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

Supplementary Information.

Enhancing catalytic performance of AuPd catalysts towards the direct synthesis of H_2O_2 through incorporation of base metals.

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Table S.1. Synthesis details of the precursors used in the preparation of key mono-, bi- and tri-metallic 1%AuPdX/TiO_2 catalysts.

Catalyst	Au precursor	Precursor vol. / µL (mgmL^{-1})	Pd precursor	Precursor vol. / µL (mgmL^{-1})	Tertiary metal precursor	Precursor vol. / µL (mgmL^{-1})
1%Au/TiO_2	$HAuCl_4.3H_2O$	816 (12.25)	-	-	-	-
1%Pd/TiO_2	-	-	$PdCl_2$	1667 (6.00)	-	-
1%$AuPd_{(1.00)}$/TiO_2	$HAuCl_4.3H_2O$	530 (12.25)	$PdCl_2$	585 (6.00)	-	-
1%$AuPd_{(0.975)}Pt_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$H_2PtCl_6.6H_2O$	231 (1.08)
1%$AuPd_{(0.975)}Ni_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$Ni(NO_3)_2$	115 (2.18)
1%$AuPd_{(0.975)}Sn_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$SnCl_2$	52 (4.84)
1%$AuPd_{(0.975)}Cu_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$CuCl_2$	106 (2.36)
1%$AuPd_{(0.975)}Co_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$CoCl_2.6H_2O$	49 (5.10)
1%$AuPd_{(0.975)}In_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$InCl_3$	49 (5.11)
1%$AuPd_{(0.975)}Ga_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$Ga(NO_3)_3.xH_2O$	45 (5.50)
1%$AuPd_{(0.975)}Zn_{(0.025)}$/$TiO_2$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$Zn(NO_3)_2.6H_2O$	46 (5.43)

Note1 : In the case of the tri-metallic catalysts the combined loading of Au and Pd is 0.975 wt.% (Au: Pd = (1:1 mol/mol)) and that of the tertiary metal (Pt, Ni, Sn, Cu, Co, In, Ga or Zn) is 0.025 wt.%. In all cases catalyst are exposed to an oxidative heat treatment prior to use (static air, 3 h, 400 °C, 10°Cmin^{-1}). **Note 2:** Values in parentheses refer to metal loading of (Au+Pd) or tertiary metal. In all instances total metal loading is 1 wt.% and Au: Pd: X = 1: 1 (mol/mol).

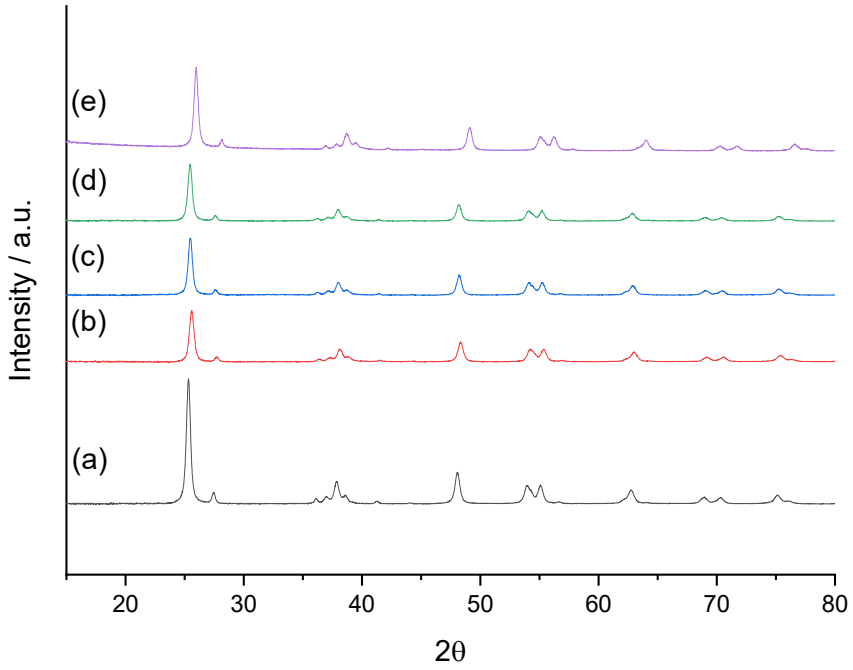

Figure S.1. X-ray diffractograms of 1%$AuPd_{(0.975)}X_{(0.025)}/TiO_2$ catalysts, prepared by sol-immobilisation. **(a)** TiO_2, **(b)** 1%$AuPd_{(1.00)}/TiO_2$, **(c)** 1%$AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$, **(d)** 1%$AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$ and **(e)** 1%$AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$. **Note 1:** No reflections associated with immobilised metal species are observed in any of the as-prepared catalysts. ICDD patterns are provided for reference (TiO_2 anatase ICDD: 01-089-4921, TiO_2 rutile ICDD:07-089-0555). **Note 2:** All catalysts exposed to an oxidative heat treatment (400 °C, 3 h, static air, ramp rate = 10°Cmin[1]).

Table S.2. Actual metal loading of 1%$AuPd_{(0.975)}X_{(0.025)}/TiO_2$ catalysts, as determined by ICP-OES microwave assisted HF digestion.

Catalyst	Theoretical loading / wt.%			Actual loading / wt.%		
	Au	Pd	X	Au	Pd	X
1%$AuPd_{(1.00)}/TiO_2$	0.649	0.351	-	0.645	0.437	-
1%$AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$	0.633	0.342	0.025	0.640	0.416	0.001
1%$AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$	0.633	0.342	0.025	0.644	0.415	0.002
1%$AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$	0.633	0.342	0.025	0.637	0.405	0.001

Note: Values in parentheses refer to metal loading of (Au+Pd) or tertiary metal. In all instances total metal loading is 1 wt.% and Au: Pd: X = 1: 1 (mol/mol).

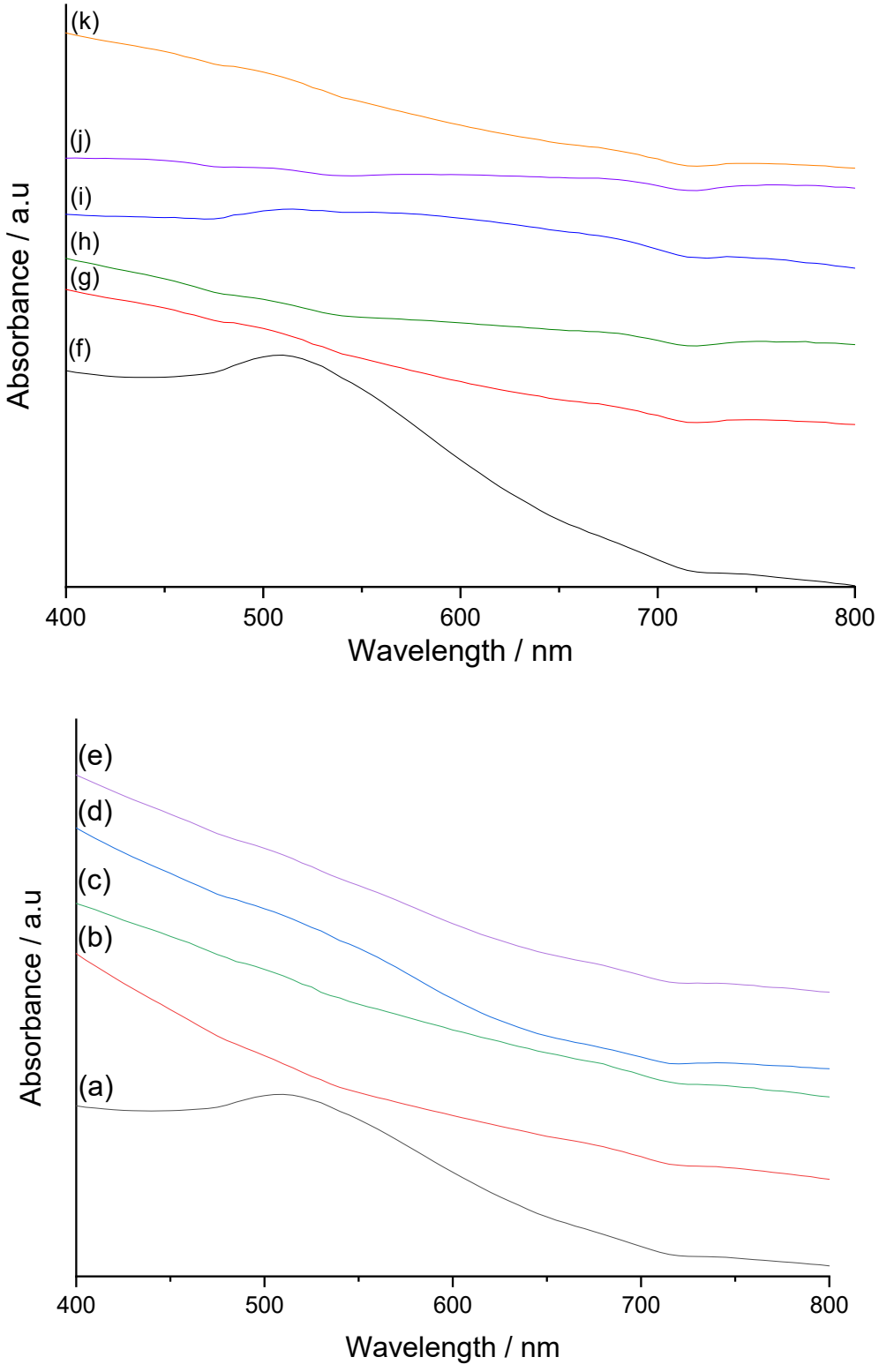

Figure S.2. Representative UV-vis spectra from aqueous sol-immobilisation prepared bi-metallic Au-based colloids. **(a)** Au, **(b)** AuPd, **(c)** AuCu, (d) AuZn and **(e)** AuNi, **(f)** Au, **(g)** AuCo, **(h)** AuPt, **(i)** AuGa, **(j)** AuIn, **(k)** AuSn. The absence of the Au plasmon peak (at approx. 520 nm) in the bimetallic colloids is indicative of alloy formation.

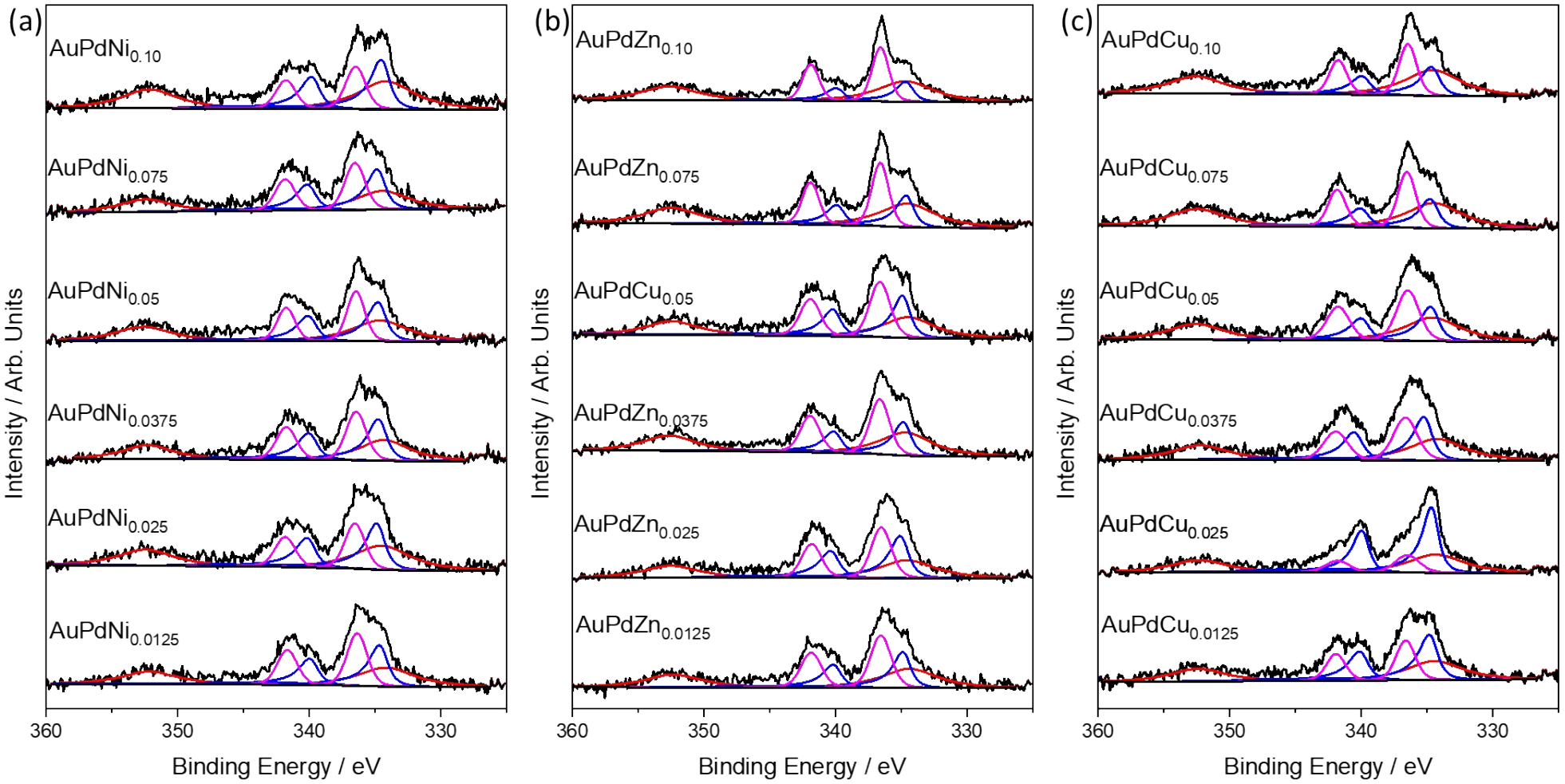

Figure S.3. XPS spectra of Pd(3d) regions for as-prepared **(a)** 1%$AuPd_{(X)}Ni_{(1-X)}/TiO_2$, **(b)** 1%$AuPd_{(X)}Zn_{(1-X)}/TiO_2$ and **(c)** 1%$AuPd_{(X)}Cu_{(1-X)}/TiO_2$ catalysts as a function of tertiary metal concentration. ***Key:*** Au(4d) (*red*), Pd^0 (*blue*), Pd^{2+} (*magenta*), Ca^{2+} (*green*).

Table S.3. Comparison of catalytic selectivity towards H_2O_2 at iso-conversion.

Catalyst	Reaction time / min	H_2 Conversion / %	H_2O_2 Selectivity / %	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	H_2O_2 Conc. / wt.%
$1\%AuPd_{(1.00)}/TiO_2$	30	12	59	61	0.125
	60	22	55	51	0.207
	75	32	47	51	0.258
$1\%AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$	30	32	41	107	0.215
$1\%AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$	30	31	40	94	0.188
$1\%AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$	30	24	50	98	0.197

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:** Values in parentheses refer to metal loading of (Au+Pd) or tertiary metal. In all instances total metal loading is 1 wt.% and Au: Pd: X = 1: 1 (mol/mol).

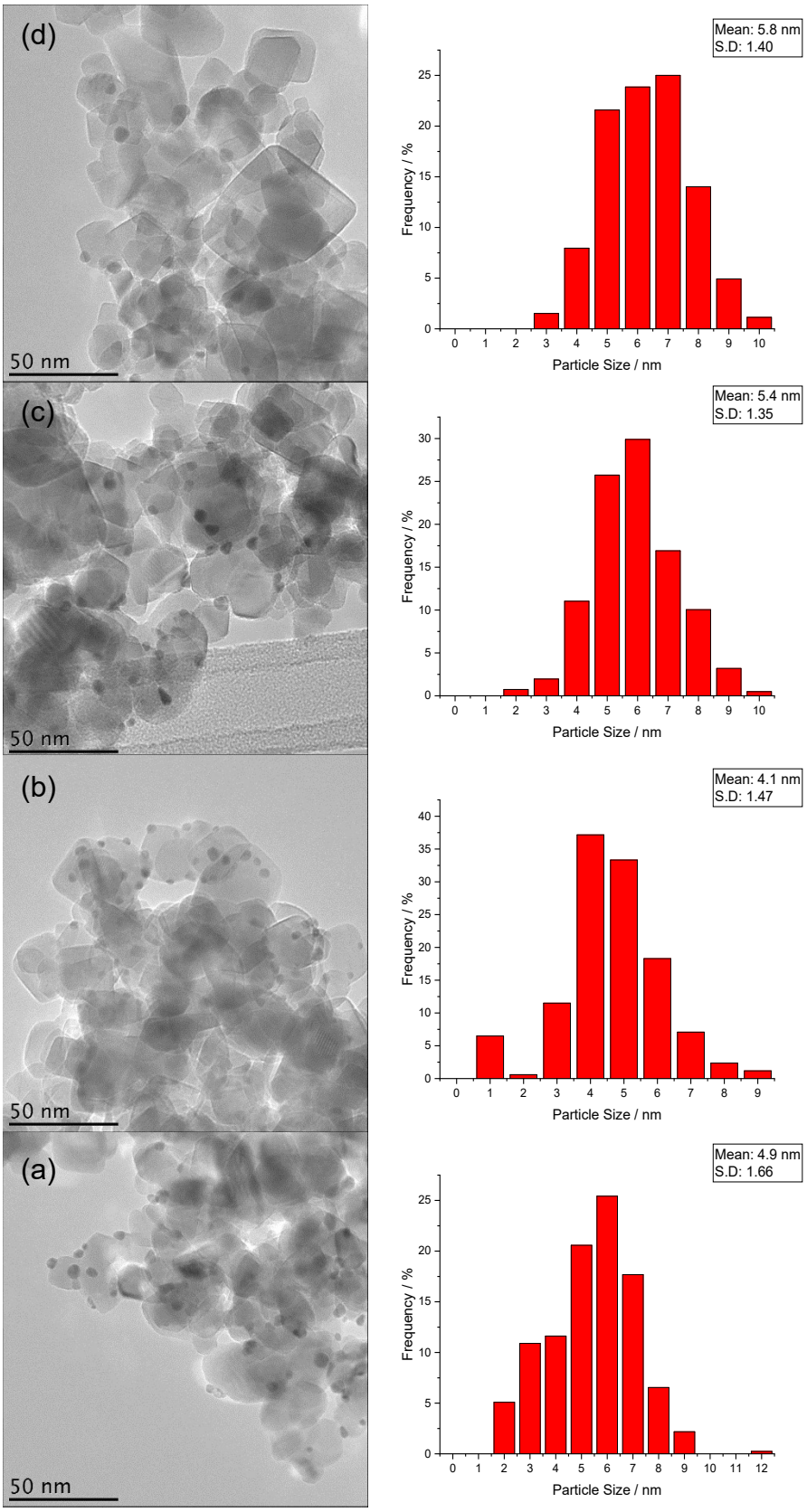

Figure S.4. Representative bright field transmission electron micrographs and corresponding particle size histograms of TiO_2 supported tri-metallic catalysts, prepared by a sol-immobilisation methodology. **(a)**1%$AuPd_{(1.00)}/TiO_2$**, (b)** 1%$AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$,**(c)** 1%$AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$, **(d)** 1%$AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$.

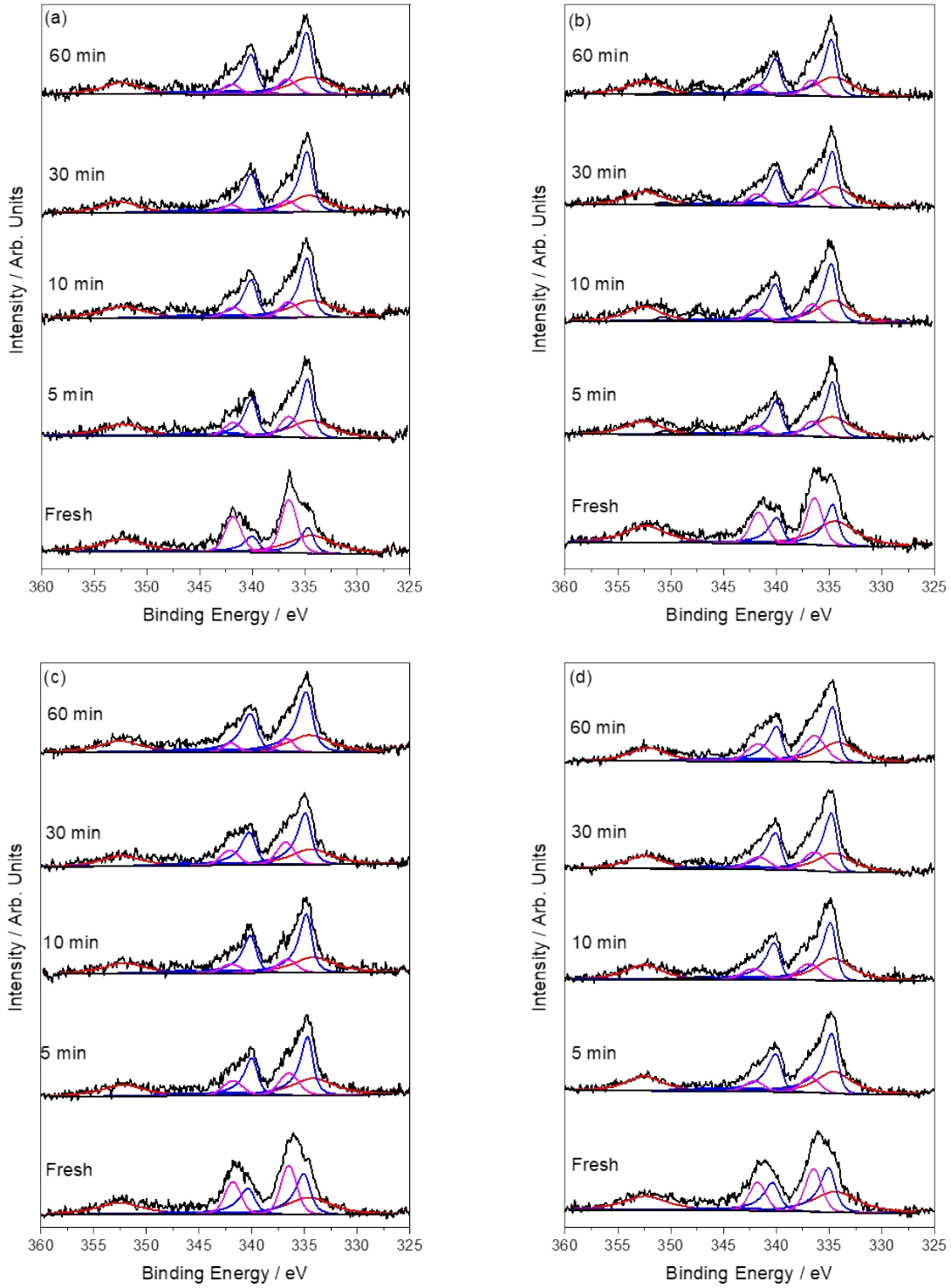

Figure S.5. XPS spectra of Pd(3d) regions for **(a)** 1%AuPd$_{(1.00)}$/TiO$_2$**, (b)** 1%AuPd$_{(0.975)}$Ni$_{(0.025)}$/TiO$_2$, **(c)** 1%AuPd$_{(0.975)}$Zn$_{(0.025)}$/TiO$_2$ and **(d)** 1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/TiO$_2$ catalysts as a function of reaction time. ***Key:*** Au(4d) (*red*), Pd^0 (*blue*), Pd^{2+} (*magenta*). **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), 2 ˚C 1200 rpm. **Note**: Used catalysts are dried under vacuum (30 °C, 16 h) prior to subsequent utilisation in the direct synthesis of H_2O_2 or XPS analysis.

Table S.4. Comparison of initial H_2O_2 synthesis rates over various TiO_2 supported catalysts.

Catalyst	Rate of reaction / $mmol_{H2O2}$ $mmol_{metal}^{-1}min^{-1}$			
	Use 1		Use 2*	
	5 min	30 min	5 min	30 min
$1\%AuPd_{(1.00)}/TiO_2$	16.40	14.06	18.22	10.54
$1\%AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$	57.19	25.16	43.43	22.37
$1\%AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$	41.87	21.39	28.37	18.94
$1\%AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$	41.86	23.30	36.77	18.40

*Catalyst used for 30 min under standard reaction conditions prior to determination of reaction rate over 0.083 or 0.5 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), 2 ˚C 1200 rpm. **Note 1**: Reaction rates upon first use (use 1) are calculated based on the actual metal loading as determined by HF digestion (see Table S.2). Reaction rates upon second use (use 2) account for metal leaching during the initial H_2O_2 synthesis reaction, as determined by ICP-MS analysis of the post reaction solutions (see Table 4). **Note 2:** Values in parentheses refer to metal loading of (Au+Pd) or tertiary metal. In all instances total metal loading is 1 wt.% and Au: Pd: X = 1: 1 (mol/mol).

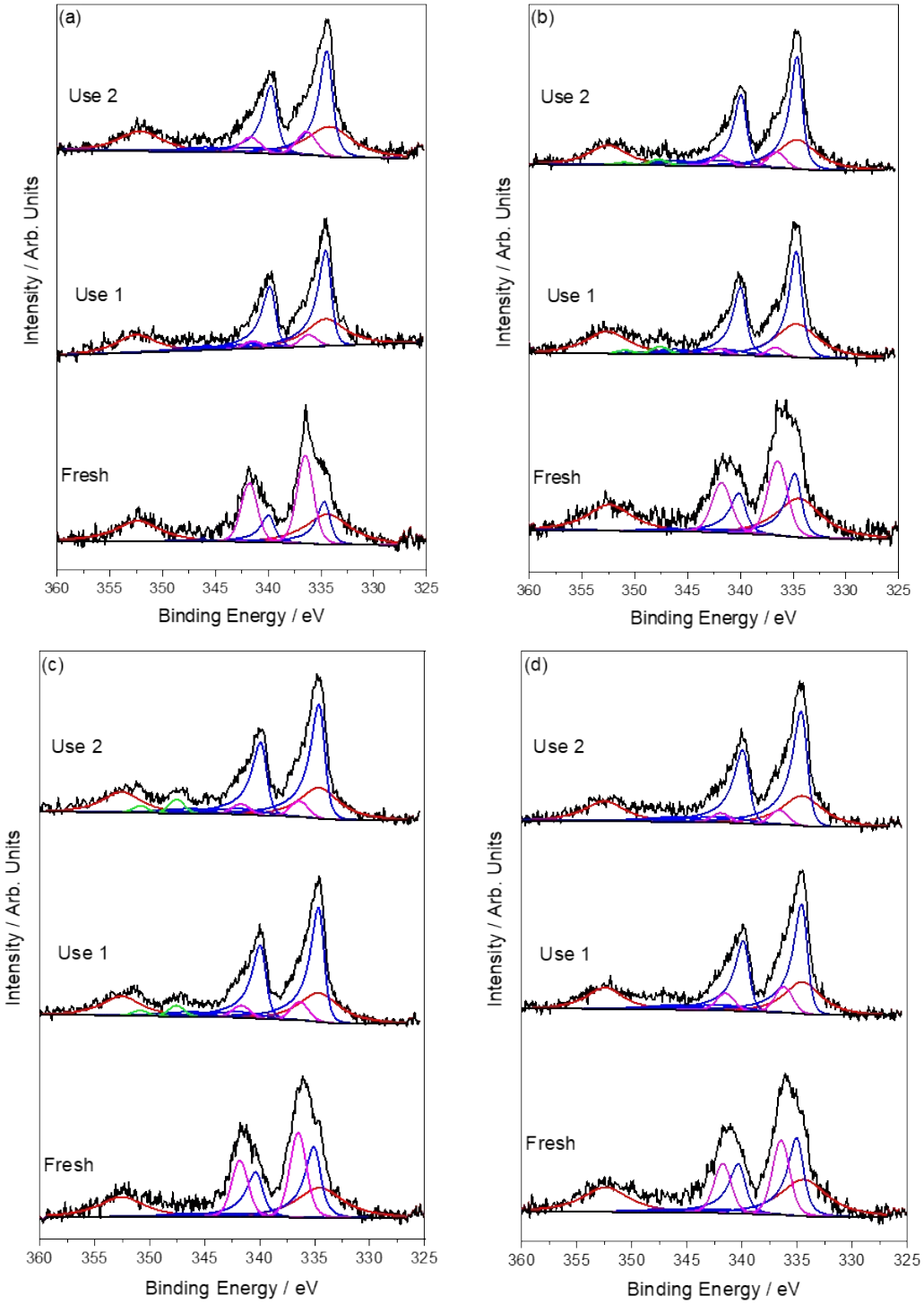

Figure S.6. XPS spectra of Pd(3d) regions for the as-prepared **(a)** 1%$AuPd_{(1.00)}/TiO_2$**, (b)** 1%$AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$, **(c)** 1%$AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$ and **(d)** 1%$AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$ catalysts in addition to corresponding spectra after one and two uses in the direct synthesis of H_2O_2. ***Key:*** Au(4d) (*red*), Pd^0 (*blue*), Pd^{2+} (*magenta*), Ca^{2+} (*green*). The presence of Ca^{2+} is considered to originate from the reaction mixture. **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. **Note**: Used catalysts are dried under vacuum (30 °C, 16 h) prior to subsequent utilisation in the direct synthesis of H_2O_2 or XPS analysis.

Table S.5. Effect of catalyst use in the direct synthesis of H_2O_2 on atomic speciation as determined by XPS.

Catalyst	As prepared		Use 1		Use 2	
	Au: Pd	Pd^{2+}: Pd^0	Au: Pd	Pd^{2+}: Pd^0	Au: Pd	Pd^{2+}: Pd^0
$1\%AuPd_{(1.00)}/TiO_2$	0.56	1.56	0.50	0.10	0.47	0.20
$1\%AuPd_{(0.975)}Ni_{(0.025)}/TiO_2$	0.58	0.91	0.55	0.20	0.53	0.14
$1\%AuPd_{(0.975)}Cu_{(0.025)}/TiO_2$	0.46	0.63	0.40	0.18	0.55	0.10
$1\%AuPd_{(0.975)}Zn_{(0.025)}/TiO_2$	0.39	0.77	0.36	0.09	0.59	0.08

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. **Note1:** All catalysts exposed to an oxidative heat treatment (400 °C, 3 h, static air, ramp rate = 10°Cmin[1]). **Note 2**: Used catalysts are dried under vacuum (30 °C, 16 h) prior to subsequent utilisation in the direct synthesis of H_2O_2 or XPS analysis. **Note3:** values in parentheses refer to metal loading of (Au+Pd) or tertiary metal. In all instances total metal loading is 1 wt.% and Au: Pd: X = 1: 1 (mol/mol).