Supporting Information.

Promoting H_2O_2 direct synthesis through Fe incorporation into AuPd Catalysts.

Rong-Jian Li[a †], Richard J. Lewis[a†*], Ángeles López-Martín[a] David J. Morgan[a,b], Thomas E. Davies[a], David Kordus[c], A. Iulian Dugulan[d], Beatriz Roldan Cuenya[c], and Graham J. Hutchings[a*]

[a]Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Translational Research Hub, Maindy Road, Cardiff, CF24 4HQ, United Kingdom.

[b]HarwellXPS, Research Complex at Harwell (RCaH), Didcot, OX11 OFA, United Kingdom.

[c]Department of Interface Science, Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany

[d]Laboratory of Fundamentals Aspects of Materials and Energy, Department of Radiation Science & Technology, Delft University of Technology, Mekelweg 15, 2628 CD, Delft, The Netherlands

[†]These authors contributed equally to this work.

*LewisR27@Cardiff.ac.uk, Hutch@Cardiff.ac.uk

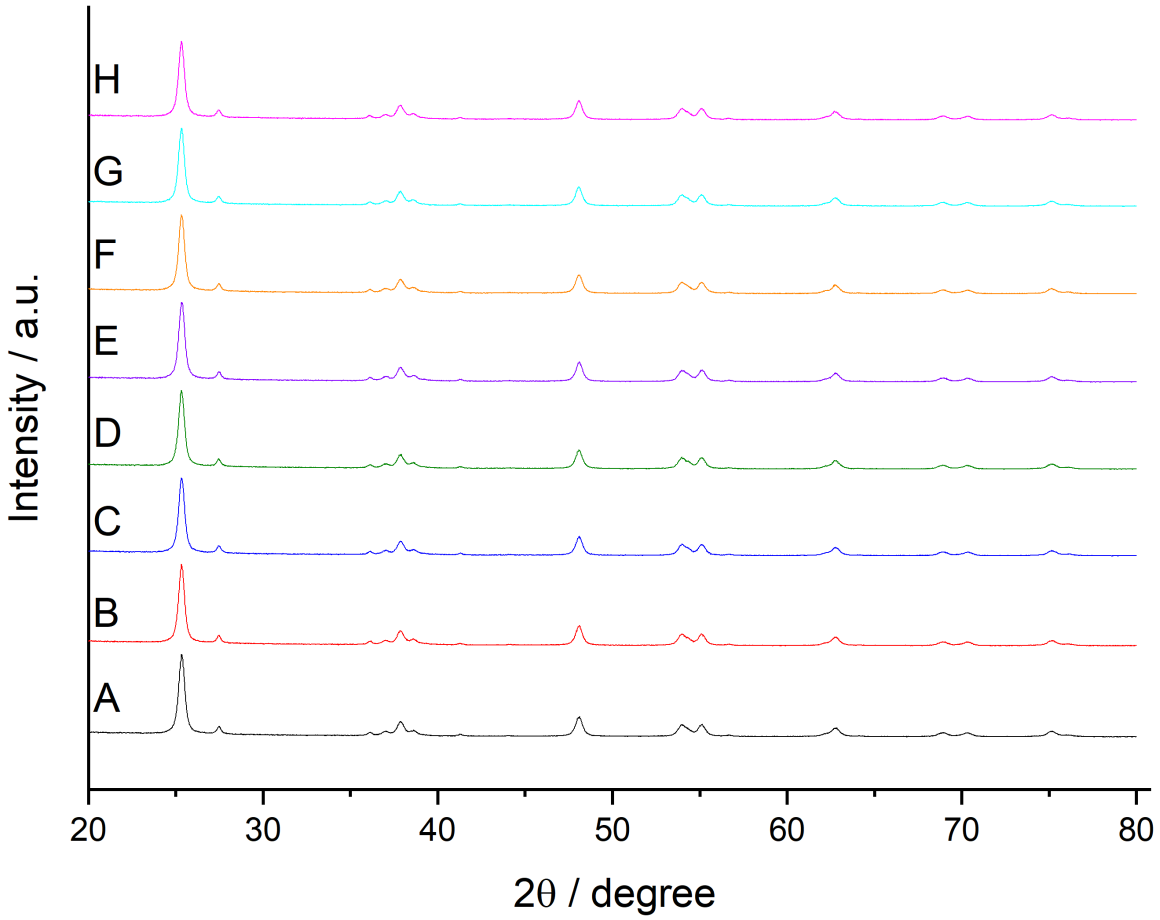

Figure S.1. X-ray diffractograms of AuPdFe/TiO_2 catalysts. **(A)** TiO_2, **(B)** 0.5%Au-0.5%Pd/TiO_2, **(C)**, 0.5%Au-0.5%Pd-0.01%Fe/TiO_2, **(D)** 0.5%Au-0.5%Pd-0.02%Fe/TiO_2, **(E)** 0.5%Au-0.5%Pd-0.05%Fe/TiO_2, **(F)** 0.5%Au-0.5%Pd-0.1%Fe/TiO_2, **(G)** 0.5%Au-0.5%Pd-0.5%Fe/TiO_2 and **(H)** 0.5%Au-0.5%Pd-0.1%Fe/TiO_2. **Note:** Catalysts exposed to a reductive heat treatment (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}). Support (P25), used as received.

Table S.1. Actual metal loading of AuPdFe/TiO_2 catalysts, as determined by ICP analysis of microwave-assisted aqua regia digested catalysts.

Catalyst	Actual metal loading / wt.%		
	Au	Pd	Fe
1%Au/TiO_2	1.01	-	-
1%Pd/TiO_2	-	0.91	-
0.5%Au-0.5%Pd/TiO_2	0.48	0.46	-
0.5%Au-0.5%Pd-0.01%Fe/TiO_2	0.45	0.47	0.01
0.5%Au-0.5%Pd-0.02%Fe/TiO_2	0.48	0.49	0.02
0.5%Au-0.5%Pd-0.05%Fe/TiO_2	0.52	0.52	0.05
0.5%Au-0.5%Pd-0.1%Fe/TiO_2	0.48	0.47	0.11
0.5%Au-0.5%Pd-0.5%Fe/TiO_2	0.49	0.49	0.47
0.5%Au-0.5%Pd-1%Fe/TiO_2	0.55	0.53	0.99
0.5%Au-0.02%Fe/TiO_2	0.46	-	0.03
0.5%Pd-0.02%Fe/TiO_2	-	0.47	0.02
1%Au-0.02%Fe/TiO_2	1.04	-	0.03
1%Pd-0.02%Fe/TiO_2	-	0.97	0.03

Table S.2. Catalytic performance towards the direct synthesis of H_2O_2, as a function of Fe loading.

Catalyst	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	H_2O_2 Conc. / wt.%	H_2 Conv. / %	H_2O_2 Sel. / %	Initial rate of reaction / $mmol_{H2O2}$ $mmol_{metal}^{-1}min^{-1}$	Degradation / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$
1%Au/TiO_2	4	0.008	3.0	14	1.76×10^2	28
1%Pd/TiO_2	50	0.100	13	41	9.99×10^2	224
0.5%Au-0.5%Pd/TiO_2	70	0.139	19	39	2.46×10^3	208
0.5%Au-0.5%Pd-0.01%Fe/TiO_2	78	0.155	26	32	1.30×10^3	331
0.5%Au-0.5%Pd-0.02%Fe/TiO_2	121	0.242	40	31	3.00×10^3	451
0.5%Au-0.5%Pd-0.05%Fe/TiO_2	110	0.213	36	32	1.89×10^3	365
0.5%Au-0.5%Pd-0.1%Fe/TiO_2	105	0.210	33	32	2.26×10^3	353
0.5%Au-0.5%Pd-0.5%Fe/TiO_2	94	0.186	25	39	1.33×10^3	307
0.5%Au-0.5%Pd-1%Fe/TiO_2	65	0.129	16	42	4.65×10^2	287
0.5%Au-0.02%Fe/TiO_2	3	0.006	2	16	3.18×10^2	52
0.5%Pd-0.02%Fe/TiO_2	35	0.070	9	40	1.03×10^3	151
1%Au-0.02%Fe/TiO_2	3	0.006	2	13	1.74×10^2	24
1%Pd-0.02%Fe/TiO_2	41	0.082	11	38	7.24×10^2	233

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2 °C 1200 rpm. **H_2O_2 degradation reaction conditions:** Catalyst (0.01 g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 0.5 h, 2 °C 1200 rpm. **Note:** Initial reaction rate measured over a reaction time of 0.083 h, calculated based on actual metal loading.

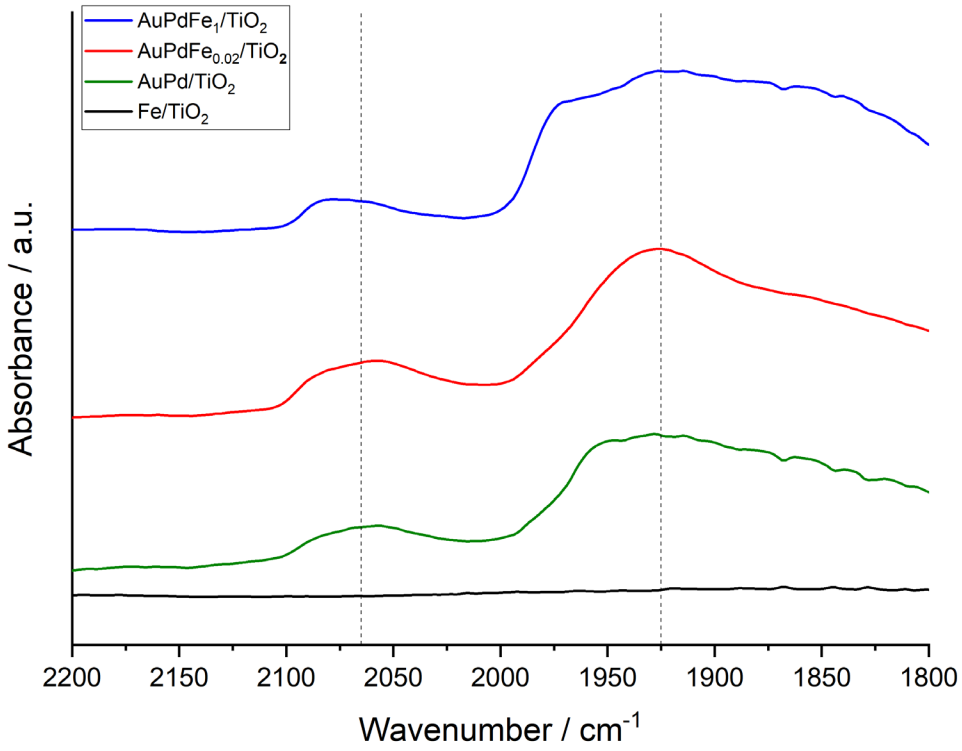

Figure S.2. CO-DRFITS spectra for AuPdFe/TiO_2 catalysts, with analysis of a 1%Fe/TiO_2 formulation included for reference. **Note:** No bands which may be associated with the redox process of FeOx, (typically at 3700 cm^{-1}) were observed and the x-axis range has been restricted to allow for improved clarity of the Pd-CO region.[1]

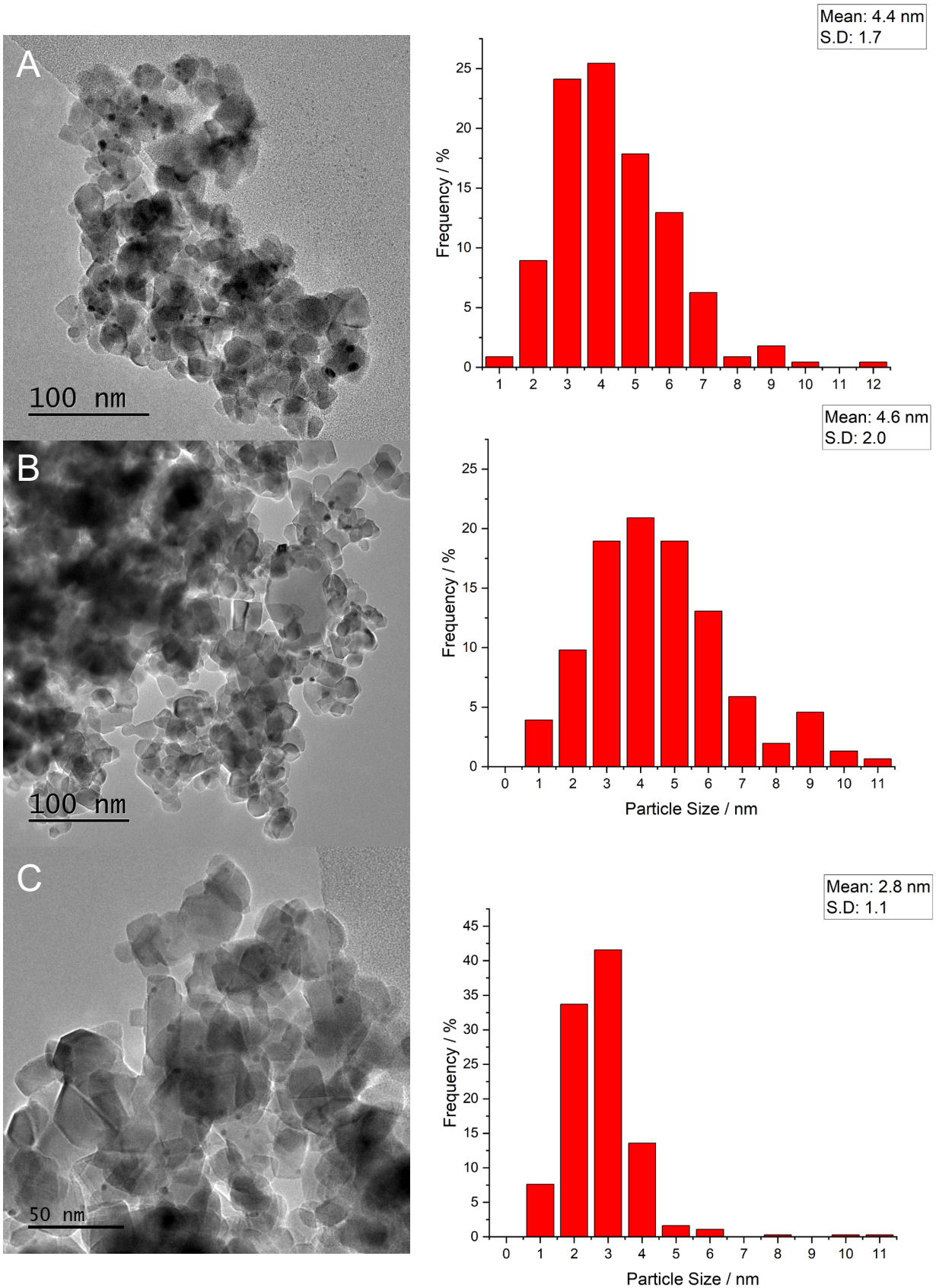

Figure S.3.A Representative bright field transmission electron micrographs and corresponding particle size histograms of **(A)** 0.5%Au-0.5%Pd/TiO_2 **(B)** 0.5%Au-0.5%Pd-0.01%Fe/TiO_2 and **(C)** 0.5%Au-0.5%Pd-0.02Fe%/TiO_2 catalysts. **Note:** All catalysts exposed to a reductive heat treatment (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1})

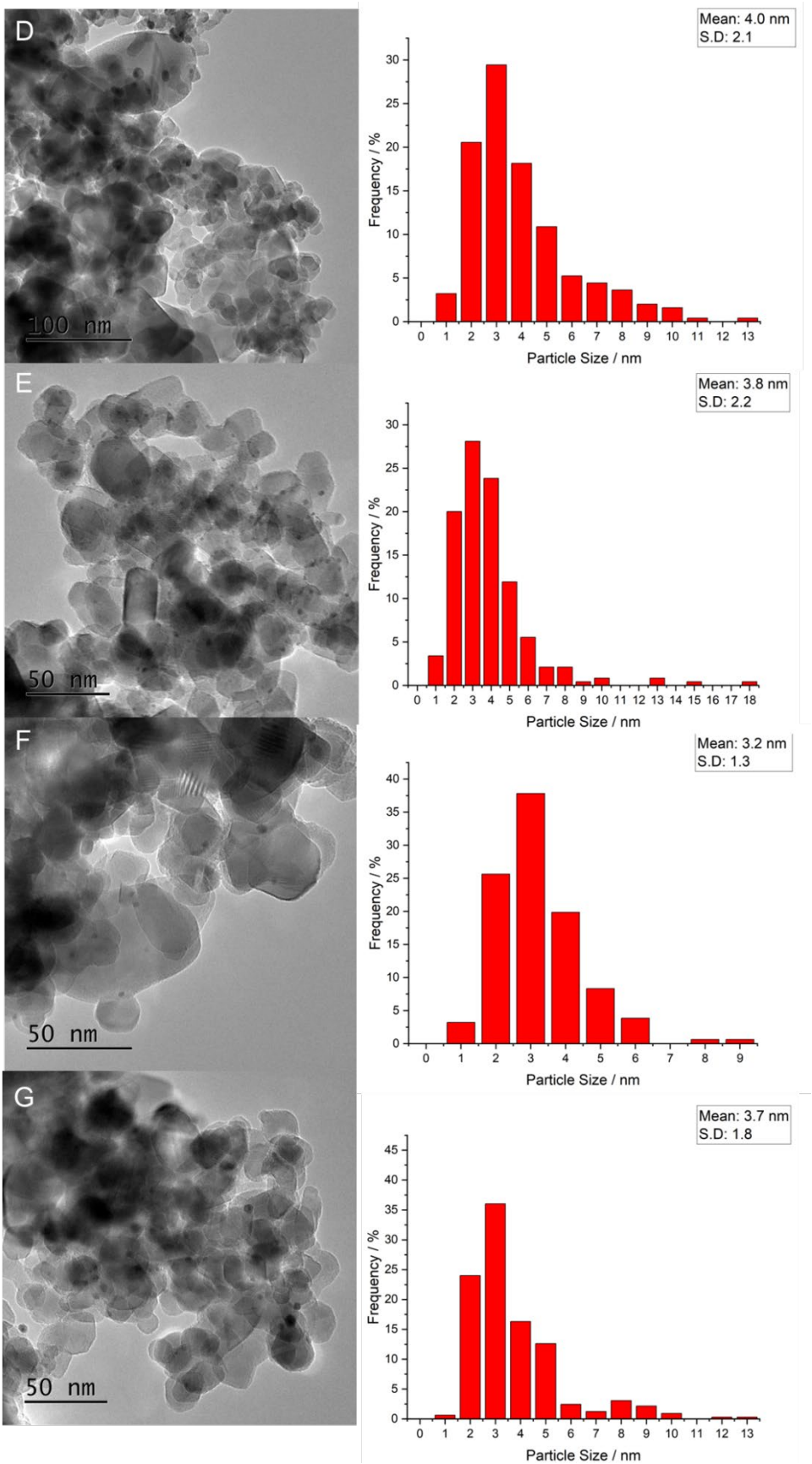

Figure 3. B. Representative bright field transmission electron micrographs and corresponding particle size histograms of **(D)** 0.5%Au-0.5%Pd0.05%Fe/TiO_2, **(E)** 0.5%Au-0.5%Pd-0.1%Fe/TiO_2, **(F)** 0.5%Au-0.5%Pd-0.5%Fe/TiO_2 and **(G)** 0.5%Au-0.5%Pd-1%Fe/TiO_2 catalysts. **Note:** All catalysts exposed to a reductive heat treatment (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}).

Table S.3. A comparison of catalytic performance of trimetallic catalysts towards the direct synthesis of H_2O_2.

Catalyst	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	Solvent	Temp / °C	Time / h	H_2O_2 Conc. / wt.%	H_2 Conv. / %	H_2O_2 Sel. / %	Rate of reaction / $mol_{H2O2}mol_{metal}^{-1}h^{-1}$	Reference
1% $Au_1Pd_1Pt_{0.01}/TiO_2$	112	H_2O/MeOH	2	0.5	0.22	43	37	1.70 x10^3	2
1%$AuPd_{(0.975)}Pt_{(0.025)}/TiO_2$	106	H_2O/MeOH	2	0.5	0.22	-	-	1.62 x10^3	3
1%$AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$	107	H_2O/MeOH	2	0.5	0.22	32	41	1.56 x10^3	3
1%$AuPd_{(0.975)}Sn_{(0.025)}/TiO_2$	78	H_2O/MeOH	2	0.5	0.16	-	-	1.18 x10^3	3
1%$AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$	94	H_2O/MeOH	2	0.5	0.19	31	40	1.38 x10^3	3
1%$AuPd_{(0.975)}Co_{(0.025)}/TiO_2$	71	H_2O/MeOH	2	0.5	0.14	-	-	1.04 x10^3	3
1%$AuPd_{(0.975)}In_{(0.025)}/TiO_2$	77	H_2O/MeOH	2	0.5	0.15	-	-	1.16 x10^3	3
1%$AuPd_{(0.975)}Ga_{(0.025)}/TiO_2$	70	H_2O/MeOH	2	0.5	0.14	-	-	1.03 x10^3	3
1%$AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$	100	H_2O/MeOH	2	0.5	0.20	24	50	1.47 x10^3	3
0.2%Au-4.60%Pd-0.2%Pt/TiO_2	184	H_2O/MeOH	2	0.5	0.37	-	-	4.06 x10^2	4
1%$AuPd_{(0.975)}Cu_{(0.025)}$/ZSM-5	115	H_2O/MeOH	2	0.5	0.23	19	72	1.69 x10^3	5
1%$AuPd_{(0.975)}Ni_{(0.025)}$/ZSM-5	81	H_2O/MeOH	2	0.5	0.16	-	-	1.19 x10^3	5
1%$AuPd_{(0.975)}Zn_{(0.025)}$/ZSM-5	77	H_2O/MeOH	2	0.5	0.16	-	-	1.13 x10^3	5
2.4%Au-2.4%Pd-0.2%Pt/TS-1	167	H_2O/MeOH	2	0.5	0.33	-	-	4.67 x10^2	6
0.275%Au-0.275%Pd-0.11%Pt/TS-1	135	H_2O/MeOH	2	0.5	0.27	-	-	2.97 x10^3	7
2.4%Au-2.4%Pd-0.2%Pt/CeO_2	170	H_2O/MeOH	2	0.5	0.34	-	-	4.75 x10^2	8
0.5%Au-0.5%Pd-0.02%Fe/TiO_2	122	H_2O/MeOH	2	0.5	0.24	40	31	1.61 x10^3	This work

Table S.4. Comparison of catalytic selectivity towards H_2O_2 at iso-conversion.

Catalyst	Reaction time / min	H_2 Conv. / %	H_2O_2 Sel. / %	H_2O_2 Conc. / wt.%
0.5%Au-0.5%Pd/TiO_2	10	8	50	0.08
0.5%Au-0.5%Pd-0.02%Fe/TiO_2	5	9	41	0.07
0.5%Au-0.5%Pd-1%Fe/TiO_2	10	8	37	0.06

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

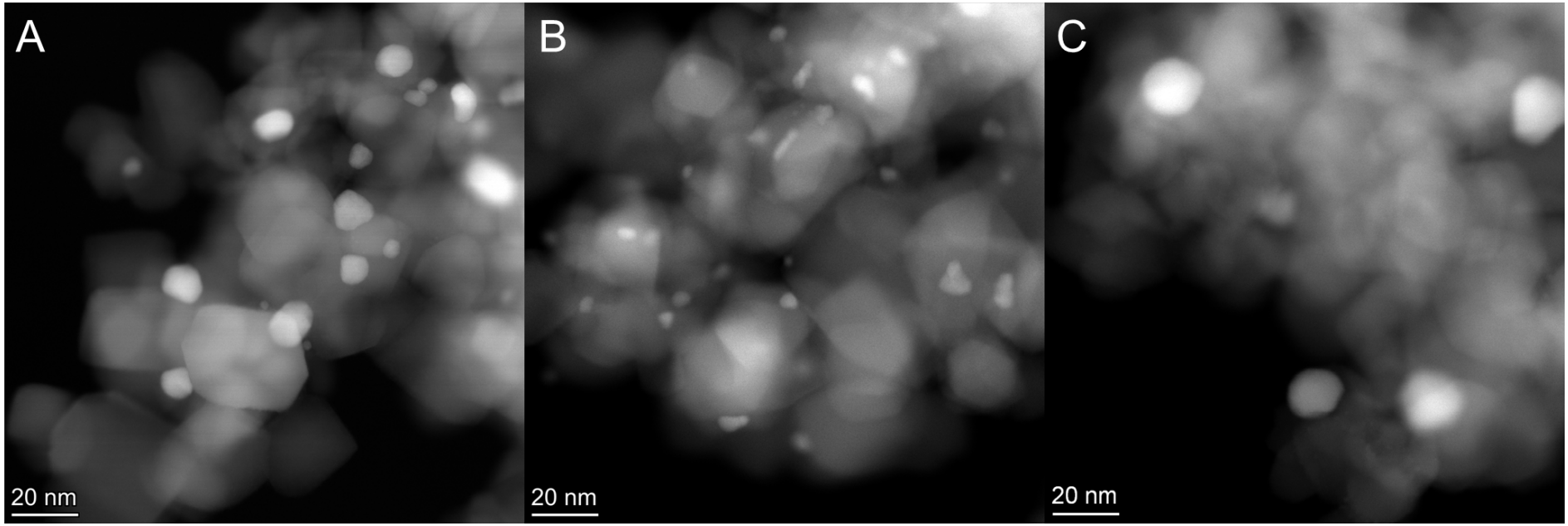

Figure S.4. HAADF-STEM analysis of the as-prepared **(A)** 0.5%Au-0.5%Pd/TiO_2 **(B)** 0.5%Au-0.5%Pd-0.02%Fe/TiO_2 and **(C)** 0.5%Au-0.5%Pd-1%Fe/TiO_2 catalysts. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}).

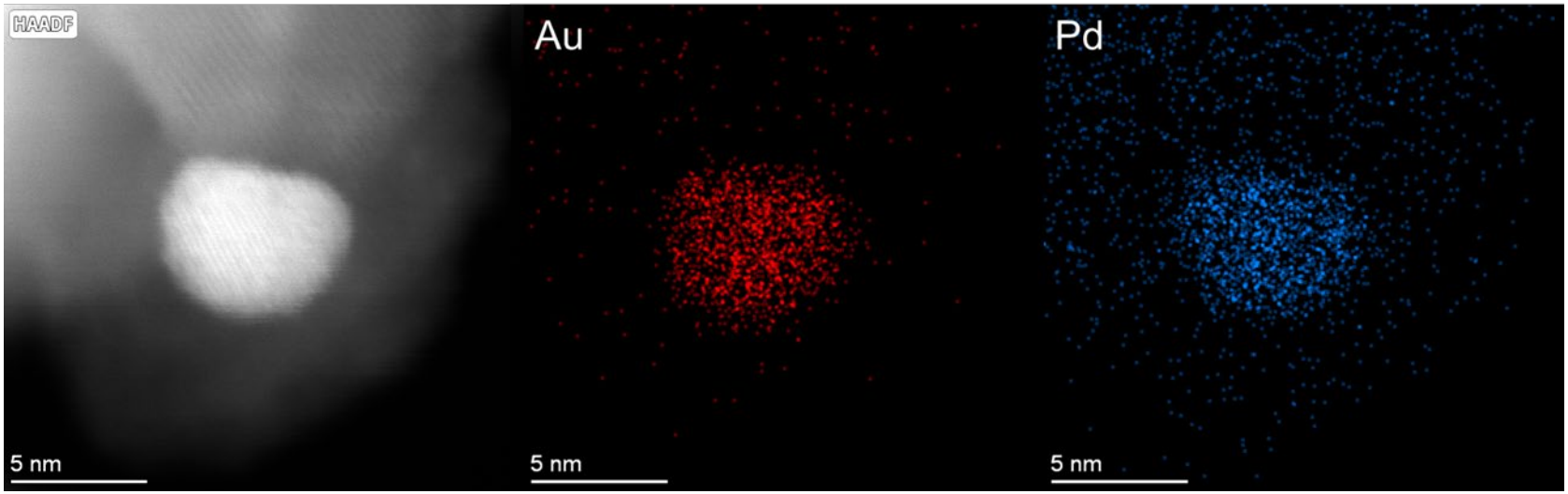

Figure S.5. HAADF-STEM and corresponding EDX analysis of the as-prepared 0.5%Au-0.5%Pd/TiO_2 catalyst. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}).

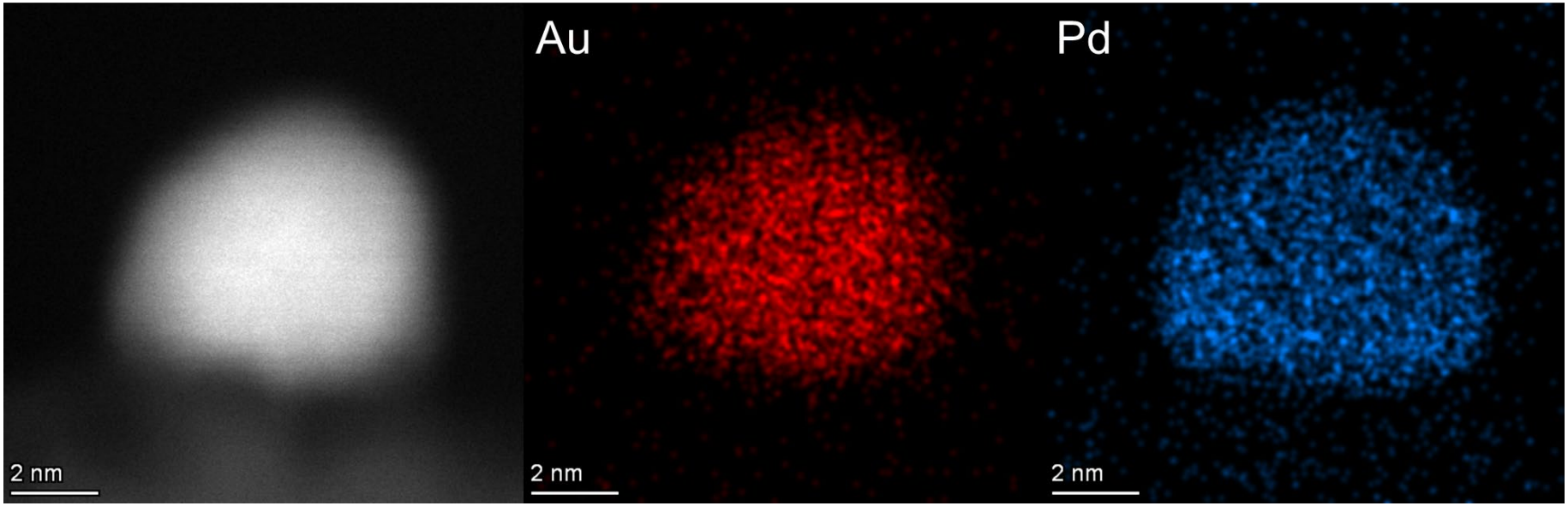

Figure S.6. HAADF-STEM and corresponding EDX analysis of the as-prepared 0.5%Au-0.5%Pd-0.02%Fe/TiO_2 catalyst. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}).

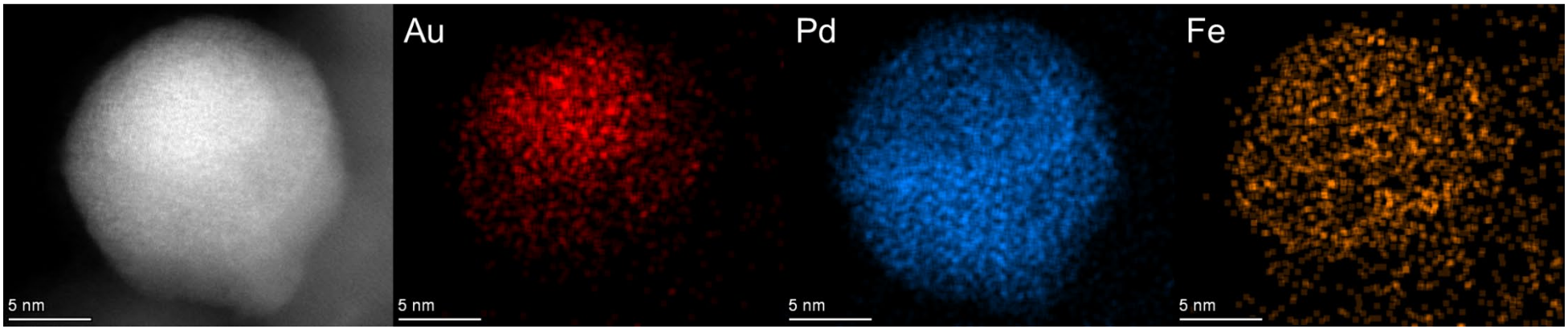

Figure S.7. HAADF-STEM and corresponding EDX analysis of the as-prepared 0.5%Au-0.5%Pd-1%Fe/TiO_2 catalyst. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}).

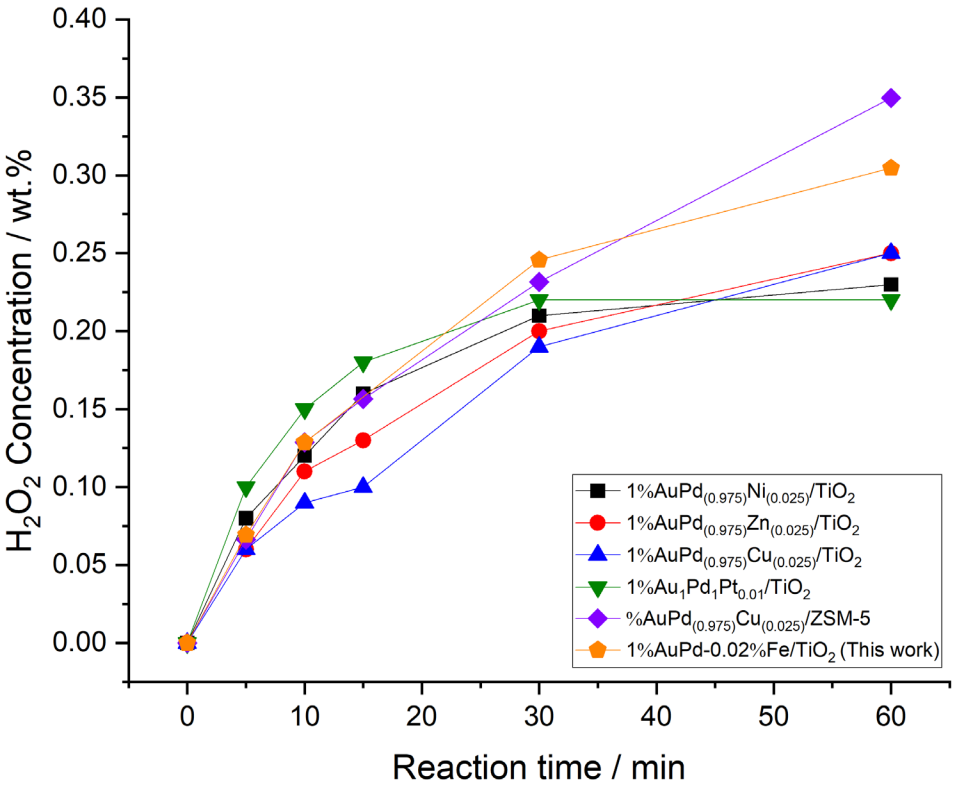

Figure S.8. A comparison of catalytic performance towards the direct synthesis of H_2O_2, as a function of reaction time. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2 °C 1200 rpm.

Table S.5. Catalyst stability as a function of reaction time, as determined by ICP analysis of post-H_2O_2 direct synthesis reaction solutions.

Catalyst	Reaction time / min	Au / ppm (%)	Pd / ppm (%)	Fe / ppm (%)
0.5%Au-0.5%Pd/TiO_2	5	0.0 (0.0)	1.9 (0.03)	-
	10	0.0 (0.0)	2.7 (0.05)	-
	30	0.0 (0.0)	3.3 (0.06)	-
	60	0.0 (0.0)	5.5 (0.10)	-
	120	0.0 (0.0)	6.0 (0.11)	-
	180	0.0 (0.0)	6.3 (0.12)	-
0.5%Au-0.5%Pd-0.02%Fe/TiO_2	5	0.0 (0.0)	1.7 (0.03)	0.0 (0.0)
	10	0.0 (0.0)	2.5 (0.05)	0.0 (0.0)
	30	0.0 (0.0)	3.0 (0.06)	0.0 (0.0)
	60	0.0 (0.0)	6.0 (0.11)	0.0 (0.0)
	120	0.0 (0.0)	6.7 (0.12)	0.0 (0.0)
	180	0.0 (0.0)	8.5 (0.16)	0.0 (0.0)
0.5%Au-0.5%Pd-1%Fe/TiO_2	5	0.0 (0.0)	3.1 (0.06)	0.0 (0.0)
	10	0.0 (0.0)	4.3 (0.08)	0.0 (0.0)
	30	0.0 (0.0)	6.3 (0.12)	0.0 (0.0)
	60	0.0 (0.0)	9.3 (0.17)	0.0 (0.0)
	120	0.0 (0.0)	13.2 (0.24)	0.0 (0.0)
	180	0.0 (0.0)	15.2 (0.28)	0.0 (0.0)

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

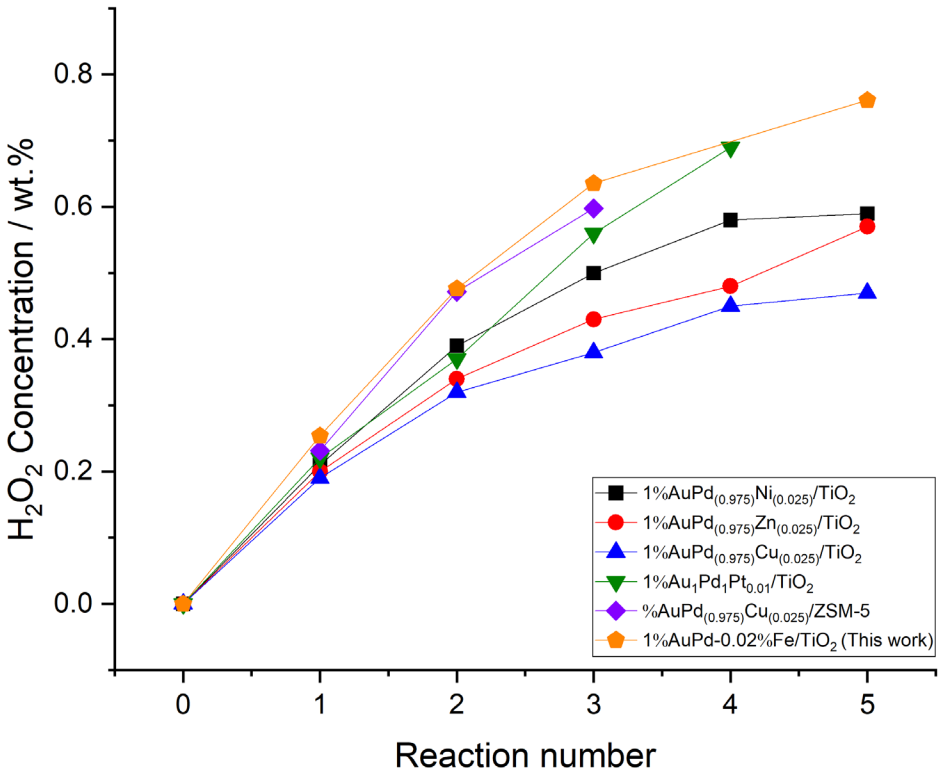

Figure S.9. Comparison of catalytic activity over sequential H_2O_2 synthesis reactions. ***Key:*** 0.5%Au-0.5%Pd/TiO_2 (green squares), 0.5%Au-0.5%Pd-0.02%Fe/TiO_2 (red circles), and 0.5%Au-0.5%Pd-1.0%Fe/TiO_2 (blue triangles). **H_2O_2 direct synthesis reaction conditions:** catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2 °C, 1200 rpm.

Table S.6. Catalyst stability after a 0.5 h H_2O_2 direct synthesis reaction, as determined by ICP analysis of post-H_2O_2 direct synthesis reaction solutions.

Catalyst	Au / ppm (%)	Pd / ppm (%)	Fe / ppm (%)
0.5%Au-0.5%Pd/TiO_2	0.0 (0.0)	3.3 (0.06)	-
0.5%Au-0.5%Pd-0.02%Fe/TiO_2	0.0 (0.0)	3.0 (0.06)	0.0 (0.0)
0.5%Au-0.5%Pd-1%Fe/TiO_2	0.0 (0.0)	6.3 (0.12)	0.0 (0.0)

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

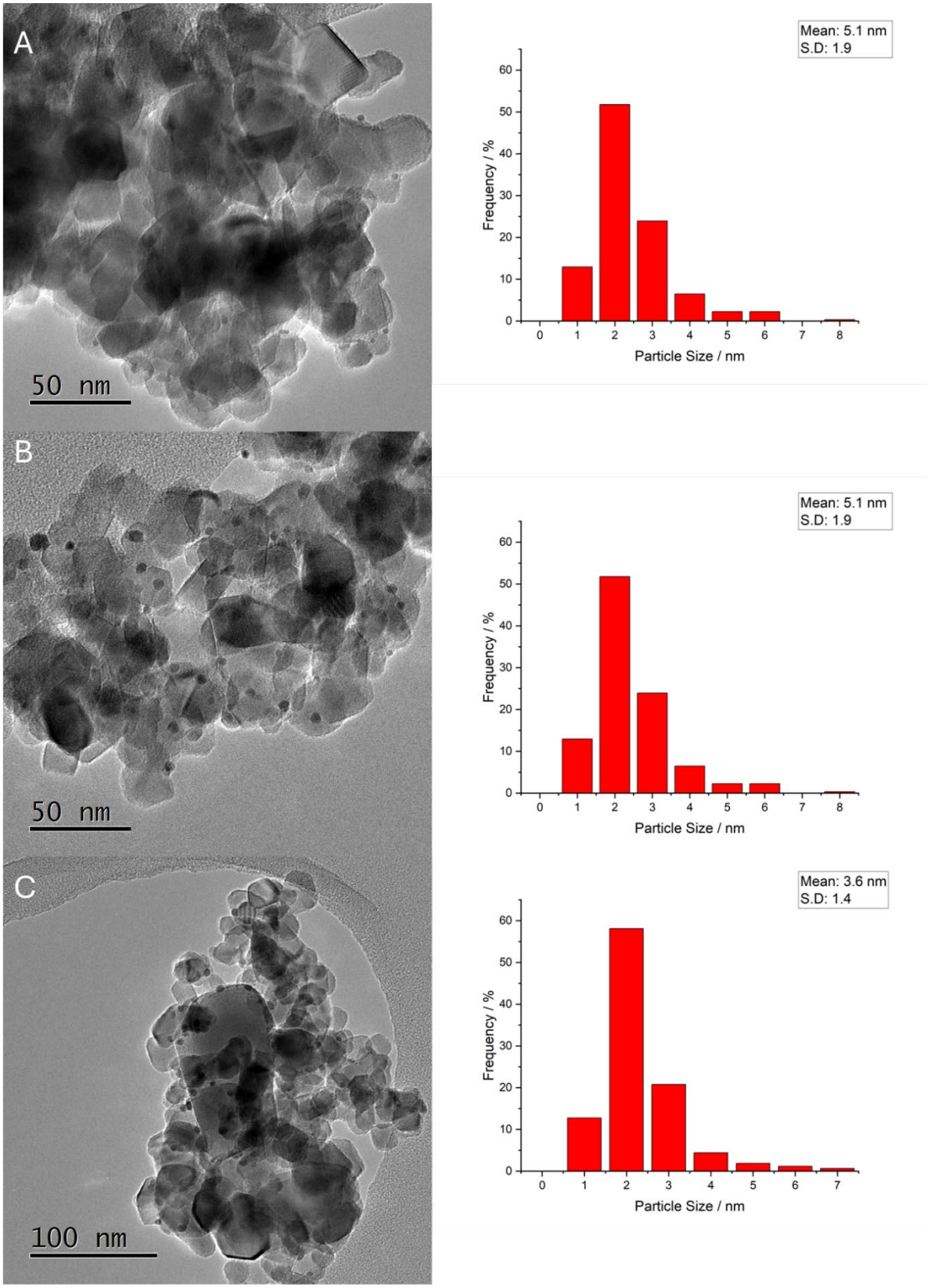

Figure S.10. Representative bright field transmission electron micrographs and corresponding particle size histograms of **(A)** 0.5%Au-0.5%Pd/TiO_2 **(B)** 0.5%Au-0.5%Pd-0.02%Fe/TiO_2 and **(C)** 0.5%Au-0.5%Pd-1%Fe/TiO_2 catalysts after use in the direct synthesis of H_2O_2. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2 °C 1200 rpm. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}). Spent samples were dried (30 °C, 16 h, under vacuum).

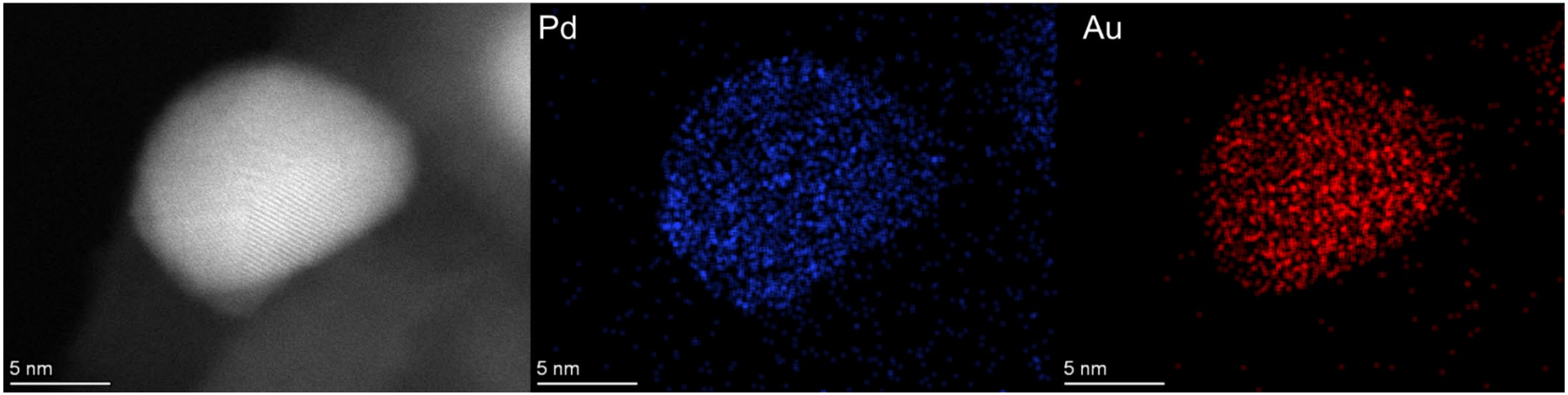

Figure S.11. HAADF-STEM and corresponding EDX analysis of the 0.5%Au-0.5%Pd/TiO_2 catalyst after use in the direct synthesis of H_2O_2. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 2° C, 1200 rpm. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}). Spent samples were dried (30 °C, 16 h, under vacuum).

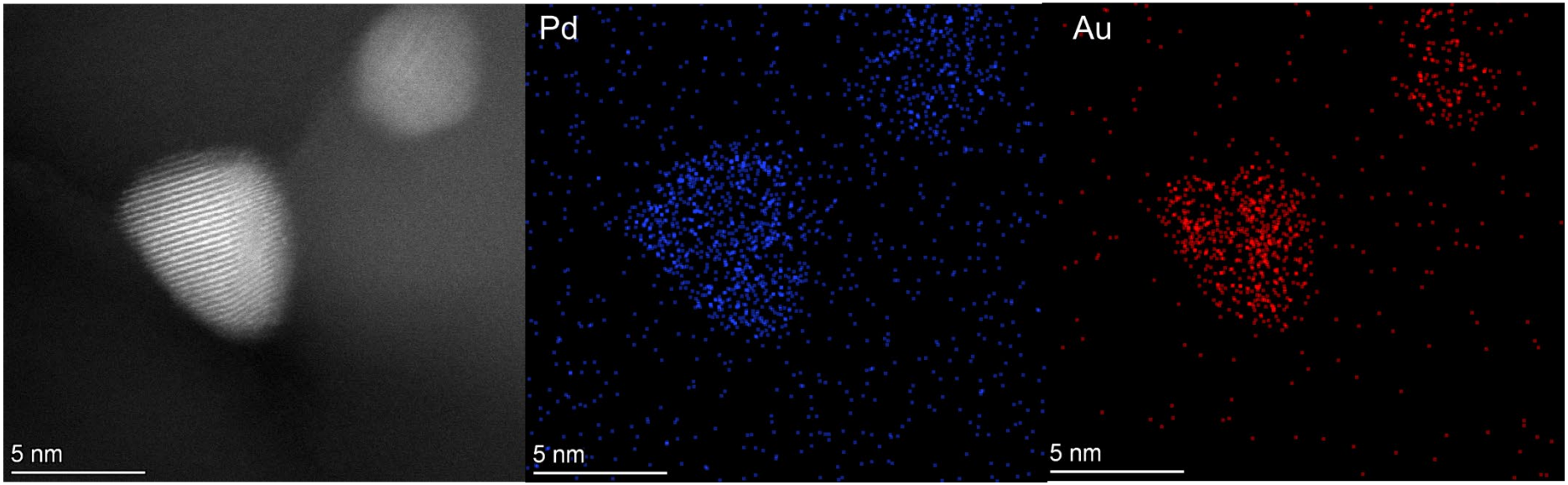

Figure S.12. HAADF-STEM and corresponding EDX analysis of the 0.5%Au-0.5%Pd-0.02%Fe/TiO_2 catalyst after use in the direct synthesis of H_2O_2. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 2° C, 1200 rpm. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}). Spent samples were dried (30 °C, 16 h, under vacuum).

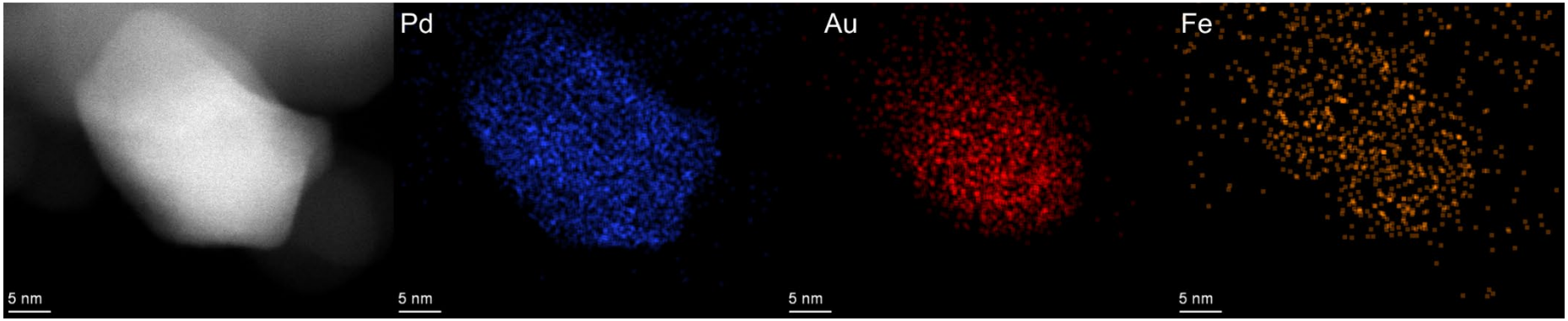

Figure S.13. HAADF-STEM and corresponding EDX analysis of the 0.5%Au-0.5%Pd-1%Fe/TiO_2 catalyst after use in the direct synthesis of H_2O_2. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 2° C, 1200 rpm. **Note:** Catalysts exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4h, 10 °Cmin^{-1}). Spent samples were dried (30 °C, 16 h, under vacuum).

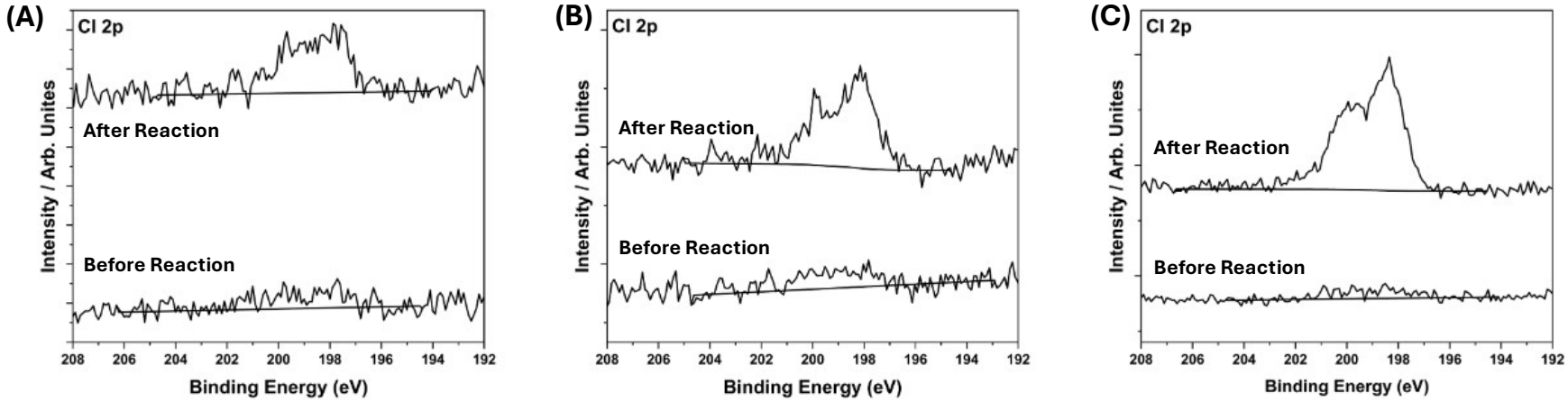

Figure S.14. XPS analysis of the loss of Cl after reaction on **(A)** 0.5%Au-0.5%Pd/TiO_2, **(B)** 0.5%Au-0.5%Pd-0.02%Fe/TiO_2 and **(C)** 0.5%Au-0.5%Pd-1.0%Fe/TiO_2. **H_2O_2 direct synthesis reaction conditions:** catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 2 °C, 1200 rpm.

Table S.7.A. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Au_{0.5}Pd_{0.5}Fe_{0.02}/TiO_2$ catalyst reported in this work.

Catalyst		**$Au_{0.5}Pd_{0.5}Fe_{0.02}/TiO_2$**	
Metal Loading / g	Au	5.00	
	Pd	5.00	
	Fe	0.20	
Support / g	TiO_2	989.80	
Catalyst: Solvent Ratio (wt/wt)		0.0018	
Solvent Usage / t		0.56	
H_2O_2 Selectivity / %		31.00	
H_2O_2 Productivity / $mol_{H2O2}\ Kg_{Cat}^{-1}\ h^{-1}$		122.00	
H_2 Usage / Kg		189.75	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	379.51
Methanol	t	336.99	188.71
TiO_2 (P25)	Kg	1.5	7.42
Au (metal)	g	96.9	24.23
Pd (metal)	g	37.2	9.30
Fe (metal)	t	104.62	0.0000010462
Catalyst	Kg		40.95
Total Cost/ USD			**609.17**

Table S.7.B. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Au_{0.65}Pd_{0.35}Pt_{0.01}/TiO_2$ catalyst.

Catalyst		**$Au_{0.65}Pd_{0.35}Pt_{0.01}/TiO_2$**	
Metal Loading / g	Au	5.00	
	Pd	5.00	
	Pt	0.10	
Support / g	TiO_2	989.80	
Catalyst: Solvent Ratio (wt/wt)		0.0018	
Solvent Usage / t		0.56	
H_2O_2 Selectivity / %		37.00	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		112.00	
H_2 Usage / Kg		158.98	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	317.97
Methanol	t	336.99	188.71
TiO_2 (P25)	Kg	1.5	7.42
Au (metal)	g	96.9	31.49
Pd (metal)	g	37.2	6.51
Pt (metal)	g	36.3	0.18
Catalyst	Kg		45.61
Total Cost/ USD			**552.29**

Table S.7.C. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Au_{0.25}Pd_{0.25}/TiO_2$ catalyst.

Catalyst		**$Au_{0.25}Pd_{0.25}/TiO_2$**	
Metal Loading / g	Au	2.50	
	Pd	2.50	
Support / g	TiO_2	995.00	
Catalyst: Solvent Ratio (wt/wt)		0.0018	
Solvent Usage / t		0.56	
H_2O_2 Selectivity / %		59.00	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		90.00	
H_2 Usage / Kg		99.70	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	199.40
Methanol	t	336.99	188.71
TiO_2 (P25)	Kg	1.5	7.46
Au (metal)	g	96.9	12.11
Pd (metal)	g	37.2	4.65
Catalyst	Kg		24.23
Total Cost/ USD			**412.34**

Table S.7.D. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Au_{0.5}Pd_{0.5}/TiO_2$ catalyst.

Catalyst		**$Au_{0.5}Pd_{0.5}/TiO_2$**	
Metal Loading / g	Au	5.00	
	Pd	5.00	
Support / g	TiO_2	990.00	
Catalyst: Solvent Ratio (wt/wt)		0.0032	
Solvent Usage / t		0.32	
H_2SO_4 Usage / t		$9.81x10^{-3}$	
NaBr Usage / t		$2.06x10^{-6}$	
H_2O_2 Selectivity / %		88.00	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		51	
H_2 Usage / Kg		66.84	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	133.69
H_2SO_4	t	85	0.83
NaBr	t	1734	$3.57x10^{-3}$
Methanol	t	336.99	106.66
TiO_2 (P25)	Kg	1.5	7.43
Au (metal)	g	96.9	24.23
Pd (metal)	g	37.2	9.30
Catalyst	Kg		40.95
Total Cost/ USD			**282.14**

Table S.7.E. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Pd_{0.72}/TiO_2$ catalyst.

Catalyst		**$Pd_{0.72}/TiO_2$**	
Metal Loading / g	Pd	7.20	
Support / g	TiO_2	992.80	
Catalyst: Solvent Ratio (wt/wt)		0.0004	
Solvent Usage / t		2.24	
H_2O_2 Selectivity / %		80.50	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		186	
H_2 Usage / Kg		73.07	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	146.15
Methanol	t	336.99	754.86
TiO_2 (P25)	Kg	1.5	7.45
Pd (metal)	g	37.2	13.38
Catalyst	Kg		20.84
Total Cost/ USD			**921.84**

Table S.7.F. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Pd_{0.1}/TiO_2$ catalyst.

Catalyst		**$Pd_{0.1}/TiO_2$**	
Metal Loading / g	Pd	1.00	
Support / g	TiO_2	999.00	
Catalyst: Solvent Ratio (wt/wt)		0.0004	
Solvent Usage / t		2.24	
H_2O_2 Selectivity / %		99.00	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		115	
H_2 Usage / Kg		59.42	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	118.84
Methanol	t	336.99	754.86
TiO_2 (P25)	Kg	1.5	7.49
Pd (metal)	g	37.2	1.86
Catalyst	Kg		9.35
Total Cost/ USD			**883.05**

Table S.7.G. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Pd_{2.16}/TiO_2$ catalyst.

Catalyst		**$Pd_{2.16}/TiO_2$**	
Metal Loading / g	Pd	21.60	
Support / g	TiO_2	978.40	
Catalyst: Solvent Ratio (wt/wt)		0.0005	
Solvent Usage / t		2.00	
H_2SO_4 Usage / t		$3.92x10^{-3}$	
H_2O_2 Selectivity / %		41.00	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		24	
H_2 Usage / Kg		147.06	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	294.12
H_2SO_4	t	85	0.33
Methanol	t	336.99	673.98
TiO_2 (P25)	Kg	1.5	7.34
Pd (metal)	g	37.2	40.18
Catalyst	Kg		47.51
Total Cost/ USD			**1015.95**

Table S.7.H. Technoeconomic analysis of the direct synthesis of H_2O_2 over the $Pd_1/N\text{-}TiO_2$ catalyst.

Catalyst		**$Pd_1/N\text{-}TiO_2$**	
Metal Loading / g	Pd	10.00	
Support / g	TiO_2	990.00	
Catalyst: Solvent Ratio (wt/wt)		0.0011	
Solvent Usage / t		1200.00	
H_2SO_4 Usage / t		$4.11x10^{-3}$	
H_2O_2 Selectivity / %		58.0	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		41	
H_2 Usage / Kg		101.42	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	202.84
H_2SO_4	t	85	0.35
Ethanol	L	0.34	408.00
TiO_2 (P25)	Kg	1.5	7.43
Pd (metal)	g	37.2	18.60
Catalyst	Kg		26.03
Total Cost/ USD			**637.21**

Table S.7.I. Technoeconomic analysis of the direct synthesis of H_2O_2 over the Pd_1/TiO_2 catalyst.

Catalyst		**Pd_1/TiO_2**	
Metal Loading / g	Pd	10.00	
Support / g	TiO_2	990.00	
Catalyst: Solvent Ratio (wt/wt)		0.0011	
Solvent Usage / t		1200.00	
H_2SO_4 Usage / t		$4.11x10^{-3}$	
H_2O_2 Selectivity / %		61.0	
H_2O_2 Productivity / mol_{H2O2} Kg_{Cat}^{-1} h^{-1}		30	
H_2 Usage / Kg		96.43	
	Unit	**USD / Unit**	**Cost / USD**
H_2	Kg	2	192.86
H_2SO_4	t	85	0.35
Ethanol	L	0.34	408.00
TiO_2 (P25)	Kg	1.5	7.43
Pd (metal)	g	37.2	18.60
Catalyst	Kg		26.03
Total Cost/ USD			**627.24**

Table S.7.J. Costings associated with key reagents utilised in the direct synthesis of H_2O_2, used to conduct the economic analysis reported in Figure 8 and Tables S.7.A-I.

	Unit	**USD / Unit**	**Reference**
H_2	Kg	2.00	9
H_2SO_4	t	85.00	10
NaBr	t	1734.00	11
Ethanol	L	0.34	12
Methanol	t	336.99	13
TiO_2 (P25)	Kg	1.50	14
Au (metal)	g	96.90	15
Pd (metal)	g	37.20	16
Pt (metal)	g	36.30	17
Fe (metal)	t	104.62	18

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