Supplementary information

PTFE supported gold nanoparticles as photocatalyst for oxidative esterification of aldehydes.

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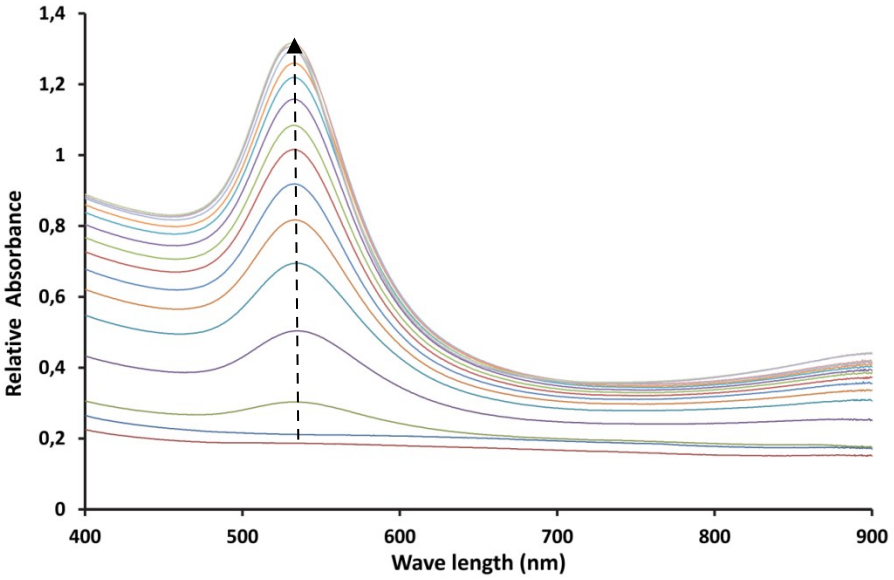

Figure SI 1. UV-Vis kinetic monitoring of AuNPs formation. The lower trace was obtained after 3 minutes. Each trace corresponds to a time increment of 1 minutes.

Table SI 1: Summary of the kinetic study during AuNPs synthesis using UV-Vis and DLS.

Time (min)	UV-Vis.		DLS		
	λ_{max} (Rel. Abs)	FWMH (nm)	Population 1 nm (%mass)	Population 2 nm(%mass)	Average particle diameter (nm)
0	///	///	///	///	///
1	///	///	///	///	///
2	///	///	///	///	///
3	534 nm (0.504)	60.0	0.69 (99%)	31.0 (1%)	1.14
4	534 nm (0.695)	58.5	2.27 (96%)	15.2 (4%)	1.25
5	533 nm (0.817)	56.5	1.11 (98%)	19.3 (2%)	1.53
6	533 nm (0.919)	55.0	1.11 (98%)	24.5 (2%)	1.73
7	533 nm (1.016)	54.5	1.11 (98%)	31.0 (2%)	1.62
8	533 nm (1.084)	54.0	0.88 (98%)	39.4 (2%)	1.54
9	533 nm (1.158)	53.5	1.11 (98%)	31.0 (2%)	1.74
10	533 nm (1.219)	50.0	2.27 (97%)	31.0 (2%)	1.5
11	533 nm (1.259)	53.5	1.11 (98%)	31.0 (2%)	1.71
12	533 nm (1.298)	53.5	1.11 (98%)	39.4 (2%)	1.84
13	531 nm (1.317)	52.5	2.27 (97%)	31.0 (2%)	1.75
14	531 nm (1.315)	51	1.72 (99%)	39.4 (1%)	1.92
15	531 nm (1.306)	50.5	1.81 (99%)	30.0 (1%)	1.83

Table SI 2: Study of AuNPs size vs irradiance of light source

AuNPs Average diameter (nm)	Power intensity (%)	Irradiance (mW.cm-1)
1.87	100	350
3.46	75	264
7.87	50	180
11.41	25	91

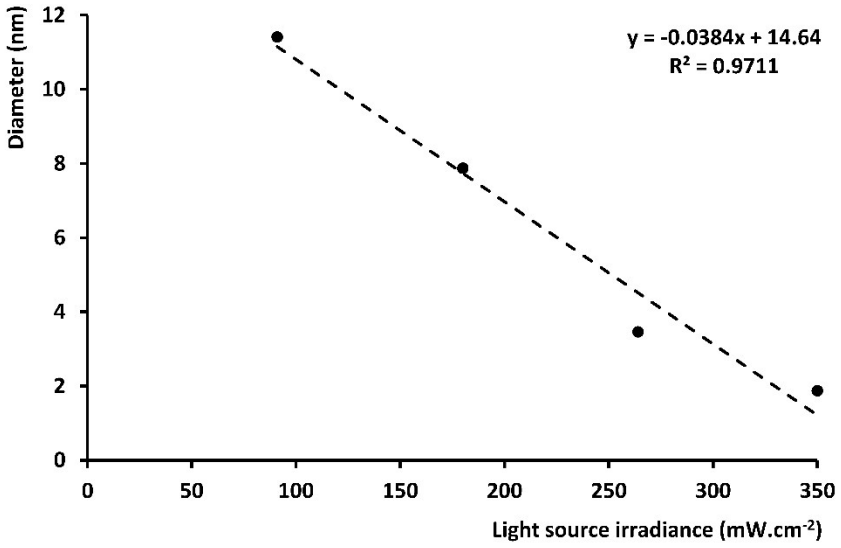

Figure SI 2. Study of AuNPs size vs irradiance of light source

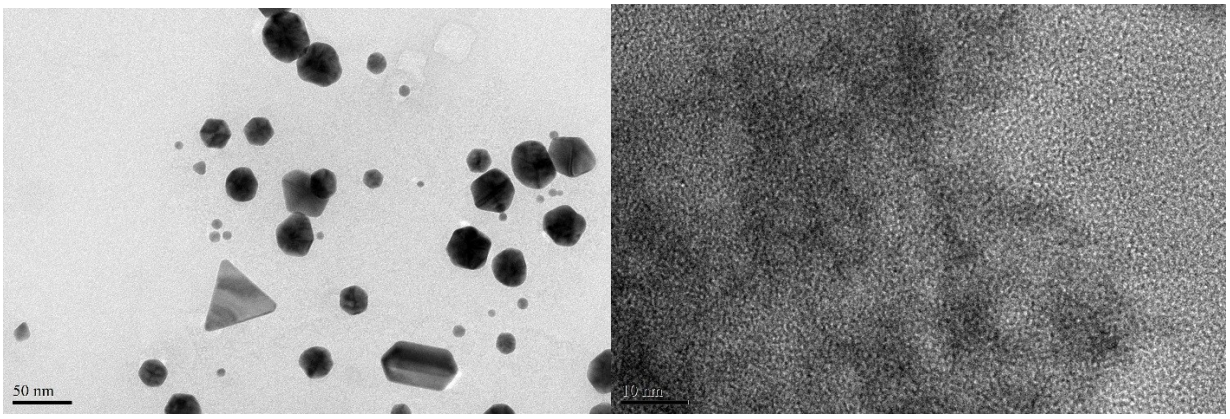

Figure SI 3. TEM analysis observed on SiO_2-MPTES grid: (left) second larger population (average diameter = 30 nm) ; (right) example of large black vesicle supposed to correspond to first population.

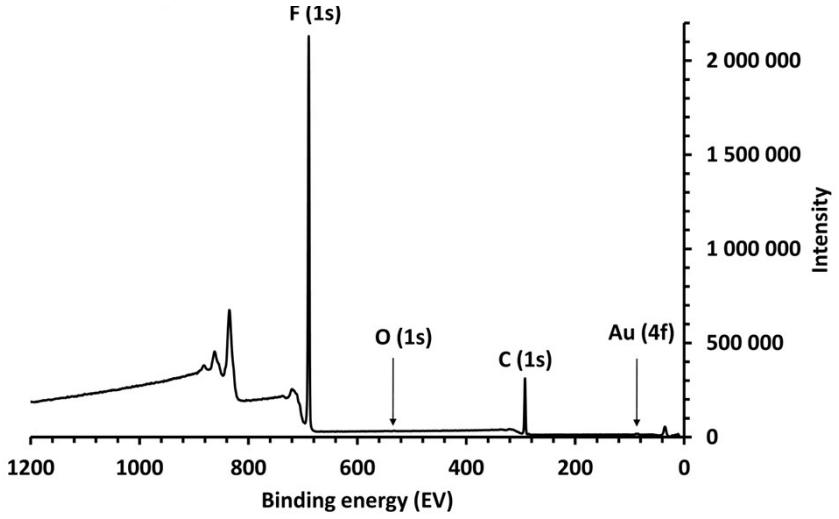

Figure SI 4. XPS spectrum of AuNPs/PTFE catalyst (PTFE particle diameter: 200 μm)

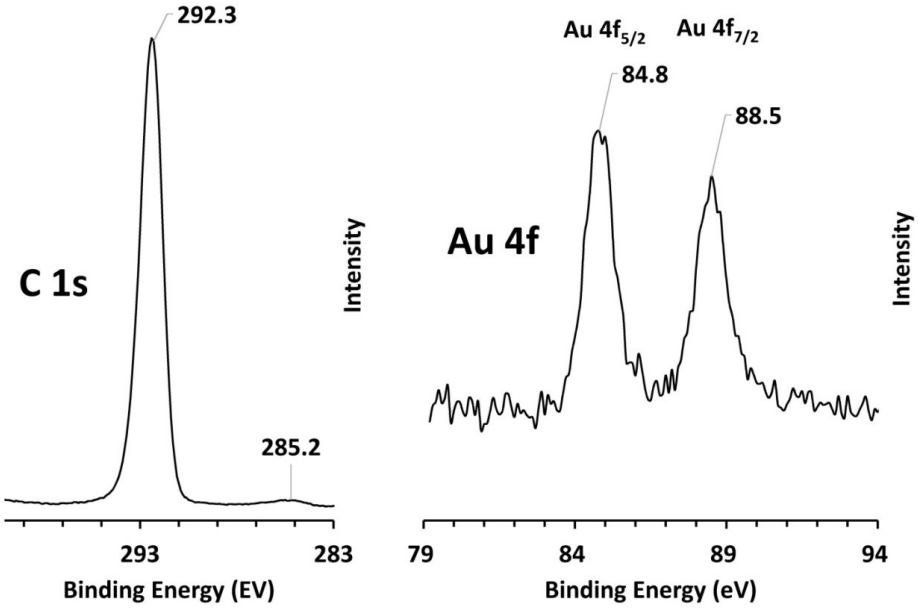

Figure SI 5. Detailed view of AuNPs/PTFE catalyst XPS spectrum for C(1s) and Au(4f) regions.

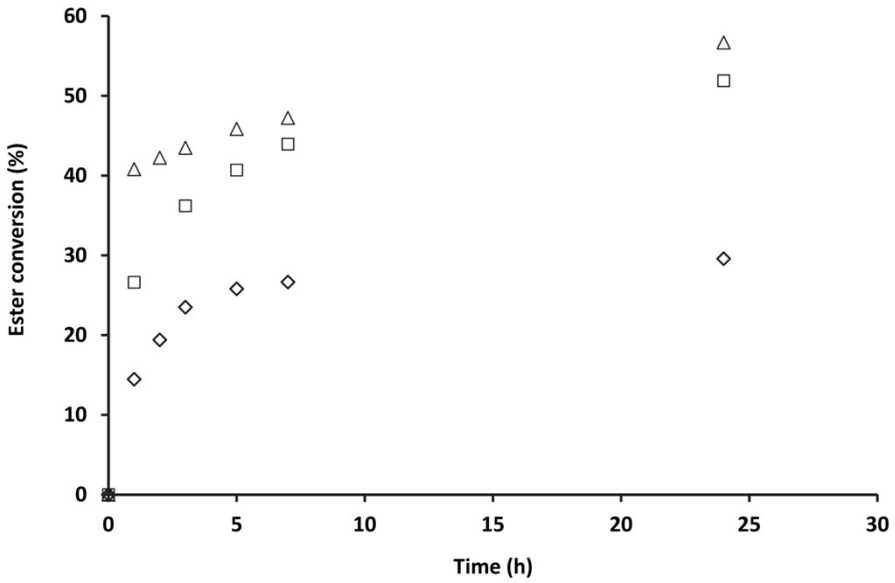

Figure SI 6. Kinetic monitoring for oxidative esterification of benzaldehyde using different bases *t*-BuONa (🕑), NaOH (⭘) and *t*-BuOK (❒).

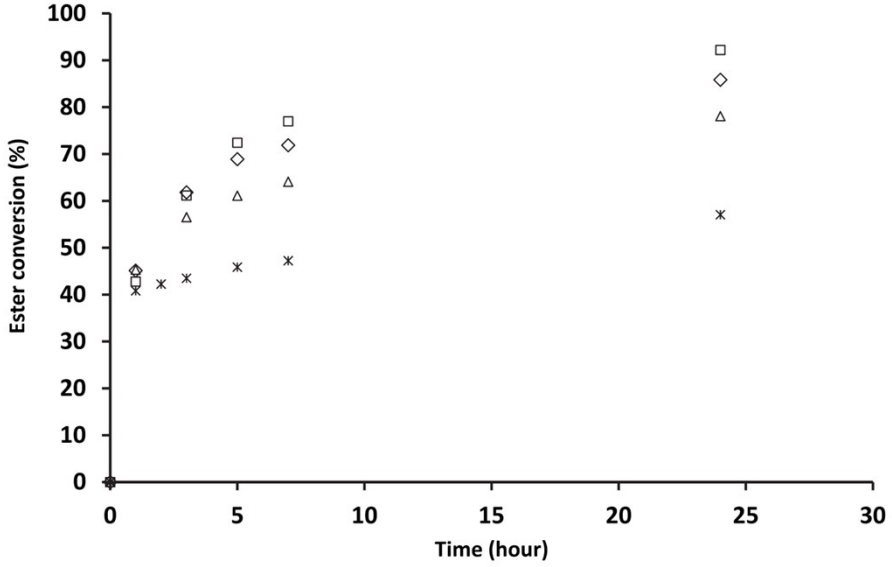

Figure SI 7. Kinetic monitoring for oxidative esterification of benzaldehyde under various conditions: (⩛) AuNPs/PTFE: 0.5%, RT, H_20_2 (1.5eq.); (❒) AuNPs/PTFE: 1%, RT, H_2O_2 (1.5eq.); (🕑) AuNPs/PTFE: 1%, 0°C, H_2O_2 (1.5eq.); (⭘) AuNPs/PTFE: 1%, RT, green lamp, H_2O_2 (1.5eq.).

Table SI 3. Kinetic results for oxidative esterification of p-substituted benzaldehydes

Aldehyde	**σ**	**run n°**	k_{obs}	$k_{obs\ average}$	**log(k_X/k_H)**
p-OCH_3	-0.27	1	1.08E-05	9.15E-06	-0.648
		2	7.49E-06		
p-CH_3	-0.17	1	5.79E-06	1.90E-05	-0.331
		2	3.22E-05		
H	0	1	2.57E-05	4.07E-05	0
		2	5.57E-05		
p-Br	0.23	1	1.64E-04	1.33E-04	0.513
		2	1.01E-04		
p-F	0.05	1	5.66E-05	6.25E-05	0.186
		2	6.84E-05		
p-Cl	0.22	1	1.44E-04	1.53E-04	0.575
		2	1.62E-04		

GC/MS data: (confirmed with standards)

- Benzaldehyde :
  - GC: retention time: 20.40 min.
  - MS (EI) m/z (relative abundance%) = 51.1 (24), 77.1 (65), 105.1 (100)
- Methyl benzoate :
  - GC: retention time: 24.97 min
  - MS (EI) m/z (relative abundance%) = 51.1 (24) , 77.1 (65) , 105.1 (100) , 136.0 (38)
- 4-tolualdehyde :
  - GC: retention time: 24.66 min
  - MS (EI) m/z (relative abundance%) = 65.1 (24) , 91.1 (82) , 119.1 (100)
- Methyl 4-methylbenzoate :
  - GC: retention time: 28.80 min
  - MS (EI) m/z (relative abundance%) = 65.1 (16), 91.1 (56), 119.1 (100), 150.0 (44)
- 4-anisaldehyde :
  - GC: retention time: 30.17 min
  - MS (EI) m/z (relative abundance%) = 63.1 (10), 77.7 (35), 92.1 (10) , 107.1 (22), 135.1 (100)
- Methyl 4-methoxybenzoate :
  - GC: retention time: 33.54 min
  - MS (EI) m/z (relative abundance%) = 63.1 (8), 77.7 (22), 92.1 (8), 107.1 (15), 135.1 (100), 166.1 (48)
- 4-chlorobenzaldehyde :
  - GC: retention time: 26.22 min
  - MS (EI) m/z (relative abundance%) = 50.0 (14), 75.1 (24), 111.0 (36), 139.0 (100)
- Methyl 4-chlorobenzoate :
  - GC: retention time: 31.13 min
  - MS (EI) m/z (relative abundance%) = 50.0 (8), 75.1 (22), 111.0 (32), 139.0 (100), 169.9 (45)
- 4-bromobenzaldehyde :
  - GC: retention time: 29.23 min
  - MS (EI) m/z (relative abundance%) = 50.1 (52.6), 51.1 (27.3), 73.1 (22.4), 74.1 (37.4), 75.1 (37.8), 76.1 (25.4), 77.1 (20.1), 155.1 (36.7), 157.0 (36.4), 183.0 (97.4), 184.1 (63.4), 185.0 (100), 186.0 (61.5)
- Methyl 4-bromobenzoate :
  - GC: retention time: 34.29 min
  - MS (EI) m/z (relative abundance%) = 50.1 (34.8), 73.1 (26.7), 74.1 (27.5), 75.1 (39.0), 76.1 (28.0), 135.2 (27.9), 147.2 (10.4), 155.1 (34.4), 157.1 (32.4), 183.0 (100), 185.0 (98.8), 214.0 (43.6), 216.0 (41.5)
- 4-fluorobenzaldehyde :
  - GC: retention time: 19.99 min
  - MS (EI) m/z= 50.1 (15.8), 74.1 (15.5), 75.1 (34.3), 95.1 (59.1), 96.2 (10.3), 123.1 (100), 124.1 (48.2)
- Methyl 4-fluorobenzoate :
  - GC retention time: 24.20 min
  - MS (EI) m/z (relative abundance%) = 73.2 (19.3), 74.1 (10.7), 75.1 (31.7), 95.1 (48.1), 123.1 (100), 153.1 (22.2), 154.0 (30.5)

Table SI 4. Equilibrium constants calculation details determined by ^{1}H NMR.

4-methoxybenzaldehyde sigma -0.27

Aldehyde integration	Hemiacetal Integration	% Aldehyde	% Hemiacetal	*Keq*	log K_X/K_H
1	0.05	95.24	4.76	0.050	-0.72

4-methylbenzaldehyde sigma -0.17

Aldehyde integration	Hemiacetal Integration	% Aldehyde	% Hemiacetal	*Keq*	log K_X/K_H
1	0.11	90.09	9.91	0.110	-0.37

benzaldehyde sigma 0

Aldehyde integration	Hemiacetal Integration	% Aldehyde	% Hemiacetal	*Keq*	log K_X/K_H
1	0.29	77.52	22.48	0.290	0.05

4-fluorobenzaldehyde sigma 0.05

Aldehyde integration	Hemiacetal Integration	% Aldehyde	% Hemiacetal	*Keq*	log K_X/K_H
1	0.3325	75.05	24.95	0.332	0.11

4-chlorobenzaldehyde sigma 0.22

Aldehyde integration	Hemiacetal Integration	% Aldehyde	% Hemiacetal	*Keq*	log K_X/K_H
1	0.67	59.88	40.12	0.670	0.41

4-bromobenzaldehyde sigma 0.23

Aldehyde integration	Hemiacetal Integration	% Aldehyde	% Hemiacetal	*Keq*	log K_X/K_H
1	0.869	53.50	46.50	0.869	0.52

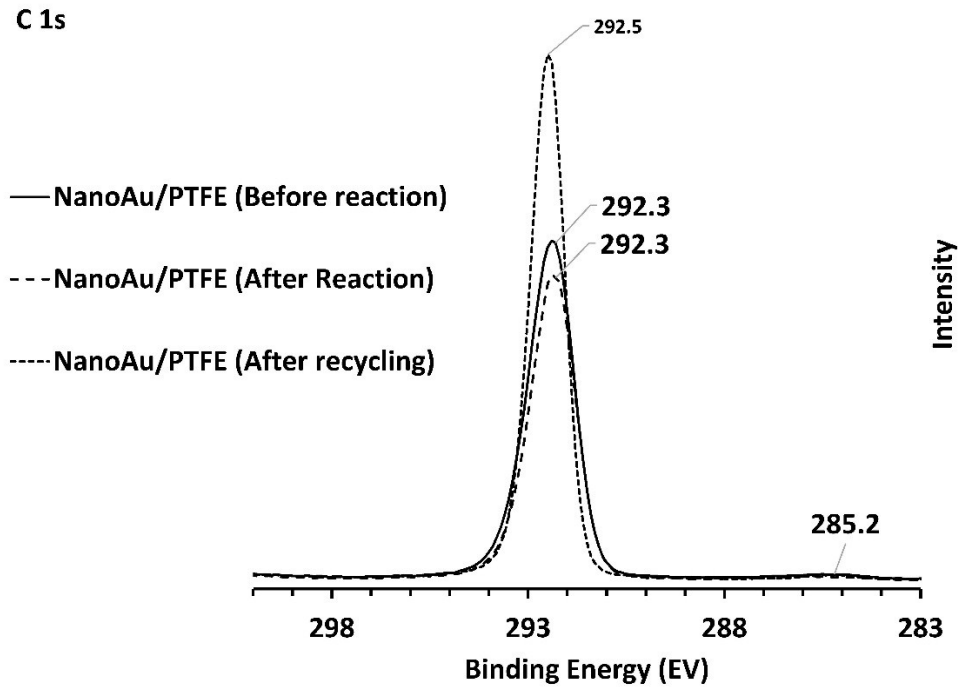

Figure SI 8. XPS study of the C (1s) region before and after reaction and after recycling step.

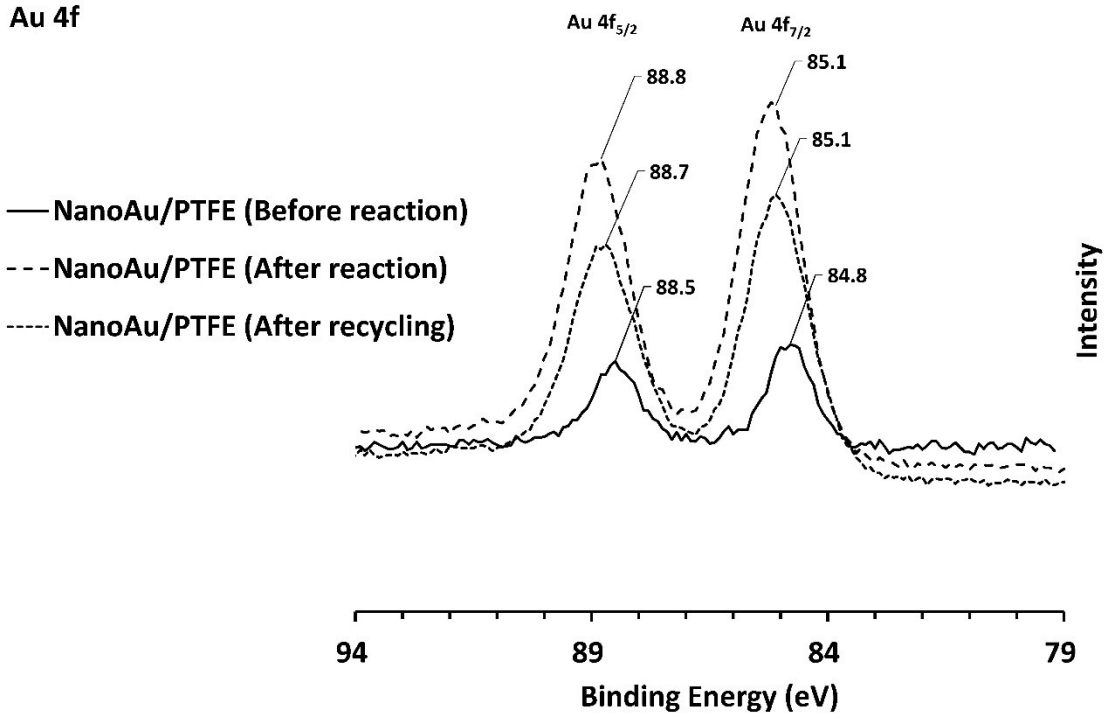

Figure SI 9. XPS study of the Au (4f) region before and after reaction and after recycling step.

Table SI 5. Summary of XPS quantitative analyses of the AuNPs/PTFE surface at different stages

Element	Orbital	AuNPs/PTFE (Step 0)[a]		AuNPs/PTFE (Step 1)[b]		AuNPs/PTFE (Step 2)[c]	
		BE (eV)	$\%_{atom}$	BE (eV)	$\%_{atom}$	BE (eV)	$\%_{atom}$
F	1s	689.7	68.40	689.5	67.15	689.3	66.48
O	1s	532.5	0.058	532.9	0.25	532.8	0.28
C	1s	292.5	31.56	292.4	32.39	292.4	33.04
	1s	285.2		285.2		285.2	
Au	$4f_{7/2}$	84.8	0.035	85.2	0.020	85.1	0.018
	$4f_{5/2}$	88.5		88.9		88.8	

[a] Step 0: AuNPs/PTFE after immobilisation on surface.
[b] Step 1: AuNPs/PTFE after oxidative esterification.
[c] Step 2: AuNPs/PTFE after recycling conditions (H_2O_2 / Acetone / Water).

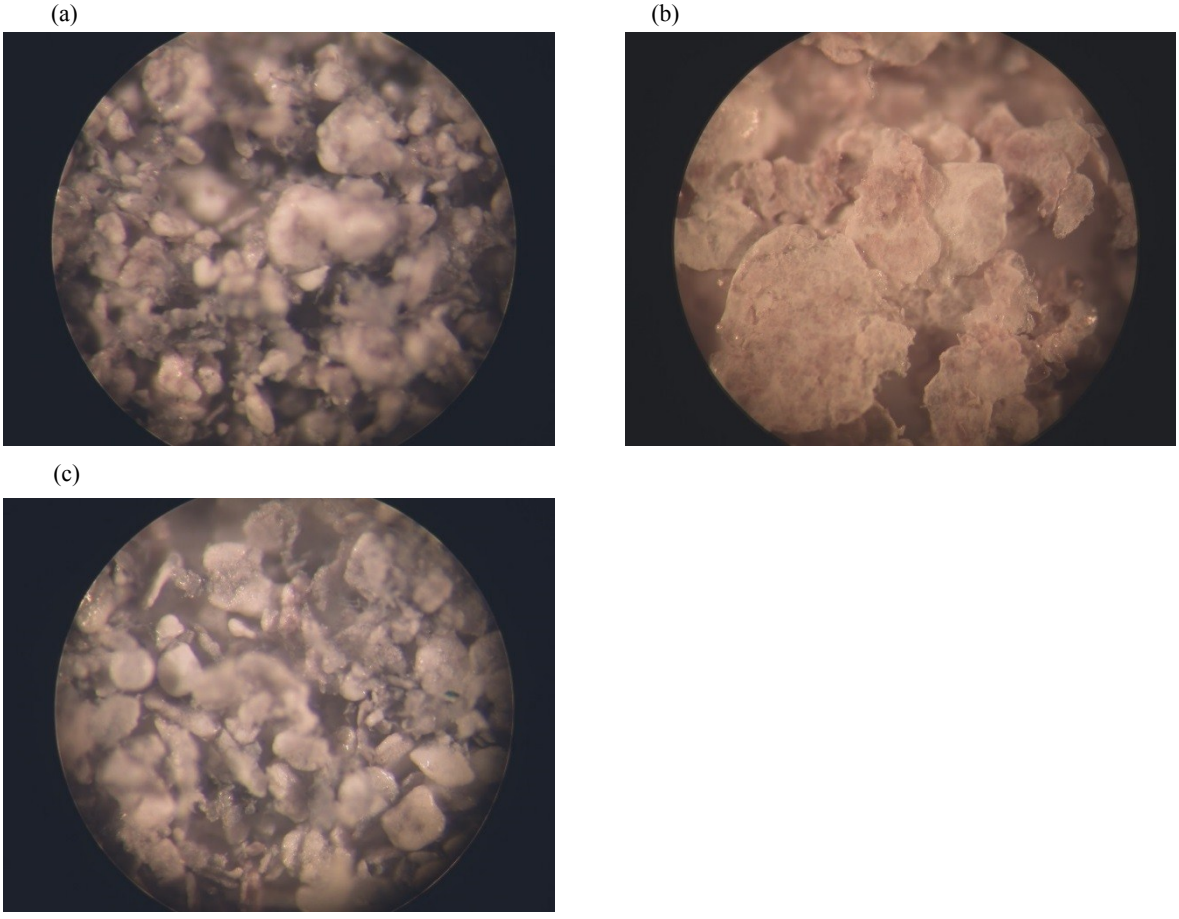

Figure SI 10. Binocular loop study of the AuNPs/PTFE before reaction (a), after 3 successive reactions without recycling procedure (b), after 10 successive reactions using recycling procedure (c).

Eley-Rideal kinetic model

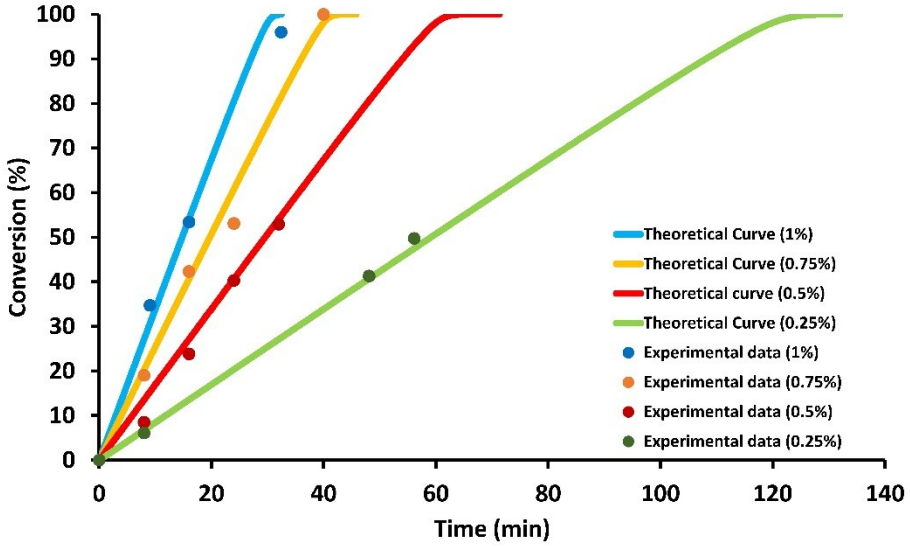

Figure SI 11. Eley-Rideal model fitting for benzaldehyde photocatalytic oxidative esterification reaction depending on catalyst loading kinetic study – comparison study between theoretical model and experimental data with fixed *kr* (1700 L.mol^{-1}.s^{-1}) and K_{Ads} (3.1×10^{-3}) values according to the following equations:

$$r_0 = -\frac{dC_{Benz}}{dt} = k_r C_S C_{H2O2} \frac{K_{Ads} K_{Hemi} C_{Benz}}{(1 + K_{Ads} K_{Hemi} C_{Benz})}$$

With:

k_r: Kinetic constant for hemiacetal anion oxydation on surface (L.mol^{-1}.s^{-1})

K_{Ads}: Hemiacetal anion adsorption equilibrium constant

K_{Hemi}: Hemiacetal anion formation equilibrium constant

C_S: Surface gold atom concentration (mol.L^{-1}) (based on 1.87 nm diameter AuNPs for which $C_S = C(Au\ total)/2.5$ considering a spherical geometry)

C_{H2O2}: Hydrogen peroxide concentration – supposed constant at 1.5 eq.

C_{Benz}: Benzaldehyde concentration

Because H_2O_2 is added continuously to the reaction medium, we considered its concentration constant along time, the kinetic model was consequently simplified and resulted in the following integrated form:

$$K_e C_{Benz} + \ln\left(C_{Benz}\right) = k_r C_S C_{H2O2} K_e t + K_e C_{0Benz} - \ln\left(C_{0Benz}\right)$$

Giving:

$$C_{Benz} = K_e \omega\left\{\frac{C_{0Benz}}{K_e} e^{\left(\frac{C_{0Benz} - k_r C_S C_{H2O2} K_e t}{K_e}\right)}\right\}$$

With: $K_e = K_{Ads} K_{Hemi}$ and $\omega\{x\}$: Lambert function

Winitzki approximated analytical form of the Lambert function (1% error) was used for the fitting:

$$W(x) \approx ln(1 + x)\left(1 - \frac{\ln(1 + \ln(1 + x))}{2 + \ln(1 + x)}\right)$$

See reference for the use of Winitzki approximation: Winitzki S. *Lecture Notes Comput. Sci.* **2003**, *2667*, 780-789.

(2003) Lecture Notes in Computer Science, 2667, 780-789. transcen-