Electronic Supplementary Information

AuPd/TiO_2 colloidal nanoparticle system stabilized in absence of organic ligands and its efficiency in environmentally benign aqueous oxidative catalysis

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Table S1. Results of catalytic aqueous oxidation under different conditions.

Catalyst Composition	Substrate	Oxidant	Temp. (°C)	Time (hours)	% Conversion	Comments
H_2O_2 oxidation						
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	25	0.5	7.2	
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	50	0.5	29.8	
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	75	0.5	62.4	
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	90	0.5	97.6	
Air oxidation						
$Au_{70}Pd_{30}$	1-phenylethanol	air	25	28	12.3	7:1 TiO_2 to $Au_{70}Pd_{30}$
$Au_{70}Pd_{30}$	1-phenylethanol	air	50	20	41.4	7:1 TiO_2 to $Au_{70}Pd_{30}$
$Au_{70}Pd_{30}$	1-phenylethanol	air	50	20	63.1	9:1 TiO_2 to $Au_{70}Pd_{30}$
Basic conditions						
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	50	0.5	9.4	pH 5.6 (KOH addition)
$Au_{70}Pd_{30}$	1-phenylethanol	air	50	16	15.7	pH 5.6 (KOH addition)
***t*-butanol addition for increased substrate solubility**						
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	50	0.5	19.6	*t*-butanol added to reaction to help with solubility of 1-phenylethanol
Core vs. shell						
$Au_{80}Pd_{20}$	1-phenylethanol	H_2O_2	50	0.5	23.1	Au and Pd premixed (alloy instead of core/shell arrangement)

$Au_{80}Pd_{20}$	1-phenylethanol	H_2O_2	50	0.5	5.9	Pd core, Au shell
$Au_{80}Pd_{20}$	1-phenylethanol	H_2O_2	50	0.5	29.5	Au core, Pd shell
Other substrates						
$Au_{70}Pd_{30}$	2-butanol	H_2O_2	50	22	0.7	
$Au_{70}Pd_{30}$	1-octanol	H_2O_2	50	22	0	
$Au_{70}Pd_{30}$	2-octanol	H_2O_2	50	112.5	15.2	
$Au_{70}Pd_{30}$	benzyl alcohol	H_2O_2	50	0.5	3.3	1.3% benzoic acid also observed
AuPd decahedral cages						
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	50	0.5	2.6	
Platinum shell, gold core						
$Au_{70}Pt_{30}$	1-phenylethanol	H_2O_2	50	0.5	3.1	
Photocatalysis						
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	rt	0.75	3.1	exposed to a 400 W metal halide lamp, 5 cm distance
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	rt	0.75	2.9	dark reaction - same conditions as listed above, but wrapped in Al-foil to exclude light
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	rt	24	76.5	supported on β-FeOOH (instead of TiO_2), exposed to a 400 W metal halide lamp, 5 cm distance
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	rt	24	13.3	supported on TiO_2, exposed to a 400 W metal halide lamp, 5 cm distance
no AuPd NPs	1-phenylethanol	H_2O_2	rt	24	3.5	TiO_2 only, exposed to a 400 W metal halide lamp, 5 cm distance
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	rt	20	52.9	exposed to a 400 W metal halide lamp, 5 cm distance
$Au_{70}Pd_{30}$	1-phenylethanol	air	rt	20	15.9	exposed to a 400 W metal halide lamp, 5 cm distance

$Au_{70}Pd_{30}$	1-phenylethanol	air	rt	20	10	dark reaction - same conditions as listed above, but wrapped in Al-foil to exclude light
Hydrazine reduction						
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	50	1.75	4.4	N_2H_4 reduced $Au_{70}Pd_{30}$ NPs, not supported (TiO_2 leads to aggregation)
Colloidal vs. dried and sintered						
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	30	0.5	14.8	As prepared colloidal dispersion
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	30	0.5	2.9	dried and redispersed (no TiO_2)
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	30	0.5	2.7	dried and redispersed (on TiO_2)
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	30	0.5	2.3	dried, sintered and redispersed (no TiO_2)
$Au_{70}Pd_{30}$	1-phenylethanol	H_2O_2	30	0.5	2.8	dried, sintered and redispersed (on TiO_2)

Table S2. Products of 1-phenylethanol oxidation by hydrogen peroxide catalyzed with AuPd/TiO_2.

% Pd	% Au	Temp. (°C)	Time (hours)	% 1-Phenylethanol	% Acetophenone	% Ethylbenzene
0	100	90	2	57.3	42.7	0
20	80	90	2	1.4	98.6	0
40	60	90	2	10.8	88.5	0.7
60	40	90	2	43.8	48.8	7.4
80	20	90	2	41.7	42.5	15.8
100	0	90	2	24	36.9	39.1
21	79	90	16	51.3	38.7	10
21	79	90	28.5	58.9	34.6	6.5
21	79	90	75.5	10.2	84.6	5.2
21	79	50	16	75.8	22.2	2
21	79	50	29	61.4	32.8	5.8
21	79	50	76	55.6	39.7	4.7

At higher palladium content and temperatures, a side reaction for the formation of ethylbenzene was observed. For oxidative catalyst with 30% Pd content, this side reaction was not observed.

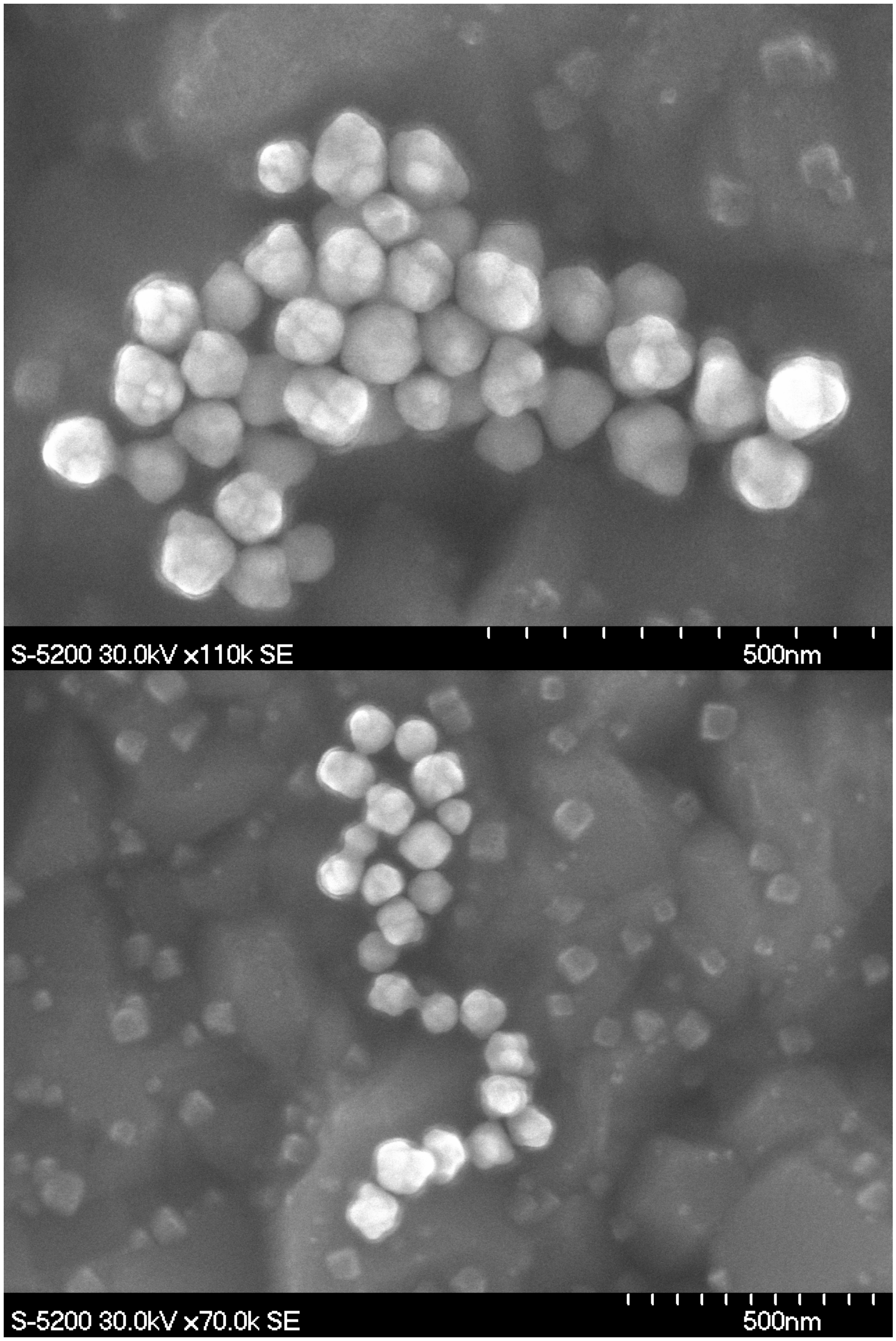

Figure S1. SEM image of hydrazine reduced Au NPs, not supported on TiO_2. TiO_2 addition was found to lead to aggregation. Hydrazine reduced Au NPs were found to have low catalytic activity, yielding only 4.4 % conversion of 1-phenylethanol to acetophenone at 50°C in 1.75 hours in the presence of H_2O_2.

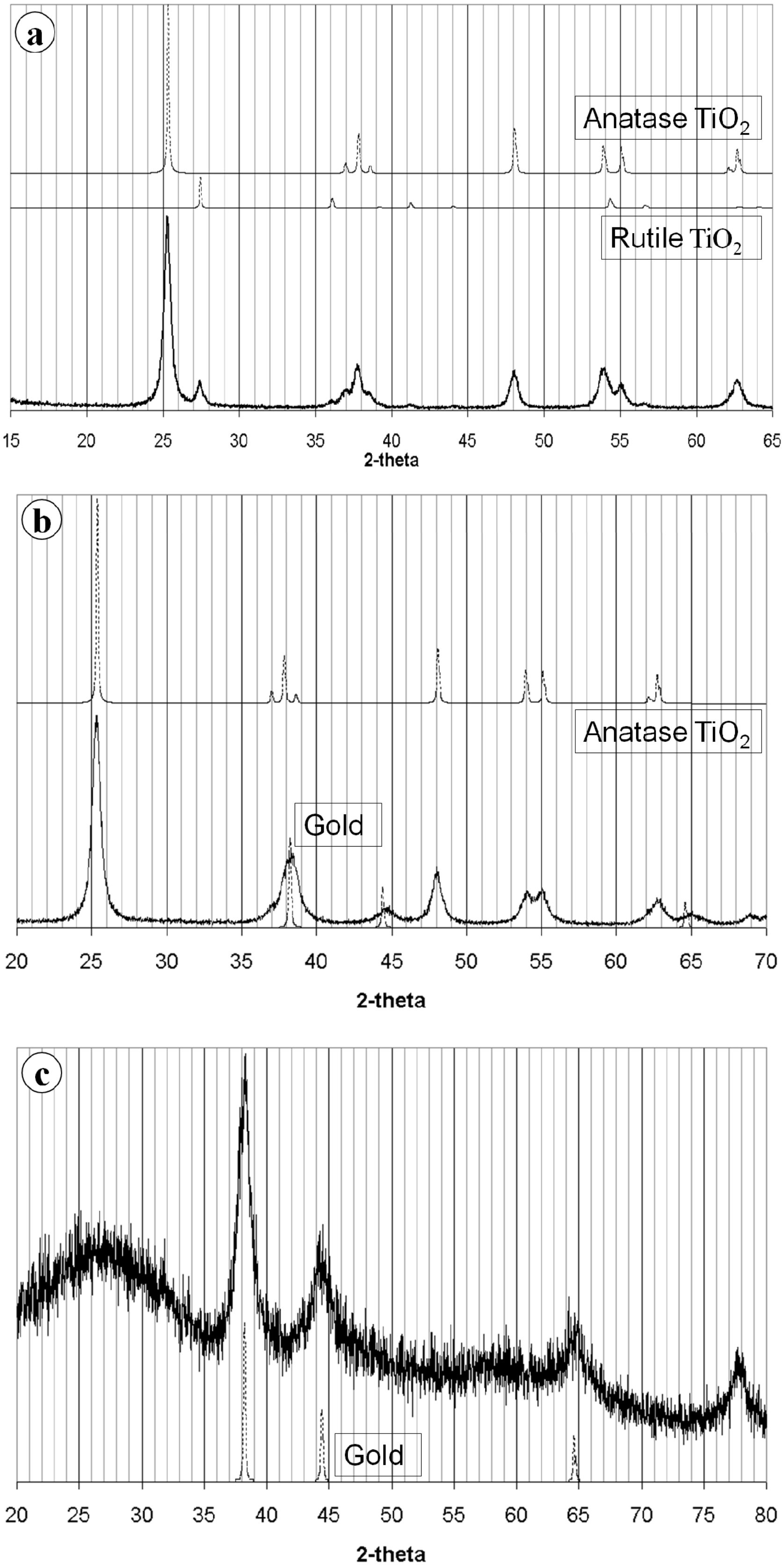

Figure S2. (a) X-ray diffraction (XRD) pattern of titania dried at 100°C. Evidence of anatase and rutile (dashed lines) can be seen.

(b) XRD pattern of $Au_{70}Pd_{30}/TiO_2$ dried at 50-60^{o}C and 10 torr, then sintered at 25°C for 30 minutes, 180°C, 350°C then 25°C for 1 hour each. Evidence of anatase (upper dashed line) and gold (lower dashed line) can be seen. No rutile or palladium was observed. This illustrates that the AuPd NP lattice is similar to that of pure gold, which indicates that there is a gold core, with a thin, palladium shell not producing enough XRD signal (Note that Pd is evident from EDX (Fig. S5).

(c) XRD pattern of Au/TiO_2 dried at 50-60^{o}C and 10 torr. Evidence of Au NPs (dashed line) is evident. The TiO_2 in this sample is amorphous.

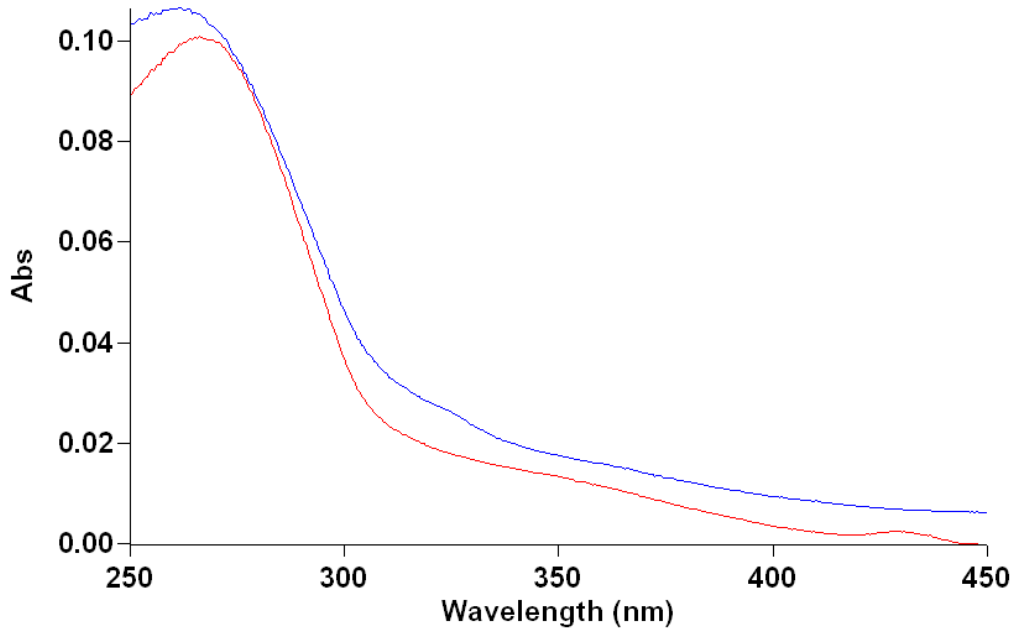

Figure S3. UV-Vis spectra of TiO_2 (red plot) and $Au_{70}Pd_{30}/TiO_2$ (blue plot) after the addition of H_2O_2. There is no strong evidence of a peak at 330 nm. A H_2O_2 solution was used as the reference sample.

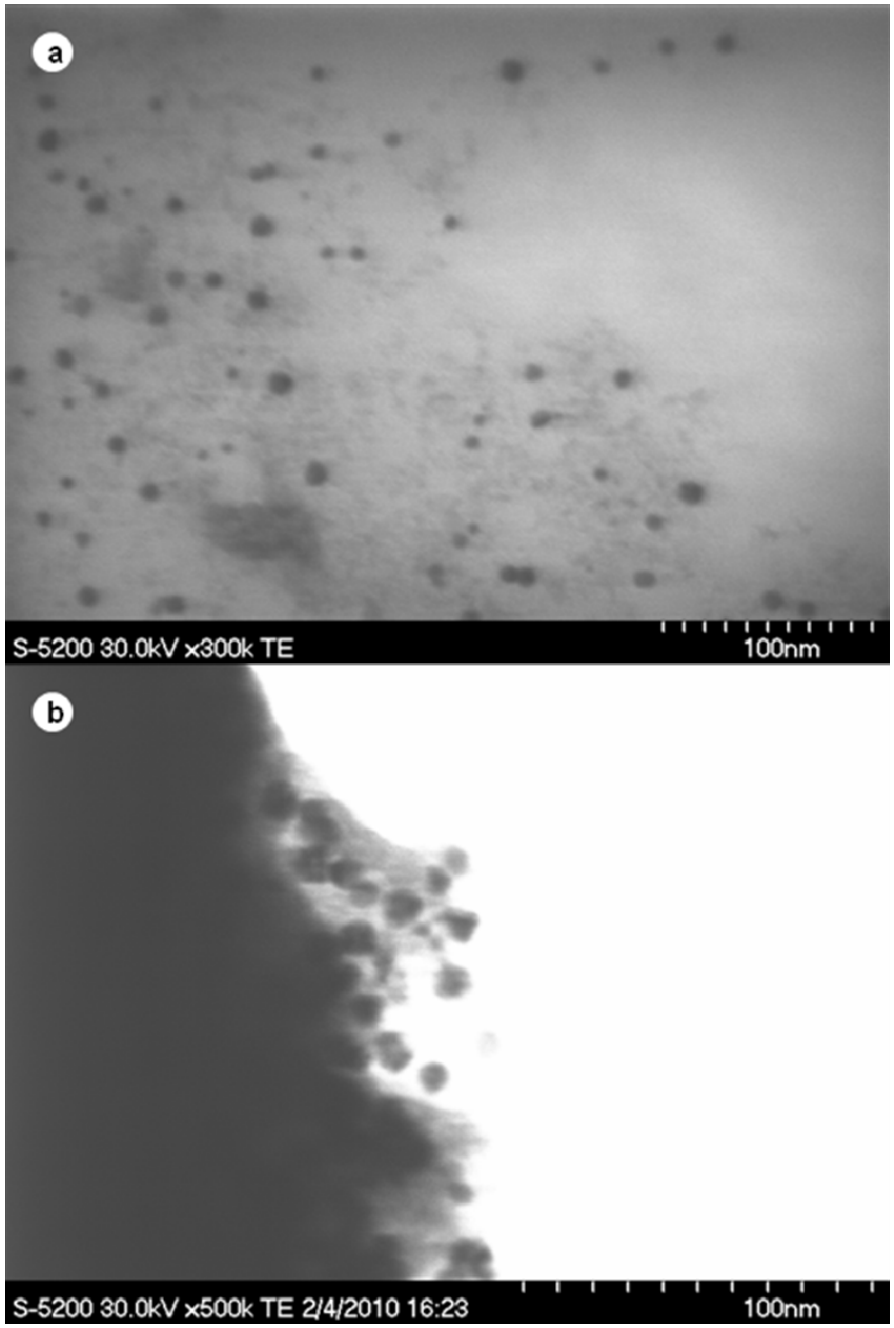

Figure S4. TEM of $Au_{70}Pd_{30}/TiO_2$ (a) before and (b) after being used for catalysis of 1-phenylethanol to acetophenone at 50°C for 30 minutes in the presence of H_2O_2. The average size of the AuPd NPs were 7.5 ± 1.5 nm before, and 7.7 ± 1.4 nm after catalysis.

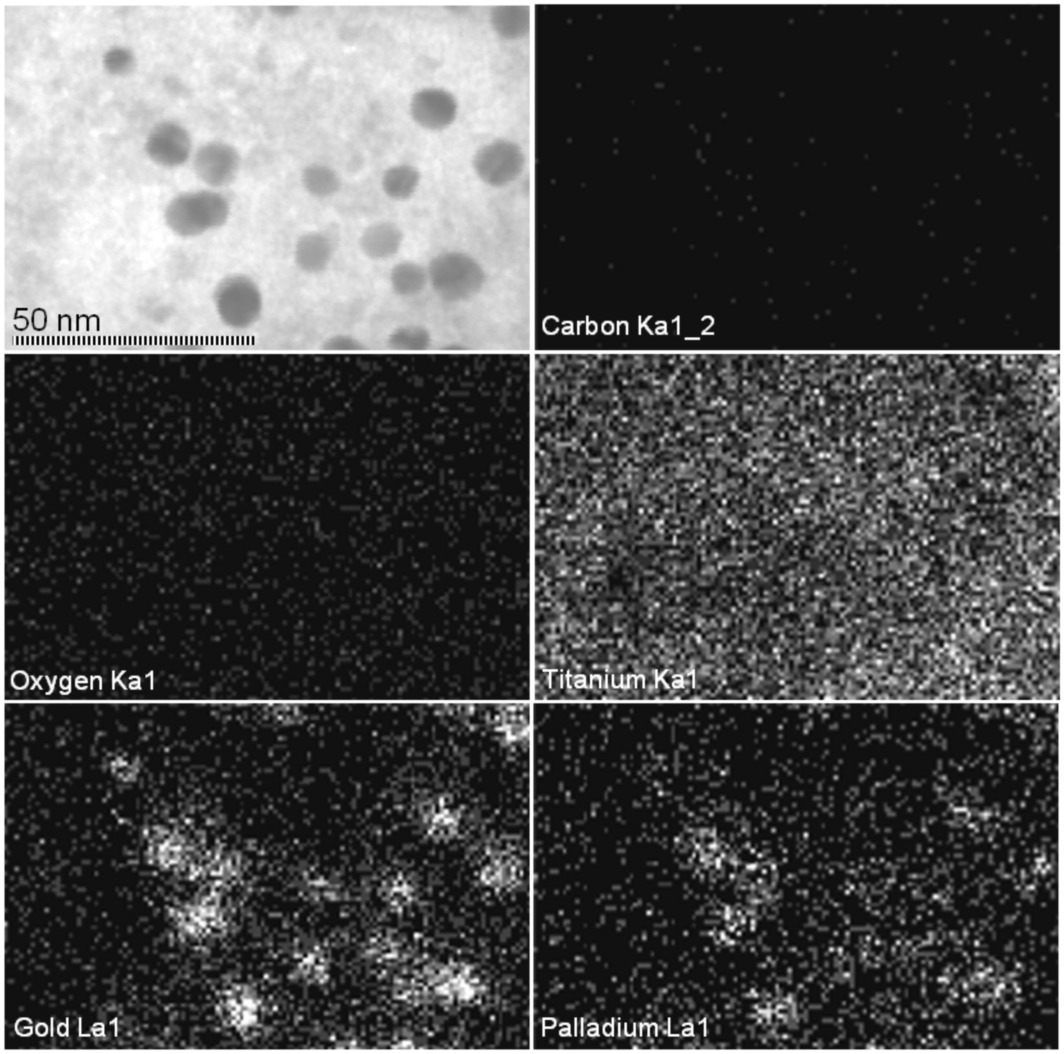

Figure S5. Energy-dispersive X-ray (EDX) map of $Au_{70}Pd_{30}/TiO_2$. In addition to confirmed presence of gold and palladium in the NPs, it can be seen that no carbon was evident in the samples exposed to peroxide, indicating complete hydrolysis and supporting all-inorganic stabilization.

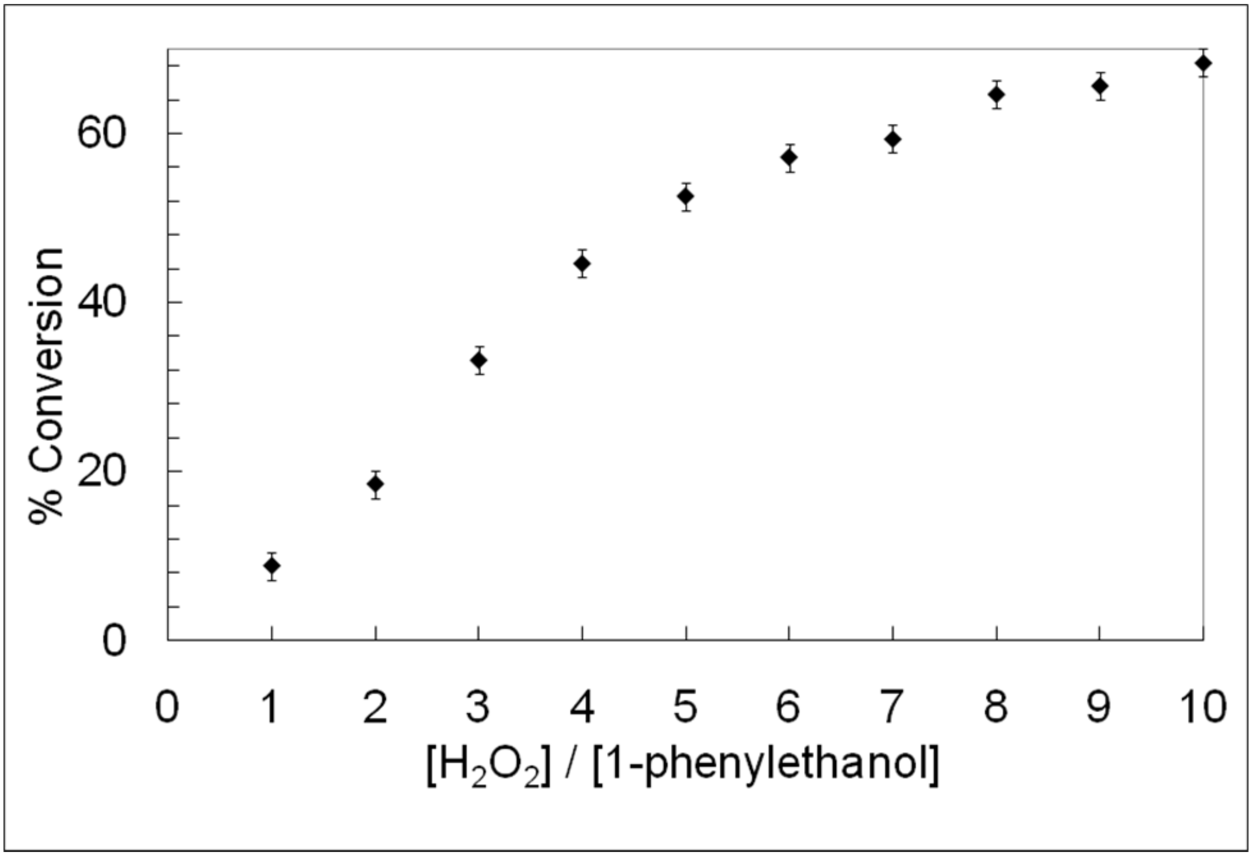

Figure S6. Plot of percentage conversion of 1-phenylethanol to acetophenone versus the ratio of H_2O_2 to 1-phenylethanol for catalysis with the $Au_{70}Pd_{30}/TiO_2$ system at 50°C for 1 hour. The minimal ratio of H_2O_2 to 1-phenylethanol for optimal conversion was found to be 6:1.

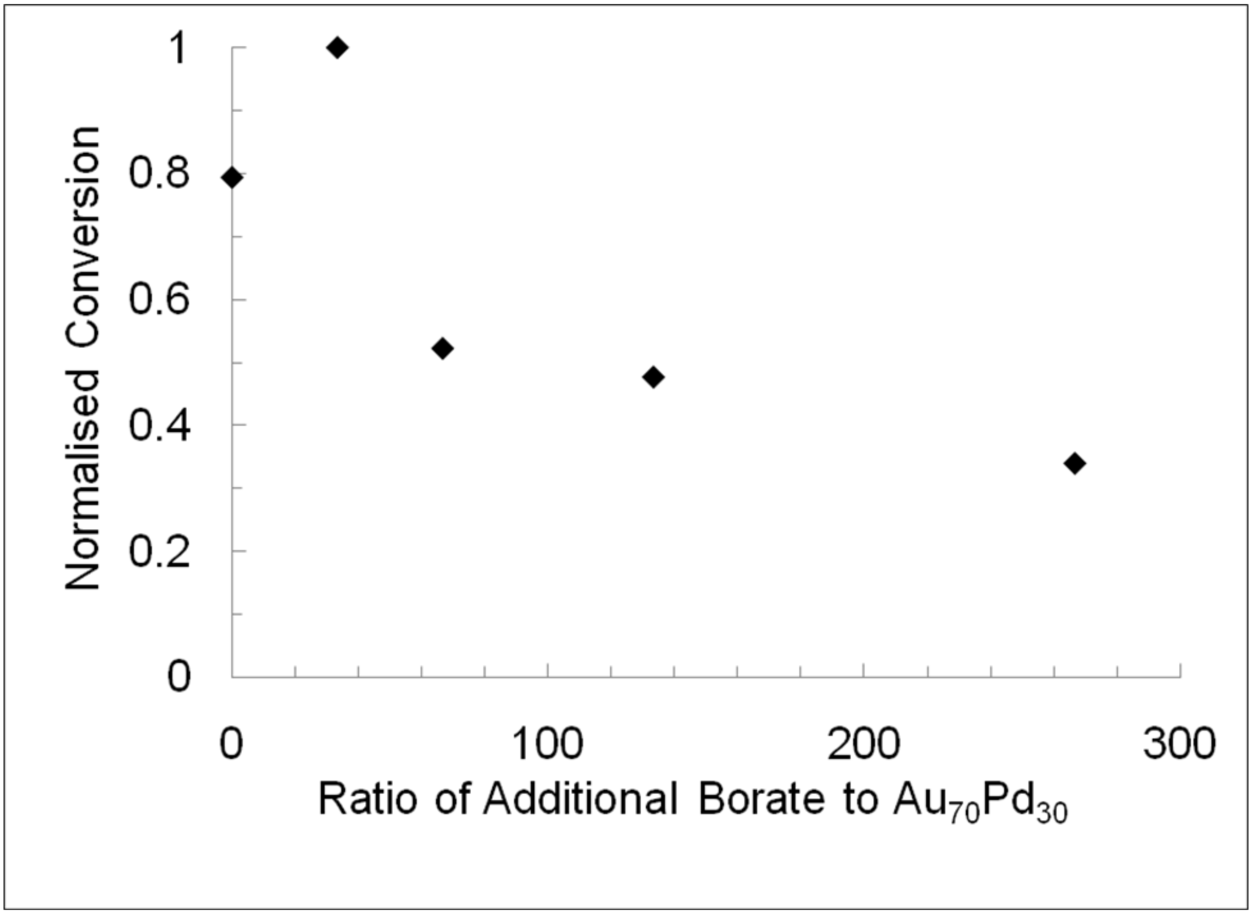

Figure S7. Normalised conversion of 1-phenylethanol to acetophenone at 50°C for 30 minutes in the presence of H_2O_2 versus the ratio of additional borate added to AuPd NPs.

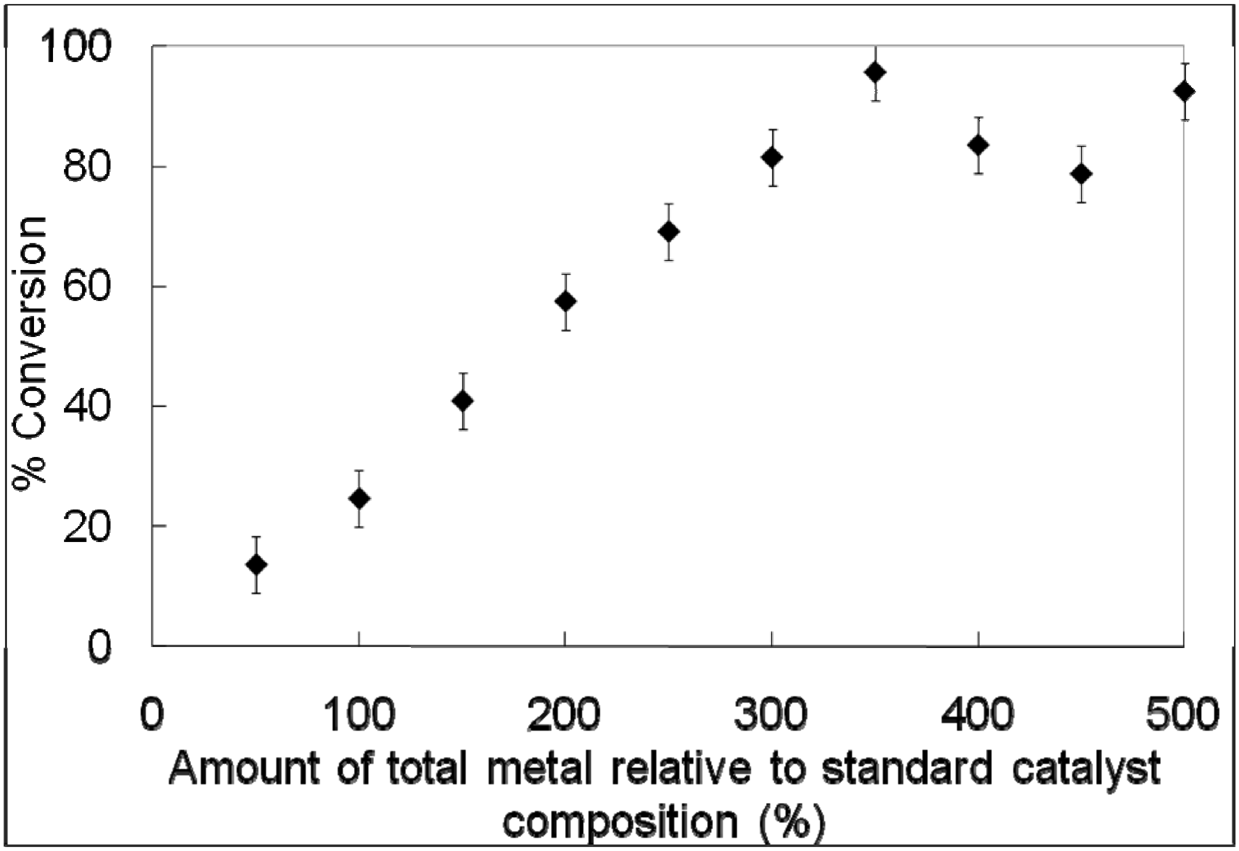

Figure S8. Different loading of $Au_{70}Pd_{30}$ NPs on TiO_2 for the conversion of 1-phenylethanol to acetophenone at 50°C for 30 minutes in the presence of H_2O_2.