Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information

Catalytic farming: reaction rotation extends catalyst performance

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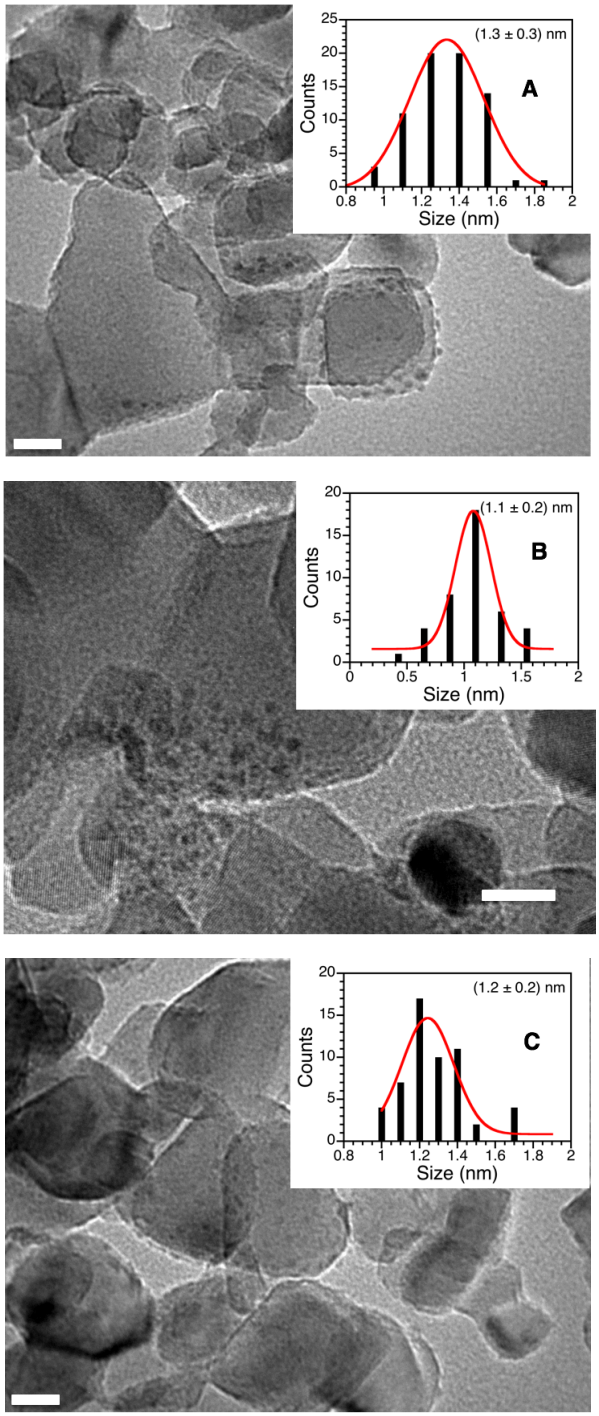
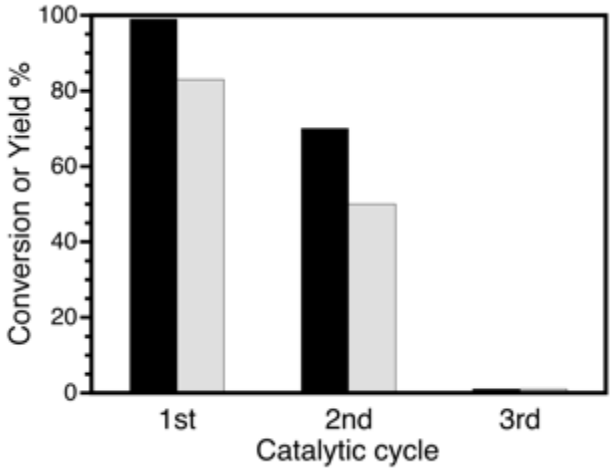
Supplementary Table S1 | Catalytic farming of Pd@TiO_2 by rotation between Ullmann homo-coupling and Sonogashira coupling: up to 6 alternating cycles.

Cycle	Reaction	% Conversion[a]	% Yield[a]			TON[b]	TOF[b] (h^{-1})
			DPA	Ar'-Ar'	Ar'-H		
1	B	97	–	65	32	967	967
2	A	98	83	–	–	2140	4280
3	B	97	–	60	35	893	893
4	A	98	85	–	–	2192	4384
5	B	96	–	56	40	833	833
6	A	65(95)	42(80)	–	–	1083 (2063)	2166 (2063)

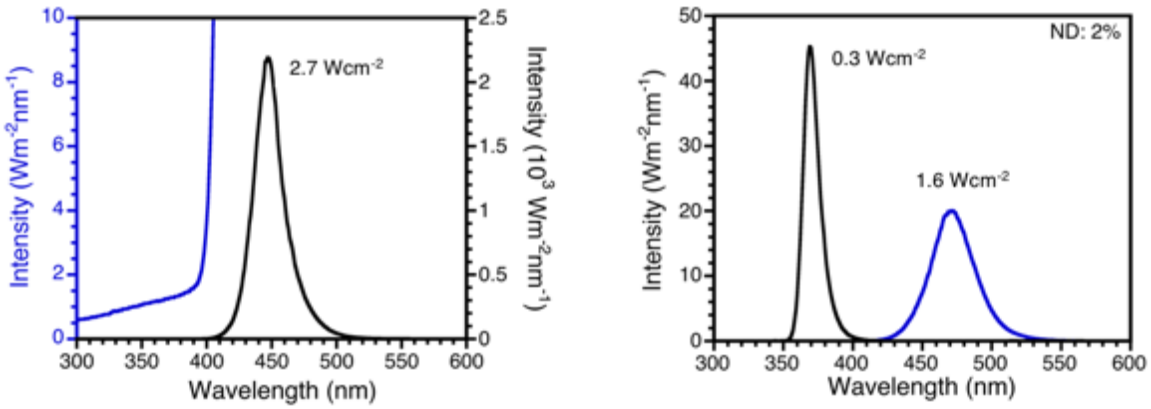
Reactions conditions: A- Sonogashira coupling: 15 mg of Pd@TiO_2, 1.3 eq. of phenylacetylene, 0.13 mmol of iodobenzene, 2 eq. of K_2CO_3, 4 mL MeOH, Ar atmosphere. Irradiation: 7x 450 nm LED working at 2.7 Wcm^{-2}. Time: 30 min. Values between brackets correspond to results obtained after 1 h of irradiation. B- Ullman homo-coupling: 20 mg Pd@TiO_2, 0.1 mmol of methyl 4-iodobenzoate, 2 eq. of Cs_2CO_3, 4 mL of THF, Ar atmosphere. Irradiation: 368 nm and 465 nm working at 0.3 and 1.6 Wcm^{-2}, respectively. Time: 1 h. [a] Yields and conversion calculated by GC-FID using *t*-butylbenzene as external standard. [b]Calculation per PdNP based on major product.



Supplementary Figure S1 | TEM image of Pd@TiO_2 and particle size distribution (insets) for fresh material (A), after 3 Sonogashira coupling cycles (B) and after 6 catalytic farming cycles (C). Scale bar: 10 nm. Size distribution of Pd nanoparticles supported on TiO_2 obtained by manual counting and sizing of particles identified by TEM.

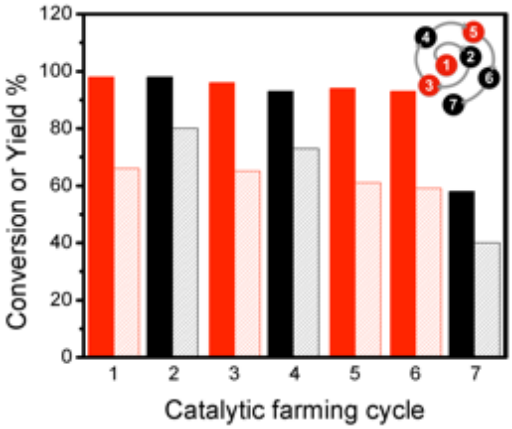


Supplementary Figure S2 | Conversions and yields obtained after several catalytic cycles of Sonogashira coupling upon 465 nm irradiation at 1.6 W cm^{-2} for 5 h.



Supplementary Figure S3 | Emission spectra of light sources used in this work. *Left:* 7x450 nm LED, showing UV contamination in blue. *Right*: 1x365 nm LED (black) and 1x465 nm LED (blue). ND: neutral density filter.

Supplementary Table S2 | Catalytic farming of Pd@TiO_2 by rotation between Ullmann homo-coupling and Sonogashira coupling: up to 7 cycles with non-alternating reactions in between.



Cycle	Reaction	% Conversion[a]	% Yield[a]			TON[b]	TOF[b] (h^{-1})
			DPA	Ar'-Ar'	Ar'-H		
1	B	98	–	66	29	982	196
2	A	98	80	–	---	2063	413
3	B	96	–	65	31	967	193
4	A	93	73	–	–	1883	377
5	B	94	–	61	33	908	182
6	B	93	–	59	34	878	176
7	A	58 (83)	40(62)	–	–	1032 (1599)	206 (67)

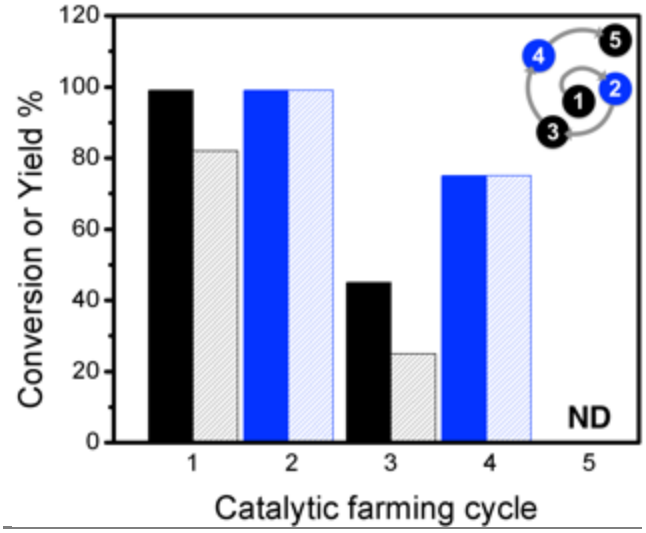
Reactions conditions: A- Sonogashira coupling: 15 mg of Pd@TiO_2, 1.3 eq. of phenylacetylene, 0.13 mmol of iodobenzene, 2 eq. of K_2CO_3, 4 mL MeOH, Ar atmosphere. Irradiation: 465 nm LED working at 1.6 Wcm^{-2}. Time: 5 h. Values between brackets correspond to results obtained after 24 h of irradiation. B- Ullman homo-coupling: 20 mg Pd@TiO_2, 0.1 mmol of methyl 4-iodobenzoate, 2 eq. of Cs_2CO_3, 4 mL of THF, Ar atmosphere. Irradiation: 368 nm LED working at 0.3 Wcm^{-2}. Time: 5 h. [a] Yields and conversion calculated by GC-FID using *t*-butylbenzene as external standard. [b]Calculation per Pd NP based on major product.

Supplementary Table S3 | Catalytic farming of $Pd@TiO_2$ by rotation between alkene isomerization, Ullmann homo-coupling and Sonogashira coupling (scheme 1).

Cycle	Reaction	Time (h)	% Conv[a]	% Yield[a]					TON[b]	TOF[b] (h^{-1})
				DPA	Ar'-Ar'	Ar'-H	A	DA		
1	C	5	97	–	–	–	71	25	1831	366
2	A	0.5	ND	ND	–	–	–	–	0	0
3	B	1	96	–	60	36	–	–	893	893
4	B	1	93	–	59	35	–	–	878	878
5	A	0.5 (3)	13(43)	ND(30)	–	–	–	–	0(774)	0(258)
1	B	1	97	–	70	27	–	–	1041	1041
2	C	6	35	–	–	–	25	~10	644	107
3	B	1	95	–	66	29	–	–	982	982
4	A	0.5(1)	74(99)	68(79)	–	–	–	–	1754(2037)	3507(2037)
5	C	6	26	–	–	–	17	~9	438	73
6[c]	C	5(9)	41(80)	–	–	–	~36(60)	ND(19)	928(1547)	186(172)
1	C	5	>99	–	–	–	67	~22	1728	346
2	C	5	98	–	–	–	69	~25	1779	356
3	B	1	96	–	65	33	–	–	967	967
4	B	1	95	–	60	~35	–	–	893	893
5	A	0.5	96	78	–	–	–	–	2011	4023

Reactions conditions: A- Sonogashira coupling: 15 mg of $Pd@TiO_2$, 1.3 eq. of phenylacetylene, 0.13 mmol of iodobenzene, 2 eq. of K_2CO_3, 4 mL MeOH, Ar atmosphere. Irradiation: 7x 450 nm LED working at 2.7 Wcm^{-2}. B- Ullmann homo-coupling: 20 mg $Pd@TiO_2$, 0.1 mmol of methyl 4-iodobenzoate, 2 eq. of Cs_2CO_3, 4 mL of THF, Ar atmosphere. Irradiation: 368 nm and 465 nm working at 0.3 and 1.6 Wcm^{-2}, respectively. C- Alkene isomerization: 15 mg of $Pd@TiO_2$, 0.16 mmol estragol, 4 mL MeOH, Ar atmosphere. Irradiation: 7x 450 nm LED working at 2.7 Wcm^{-2}. [a] Yields and conversion calculated by GC-FID using *t*-butylbenzene as external standard. [b] Calculation per Pd NP based on major product. [c] Catalyst used after reactivation with I-2959 under UVA irradiation for 5h (See ref. {Elhage, 2017 #11}).

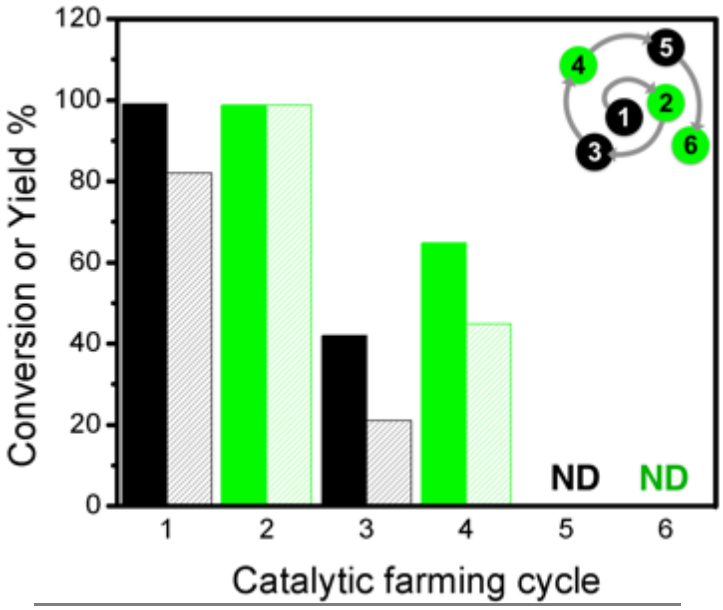
Supplementary Table S4 | Catalytic farming of Pd@TiO2 by rotation between alkene isomerization and Sonogashira coupling.



Cycle	Reaction	% Conversion[a]	% Yield[a]		
			DPA	A	DA
1	A	>99	82	–	–
2	C	>99	–	>99	–
3	A	45	25	–	–
4	C	75	–	75	–
5	A	ND	–	–	–

Reactions conditions: A- Sonogashira coupling (black): 15 mg of Pd@TiO_2, 1.3 eq. of phenylacetylene, 0.13 mmol of iodobenzene, 2 eq. of K_2CO_3, 4 mL MeOH, Ar atmosphere. Irradiation: 465 nm LED working at 1.6 Wcm^{-2}. Time: 5h. C- Alkene isomerization (blue): 15 mg of Pd@TiO_2, 0.16 mmol of estragole, Ar atmosphere. Irradiation: 465 nm irradiation at 1.6 Wcm^{-2}. Time: 24 h. [a] Yields and conversion calculated by GC-FID using *t*-butylbenzene as external standard.

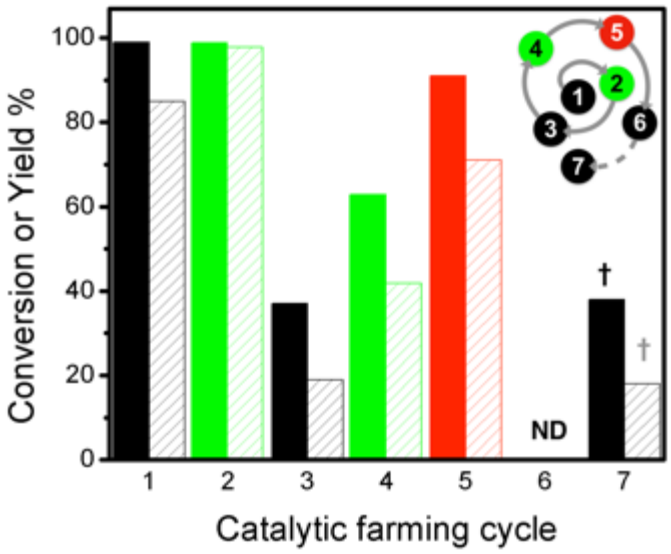
Supplementary Table S5 | Catalytic farming of Pd@TiO2 by rotation between alkene hydrogenation and Sonogashira coupling.



Cycle	Reaction	% Conversion[a]	% Yield[a]		
			DPA	A	DA
1	A	>99	82	–	–
2	D	>99	–	–	>99
3	A	42	21	–	–
4	D	65	–	20	45
5	A	ND	–	–	–
6	D	ND	–	–	–

Reactions conditions: A- Sonogashira coupling (black): 15 mg of Pd@TiO_2, 1.3 eq. of phenylacetylene, 0.13 mmol of iodobenzene, 2 eq. of K_2CO_3, 4 mL MeOH, Ar atmosphere. Irradiation: 465 nm LED working at 1.6 Wcm^{-2}. Time: 5h. D-Alkene hydrogenation (green): 15 mg of Pd@TiO_2, 0.16 mmol of estragole, Ar atmosphere Irradiation: 368 nm irradiation at 0.3 Wcm^{-2}. Time: 4 h. [a] Yields and conversion calculated by GC-FID using *t*-butylbenzene as external standard**.** ND: nothing detected.

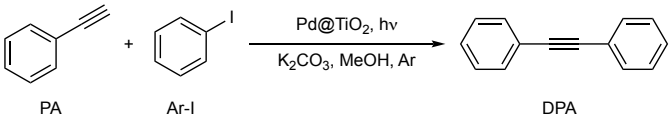
Supplementary Table S6 I Catalytic farming of $Pd@TiO_2$ by rotation between alkene hydrogenation, Ullmann reaction and Sonogashira coupling.



Cycle	Reaction	Time (h)	% Conv[a]	% Yield[a]					TON[b]	TOF[b] (h^{-1})
				DPA	Ar'-Ar'	Ar'-H	A	DA		
1	A	5	99	85	–	–	–	–	2192	438
2	D	4	99	–	–	–	–	98	3110	778
3	A	5	37	19	–	–	–	–	490	98
4	D	4	63	–	–	–	21	42	1333	333
5	B	1	91	–	71	20	–	–	1056	1056
6	A	5	ND	ND	–	–	–	–	0	0
7[c]	A	5	38	18	–	–	–	–	464	93

Reactions conditions: A- Sonogashira coupling (black): 15 mg of $Pd@TiO_2$, 1.3 eq. of phenylacetylene, 0.13 mmol of iodobenzene, 2 eq. of K_2CO_3, 4 mL MeOH, Ar atmosphere. Irradiation: 465 nm LED working at 1.6 Wcm^{-2}. Time: 5h. B- Ullman homo-coupling (red): 20 mg $Pd@TiO_2$, 0.1 mmol of methyl 4-iodobenzoate, 2 eq. of Cs_2CO_3, 4 mL of THF, Ar atmosphere. Irradiation: 368 nm and 465 nm working at 0.3 and 1.6 Wcm^{-2}, respectively. Time: 1 h. D- Alkene hydrogenation (green): 15 mg of $Pd@TiO_2$, 0.16 mmol of estragole, Ar atmosphere Irradiation: 368 nm irradiation at 0.3 Wcm^{-2}. Time: 4 h. [a] Yields and conversion calculated by GC-FID using *t*-butylbenzene as external standard. [b]Calculation per Pd NP based on major product. [c, †] Catalyst used after reactivation with THF treatment under UVA-vis irradiation for 5h. ND: nothing detected.

Supplementary Table S7 | Kinetics for photocatalytic Sonogashira C-C coupling under different irradiation intensities.

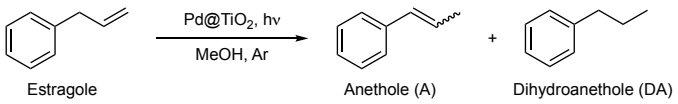


PA Ar-I DPA

	Time (h)	% Conversion[a]	% Yield[a]
465 nm @1.6 Wcm^{-2}	0	0	0
	1	56	46
	2	60	53
	3	64	61
	4.5	77	68
	6	>99	84
450 nm @2.7 Wcm^{-2}	0	0	0
	5	33	29
	10	46	40
	15	67	55
	20	72	60
	30	96	83

Reactions Conditions: 15 mg of Pd@TiO_2, 1.3 eq. of phenylacetylene, 0.13 mmol of iodobenzene, 2 eq. of K_2CO_3, 4 mL MeOH, Ar atmosphere. Irradiation: 1x 465 nm LED working at 1.6 Wcm^{-2} and 7x 450 nm LED working at 2.7 Wcm^{-2}.

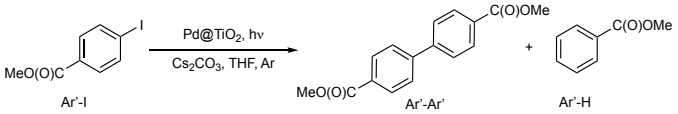
Supplementary Table S8 | Kinetics for photocatalytic alkene isomerization.



	Time (h)	% Conversion[a]	% A[a]	% DA[a]
450 nm @2.7 Wcm^{-2}	0.5	20	19	ND
	1	36	32	ND
	2	46	40	5
	3	60	44	12
	4	76	53	19
	5	94	70	21
465 nm @1.6 Wcm^{-2}	1	28	27	ND
	3	40	38	ND
	5	51	46	ND
	7	52	51	ND
	9	58	58	ND
	24	<99	94	6

Reactions Conditions: 15 mg of Pd@TiO_2, 1 eq. estragol, 4 mL MeOH, Ar atmosphere. Irradiation: 7x 450 nm LED working at 2.7 Wcm^{-2} or 1x 465 nm LED working at 1.6 Wcm^{-2}. [a] Yields and conversions calculated by GC-FID using *t*-butylbenzene as external standard. Dihydroanethole (DA) is detected as by product due to UV light contamination in the light source.(See Supplementary Figure S3)

Supplementary Table S9 | Kinetics for photocatalytic Ullmann homo-coupling.



	Time (h)	% Conversion[a]	% Ar'-H[a]	%Ar'-Ar'[a]
368 nm @0.3 Wcm^{-2}	1	36	22	14
	2	60	26	34
	3	69	25	44
	4	86	26	60
	5	96	27	69
368 nm @0.3 Wcm^{-2} 465 nm @1.6 Wcm^{-2}	0.5	61	32	29
	1	95	33	62

Reactions conditions: 20 mg Pd@TiO_2, 0.1 mmol of methyl 4-iodobenzoate, 2 eq. of Cs_2CO_3, 4 mL of THF, Ar atmosphere. [a] Yields and conversions calculated by GC-FID using t-butylbenzene as external standard.

Supplementary Table S10 | Reusability and recovery of catalytic activity of Pd@TiO_2 towards Sonogashira coupling using Ullmann homo-coupling reaction.

Cycle	% Conversion[a]	% Yield[a]
1	98 ± 1	85 ± 1
2	40 ± 1	35 ± 1
3	ND	ND
4[b]	24(57)	19(37)

Sonogashira reaction as per conditions in Supplementary table S7, 450 nmLED working at 2.7 Wcm^{-2}. [a] Yields and conversions calculated by GC-FID using t-butylbenzene as external standard. [b] Catalyst was used after one cycle of Ullmann homo-coupling reaction (95 % conversion, 57 % Ar'-Ar', 38 % Ar'-H) as per conditions described in Supplementary table S9. ND: Non detected.