Electronic Supplementary Information (ESI)

Improved Visible Photocatalytic Activity on Titania Modified with —O—Pd—Cl Species Assisted by Oxidative Addition Reaction of Pd^0

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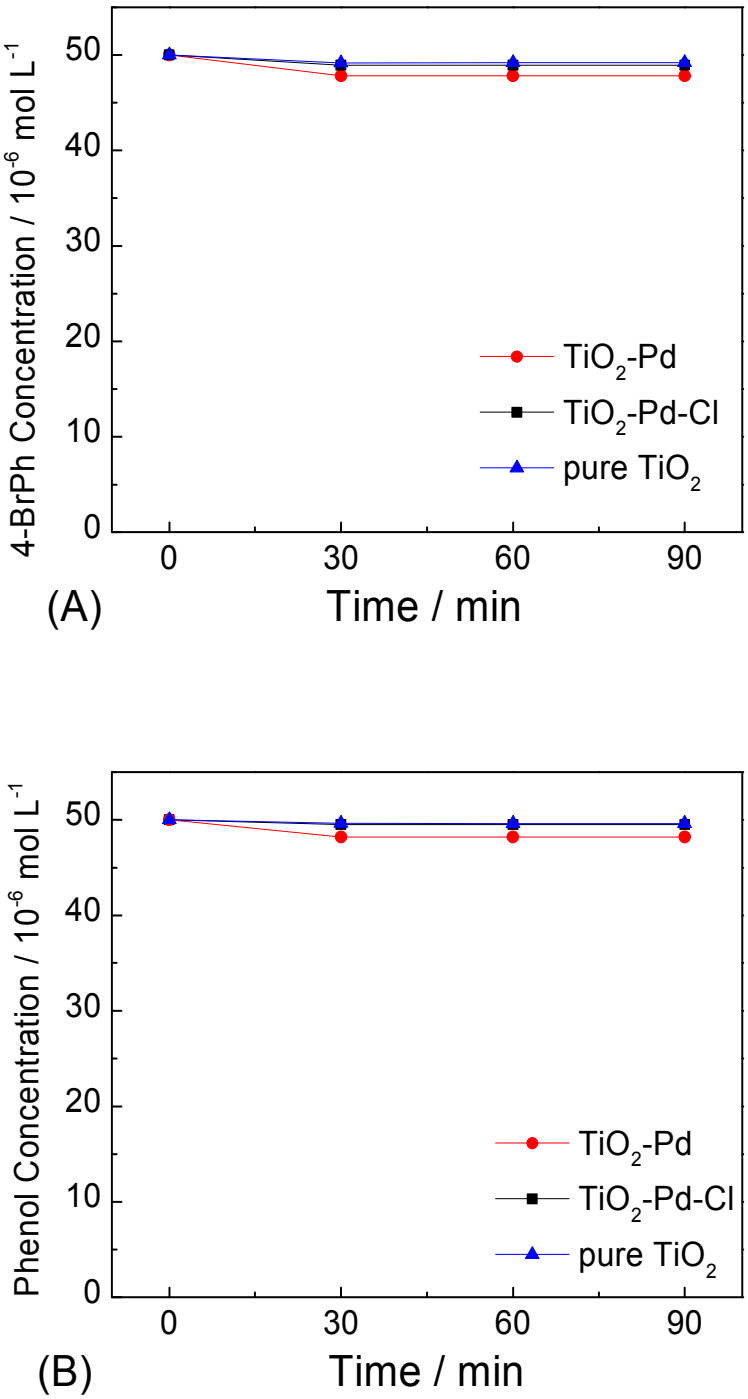


Figure S1. Adsorption curves under dark for all the samples: 4-BrPh (A) and phenol (B).

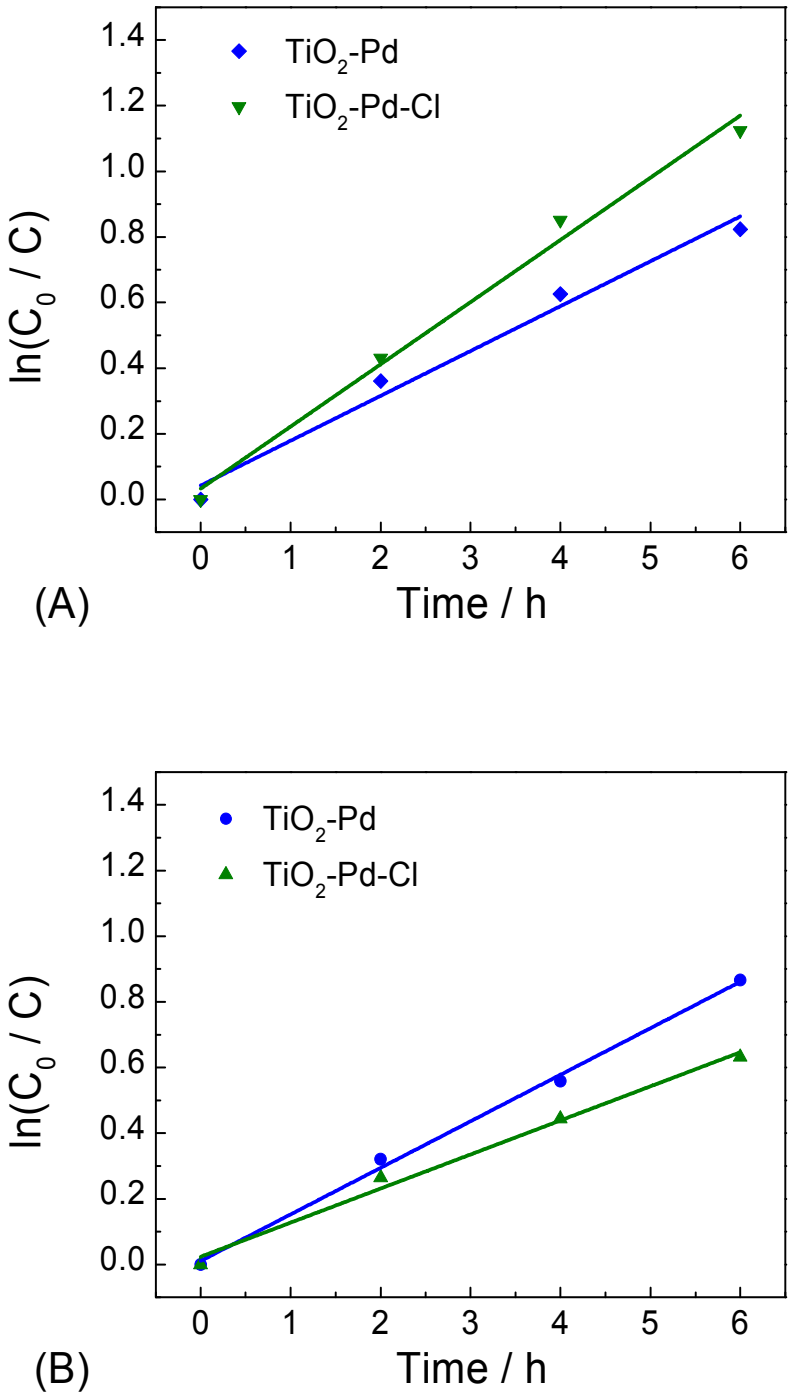
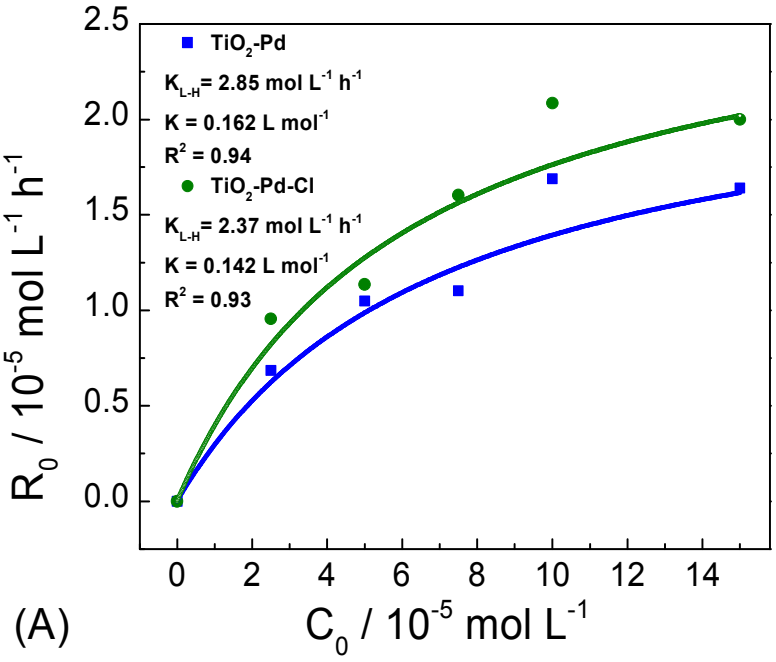


Figure S2. The linear fits to the photocatalytic degradation data represent pseudo-first-order degradation kinetics: 4-BrPh (A) and phenol (B).



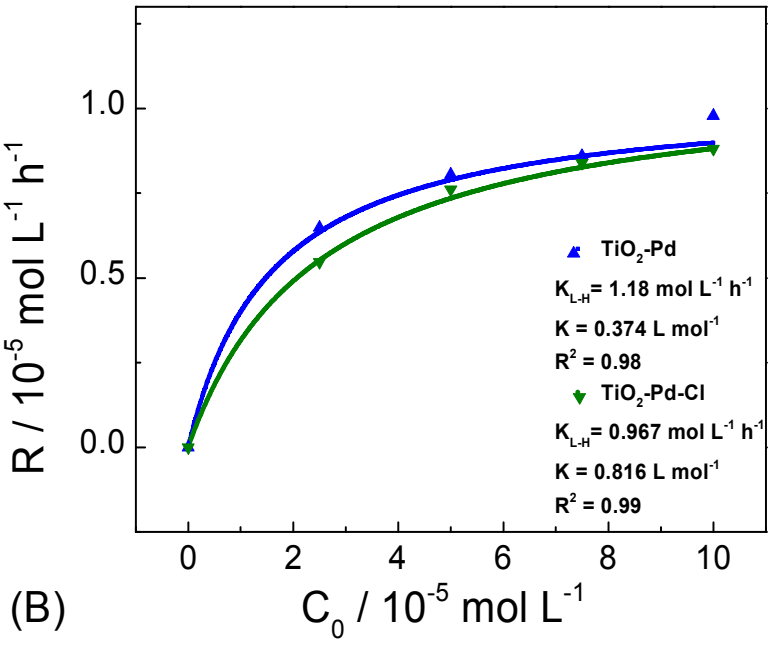
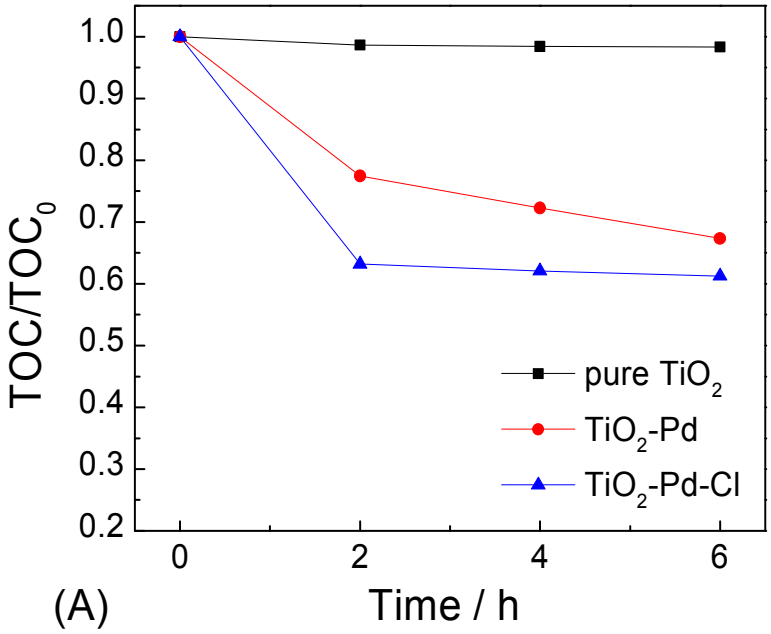
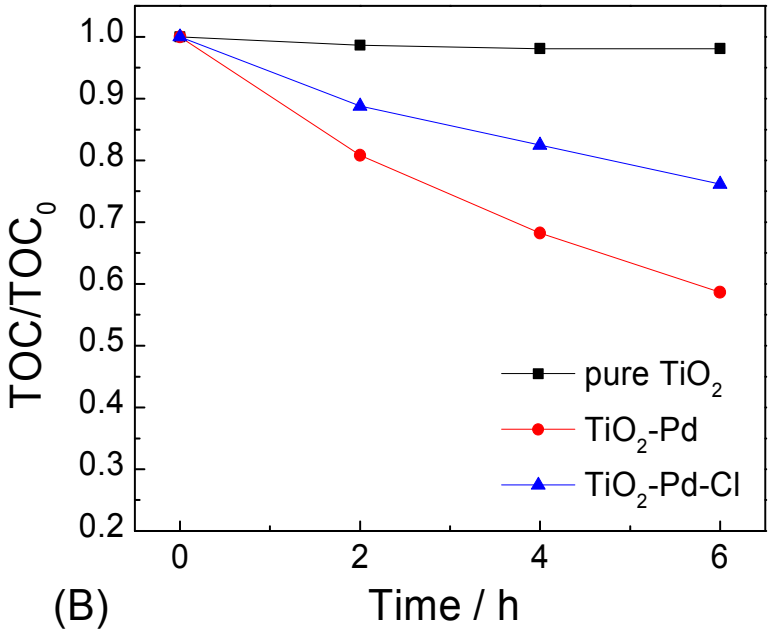


Figure S3. Initial degradation rate as a function of initial concentration and fitting curves of the Langmuir−Hinshelwood (L-H) kinetics model: 4-BrPh (A) and phenol (B). Langmuir−Hinshelwood (L-H) rate constant K_{L-H}, Langmuir adsorption coefficient (K) and regression coefficients (R_2) are also shown. Substrates photo-degradation reaction rates (R_0) are

observed to be a function of the initial concentration (C_0) by keeping the surface concentration fixed. The rate of photodegradation of the phenolic compounds is typically fitted with the Langmuir−Hinshelwood (L-H) kinetics model.[1]



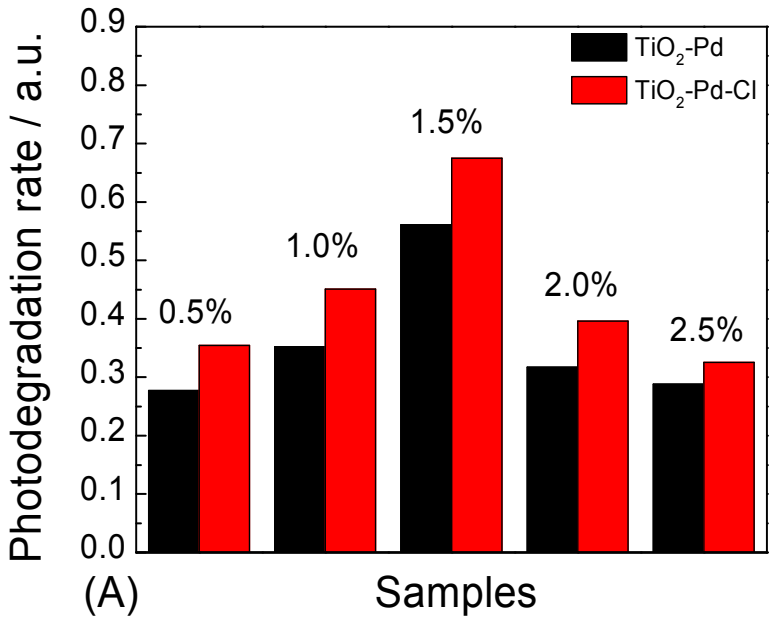
(A)



(B)

Figure S4. Kinetics of disappearance of total organic carbon (TOC): photodegradation of 4-BrPh (A) and phenol (B).

It is observed that in photodegradation of 4-BrPh, TiO_2-Pd-Cl has a higher activity than TiO_2-Pd for TOC disappearance. While in photodegradation of phenol, TiO_2-Pd has a higher activity than TiO_2-Pd-Cl for TOC disappearance.



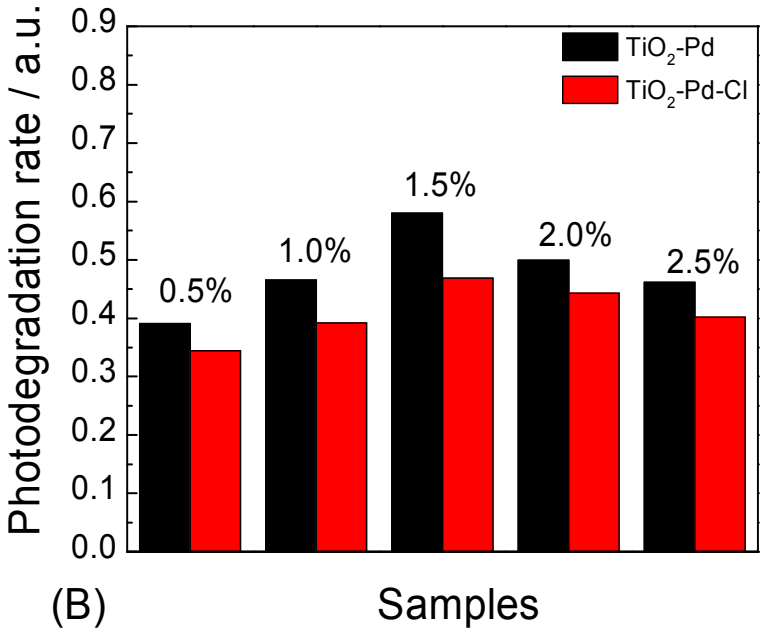


Figure S5. Photodegradation rate of 4-BrPh (A) and phenol (B) in aqueous suspension using catalysts with different molar ratio of Pd^{2+} to Ti^{4+} under visible light irradiation (λ > 420 nm) for 8 h.

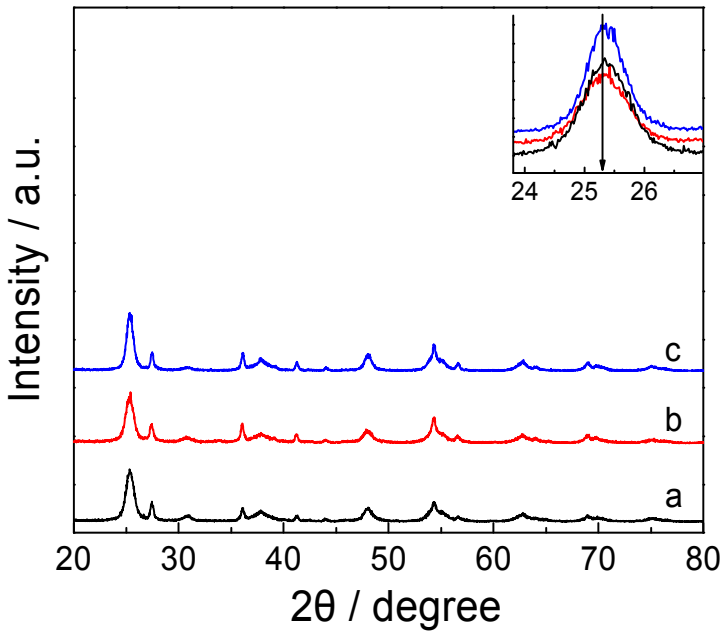


Figure S6. XRD patterns of the as-prepared samples. (a) pure TiO_2, (b) Pd-TiO_2, (c) TiO_2-Pd-Cl.

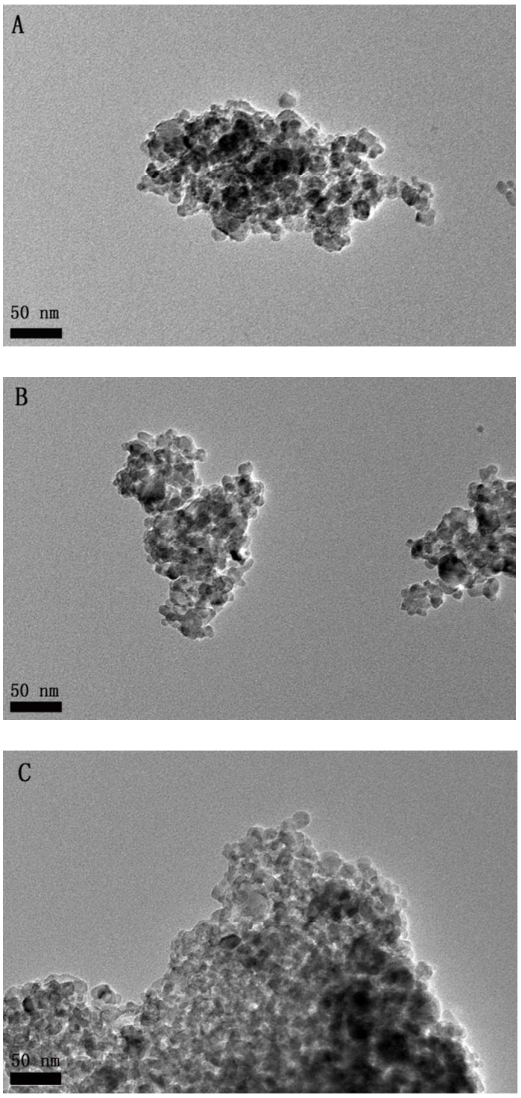


Figure S7. TEM images of the as-prepared samples: pure TiO_2 (A), TiO_2-Pd (B) and TiO_2-Pd-Cl (C).

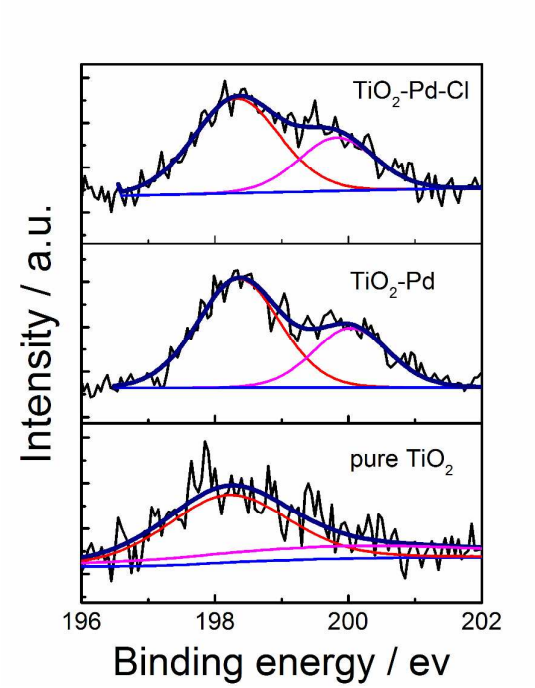


Figure S8. XPS Cl 2p spectra of as-prepared pure TiO_2, TiO_2-Pd and TiO_2-Pd-Cl.

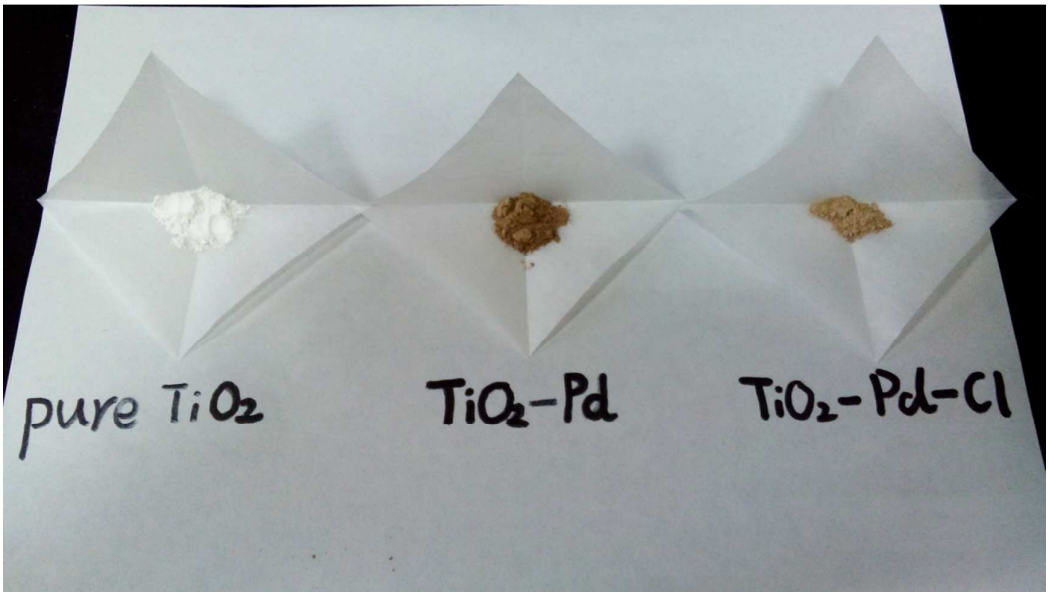
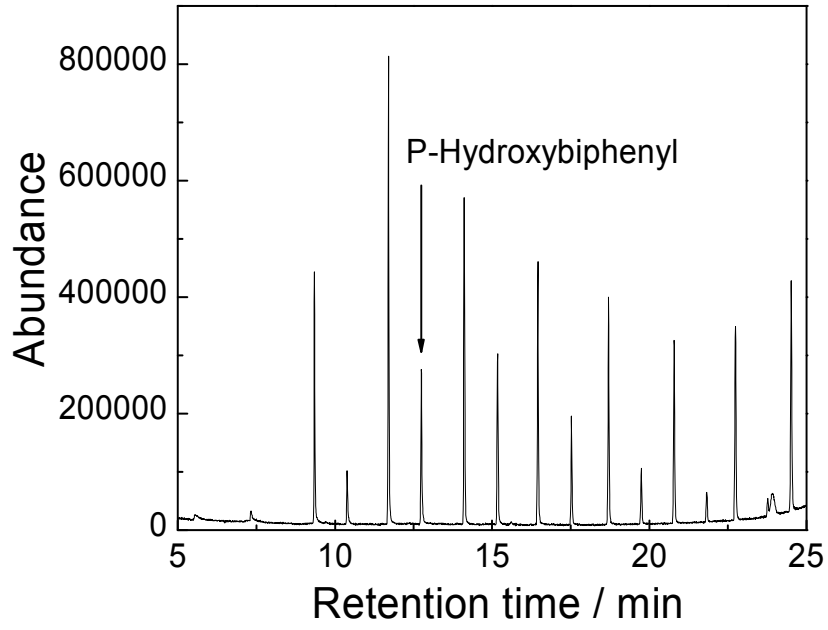
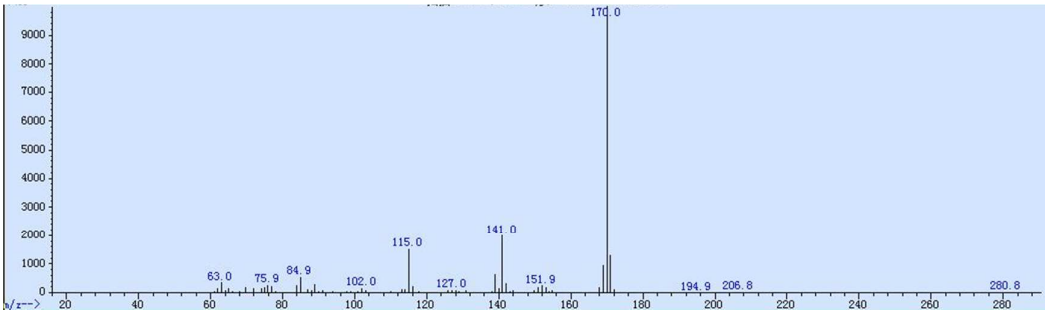


Figure S9. Photographs of the photocatalyst.



(A)



(B)

Figure S10. GC-MS total ion chromatogram (TIC) of the intermediates during photocatalytic degradation of 4-BrPh by TiO_2-Pd-Cl at 6h (A). EI mass spectrum corresponding to the retention time window from 12.7 min to 13.1 min (B).

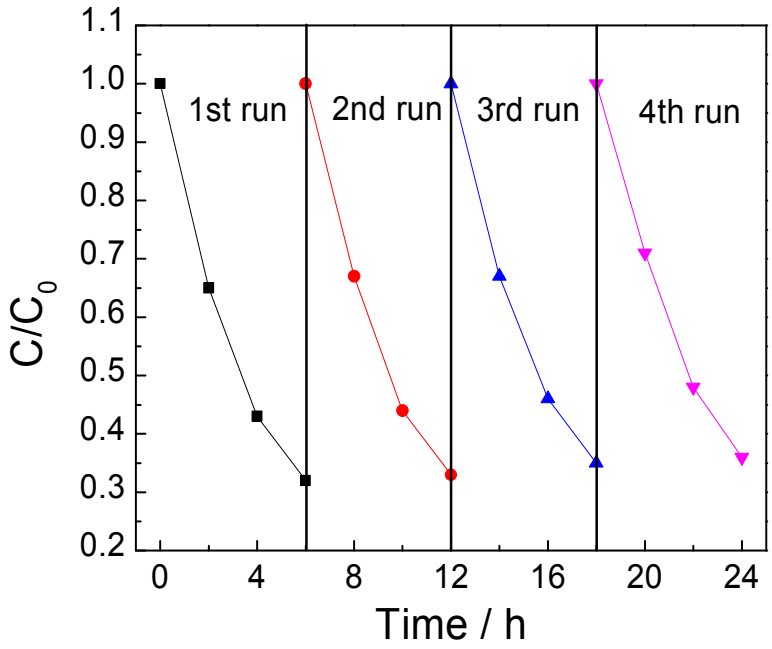


Figure S11. Reusability of TiO_2-Pd-Cl for the visible photocatalytic degradation of 4-BrPh (5×10^{-5} mol L^{-1}).

Table S1. Degradation ratio (after 6h of reaction), pseudo-first-order rate constant, half-time ($t_{1/2}$) for photodegradation reaction and specific photocatalytic activity for TiO_2-Pd and TiO_2-Pd-Cl upon photodegradation of 4-BrPh under visible-light irradiation (λ > 420 nm).

Sample	4-BrPh degraded $(C_0\text{-}C) / C_0$ (%)[a]	k ($\times 10^{-2}$ h^{-1})	$t_{1/2}$ (h)	Specific photocatalytic activity (mol g^{-1} h^{-1})	R^2
TiO_2-Pd	55.10	13.67	5.1	3.67×10^{-5}	0.97
TiO_2-Pd-Cl	71.98	20.14	3.4	4.73×10^{-5}	0.99

[a]after 6 h photodegradation reaction

Table S2. Degradation ratio (after 6h of reaction), pseudo-first-order rate constant, half-time ($t_{1/2}$) for photodegradation reaction and specific photocatalytic activity for TiO_2-Pd and TiO_2-Pd-Cl upon photodegradation of phenol under visible-light irradiation (λ> 420 nm).

Sample	Phenol	k ($\times 10^{-2}$ h^{-1})	$t_{1/2}$ (h)	Specific	R^2

	degraded (C_0-C) / C_0 (%) [a]			photocatalytic activity (mol g^{-1} h^{-1})	
TiO_2-Pd	57.95	14.17	4.9	3.86×10^{-5}	0.99
TiO_2-Pd-Cl	46.85	9.76	7.1	3.12×10^{-5}	0.99

[a]after 6 h photodegradation reaction

Table S3. Cell parameters, cell volumes, crystallite sizes and BET specific surface areas of pure TiO_2, TiO_2-Pd and TiO_2-Pd-Cl.

Sample	Anatase cell parameters (Å)		Anatase cell volume ($Å^3$)	Crystallite size (nm)	BET surface area (m^2 / g)
	a=b	c			
TiO_2-Pd-Cl	3.790	9.498	136.43	9.8	78.7
TiO_2-Pd	3.788	9.501	136.32	10.6	69.0
Pure TiO_2	3.789	9.499	136.37	11.0	64.6

Table S4. Zeta potential measurements on TiO_2-Pd and TiO_2-Pd-Cl suspensions before and after adsorption of phenol or 4-BrPh.

Sample	Before adsorption (mV)	After adsorption of phenol (mV)	After adsorption of 4-BrPh (mV)
TiO_2-Pd	36.68	20.49	18.37
TiO_2-Pd-Cl	36.42	32.59	34.56

REFERENCES

1. S. Sarkar, A. Makhal, S. Baruah, M. A. Mahmood, J. Dutta and S. K. Pal, *J. Phys. Chem. C*, 2012, **116**, 9608-9615.