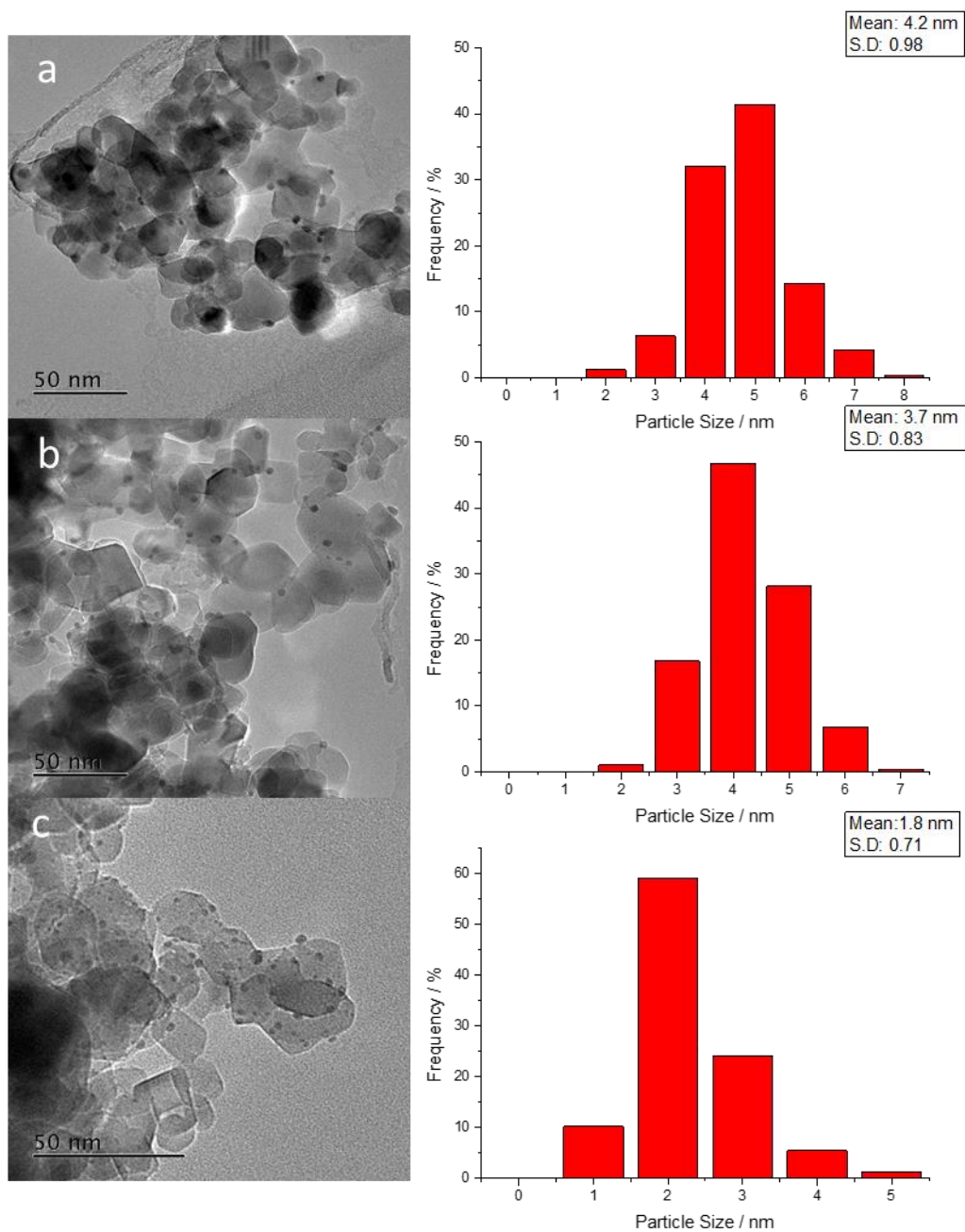


Figure S3. Representative bright field transmission electron micrographs and corresponding particle size distributions of TiO₂ supported bi- and tri-metallic catalysts prepared by a sol-immobilisation methodology, calcined 400 °C, 3h, static air, ramp rate = 10 °C min⁻¹. (a) 1%Au₁Pd₁/TiO₂, (b) 1%Au₁Pd₁Pt_{0.01}/TiO₂, and (c) 1%Au₁Pd₁Pt₁/TiO₂.

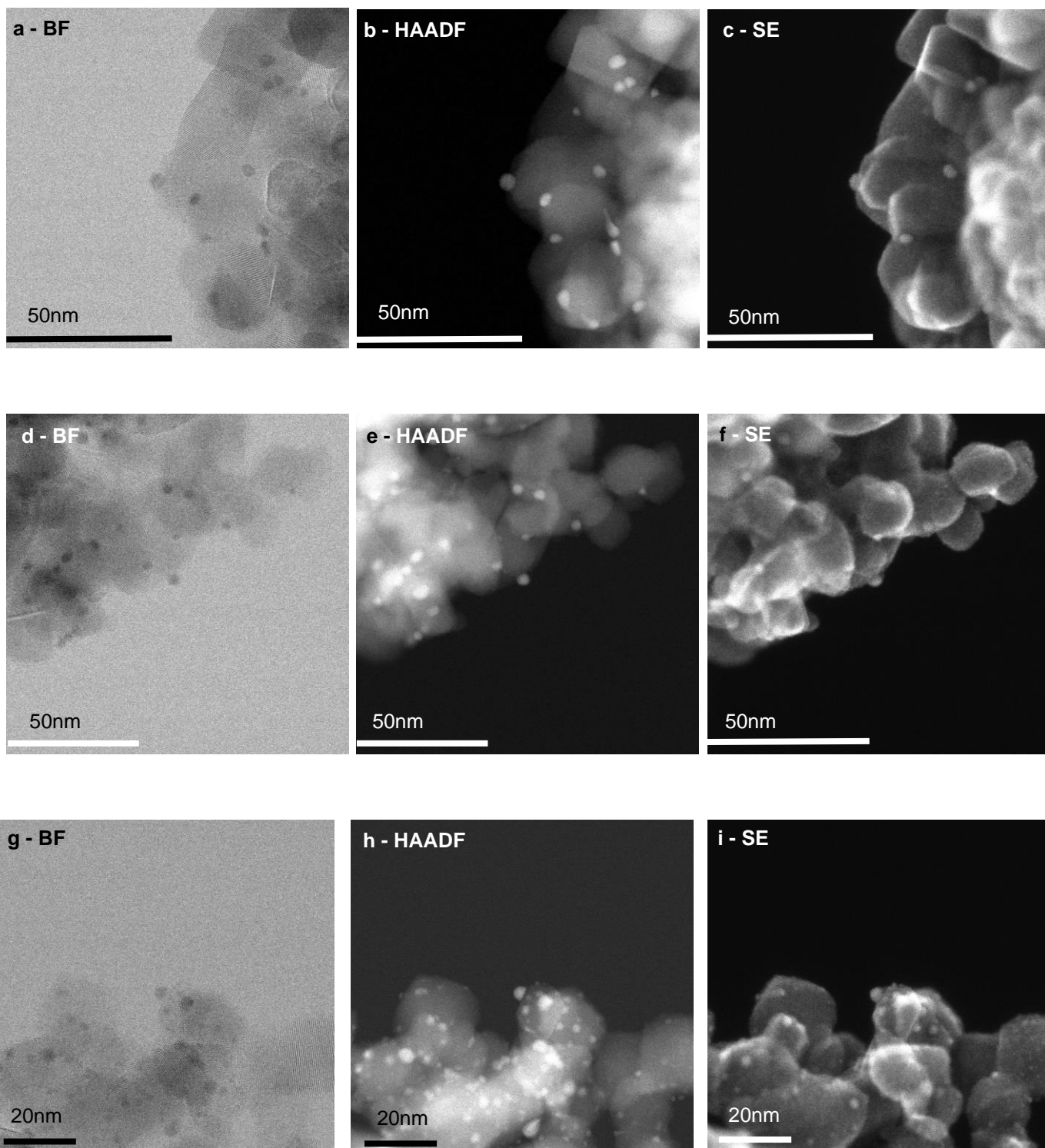


Figure S4 - Complementary bright field (BF)-STEM, high angle annular dark field (HAADF)-STEM and secondary electron (SE)-STEM images of (a, b, c) 1% Au₁Pd₁/TiO₂, (d, e, f) 1% Au₁Pd₁Pt_{0.01}/TiO₂ and (g, h, i) 1% Au₁Pd₁Pt₁/TiO₂ catalyst samples prepared by sol-immobilisation.

Table S1. Elemental composition of 1%AuPdPt/TiO₂ catalysts before and after use in the direct synthesis of H₂O₂, as determined by EDX.

Catalyst	Au (At%)	Pd (At%)	Pt (At%)
1%Au ₁ Pd ₁ /TiO ₂	0.19	0.15	-
1%Au ₁ Pd ₁ Pt _{0.01} /TiO ₂	0.17	0.18	BDL*
1%Au ₁ Pd ₁ Pt ₁ /TiO ₂	0.17	0.11	0.11

Table S2. Comparison of initial H₂O₂ synthesis rates over various TiO₂ supported AuPdPt catalysts.

Catalyst	Rate of reaction / mmol _{H₂O₂} min ⁻¹	
	Use 1	Use 2*
1%Au ₁ Pd ₁ /TiO ₂	0.034	0.042
1%Au ₁ Pd ₁ Pt _{0.01} /TiO ₂	0.049	0.056
1%Au ₁ Pd ₁ Pt 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.

H₂O₂ direct synthesis reaction conditions: Catalyst (0.01g), H₂O (2.9g), MeOH (5.6g), 5% H₂ / CO₂ (420 psi), 25% O₂ / CO₂ (160 psi), 0.083 h, 2 °C 1200 rpm

Table S3. Elemental surface composition of 1%AuPdPt/TiO₂ catalysts after use in the direct synthesis of H₂O₂, as determined by XPS analysis.

Catalyst		Au : Pt	Pd : Au	Pd ²⁺ : Pd ⁰
1%Au ₁ Pd ₁ /TiO ₂	Fresh	-	1.92	1.30
	Used	-	2.27	0.00
1%Au ₁ Pd ₁ Pt _{0.01} /TiO ₂	Fresh	n.d	1.92	0.92
	Used	n.d	2.78	0.00
1%Au ₁ Pd ₁ Pt ₁ /TiO ₂	Fresh	0.78	1.86	0.63
	Used	0.50	1.78	0.00

H₂O₂ direct synthesis reaction conditions: Catalyst (0.01g), H₂O (2.9g), MeOH (5.6g), 5% H₂ / CO₂ (420 psi), 25% O₂ / CO₂ (160 psi), 0.5 h, 2 °C 1200 rpm.

n.d: not able to determine

Table S4. Total metal leaching from various TiO₂ supported AuPdPt catalysts during H₂O₂ synthesis reaction, as determined by ICP-MS analysis.

Catalyst	Productivity (Fresh) / mol _{H₂O₂} kg _{cat} ⁻¹ h ⁻¹	Au Leaching / μg _L ⁻¹	Pd Leaching / μg _L ⁻¹	Pt Leaching / μg _L ⁻¹
1%Au ₁ Pd ₁ /TiO ₂	81	-	0.21	-
1%Au ₁ Pd ₁ Pt _{0.01} /TiO ₂	112	-	1.56	-
1%Au ₁ Pd ₁ Pt ₁ /TiO ₂	30	-	-	-

H₂O₂ direct synthesis reaction conditions: Catalyst (0.01g), H₂O (2.9g), MeOH (5.6g), 5% H₂ / CO₂ (420 psi), 25% O₂ / CO₂ (160 psi), 0.5 h, 2 °C 1200 rpm.

Table S5. Mean metal particle size of various TiO₂ supported AuPdPt catalysts, as prepared and after use in the H₂O₂ synthesis reaction, as determined by analysis of bright field TEM micrographs.

Catalyst	Mean Particle size / nm (Standard deviation)	
	Fresh *	Used **
1%Au ₁ Pd ₁ /TiO ₂	4.2 (0.98)	4.3 (0.91)
1%Au ₁ Pd ₁ Pt _{0.01} /TiO ₂	3.7 (0.55)	4.6 (1.2)
1%Au ₁ Pd ₁ Pt 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 H₂O₂ synthesis reaction.

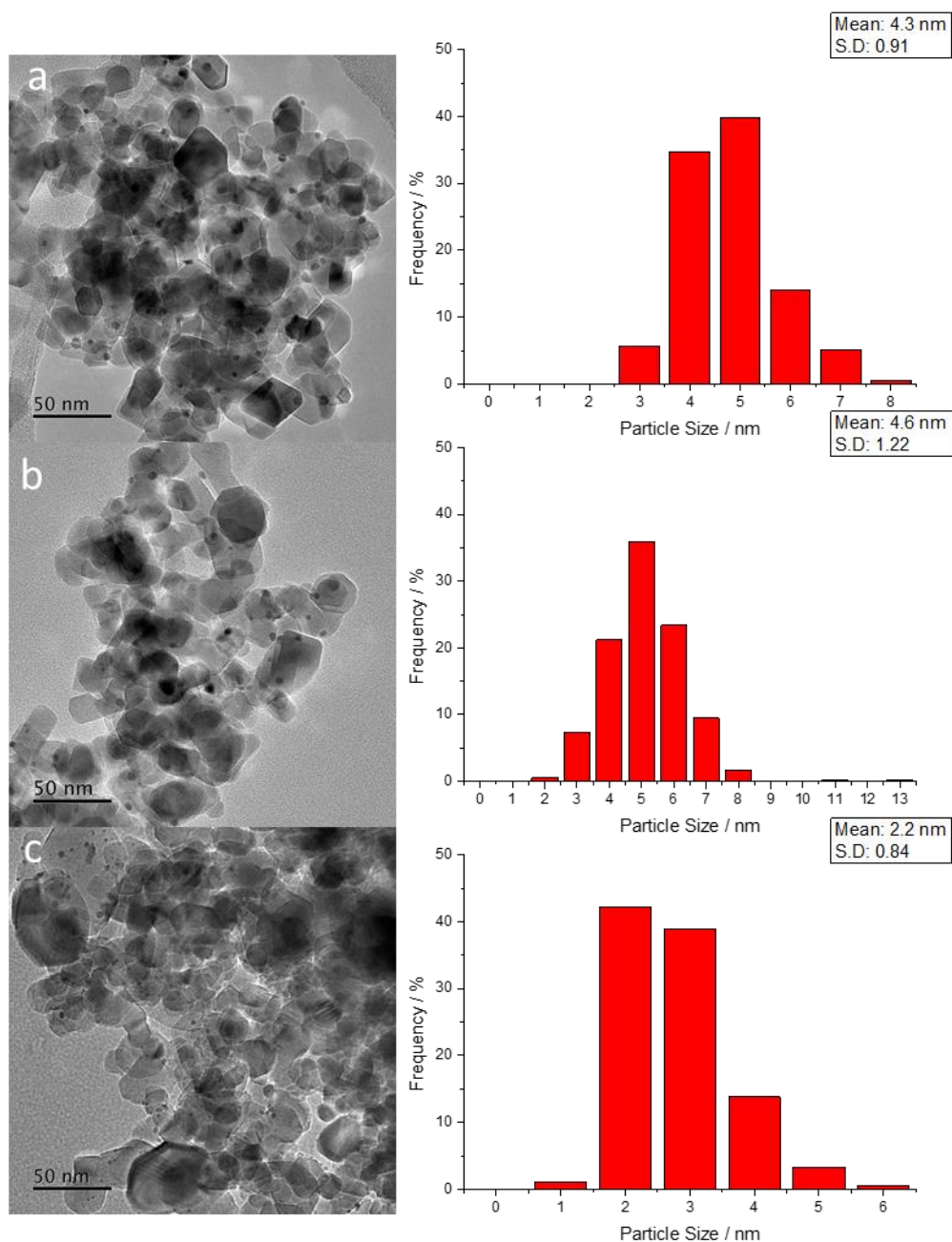


Figure S4. Representative bright field transmission electron micrographs and corresponding particle size distributions of 1% AuPdPt/TiO₂ catalysts after use in the direct synthesis of H₂O₂. Catalysts prepared by a sol-immobilisation methodology, calcined 400 °C, 3h, static air, ramp rate = 10 °C min⁻¹. (a) 1%Au₁Pd₁/TiO₂, (b) 1%Au₁Pd₁Pt_{0.01}/TiO₂ and (c) 1%Au₁Pd₁Pt₁/TiO₂.