Electronic Supplementary Information (ESI)

Tandem catalysis induced by hollow PdO: highly efficient H_2 generation coupled with organic dye degradation via sodium formate reforming at room temperature

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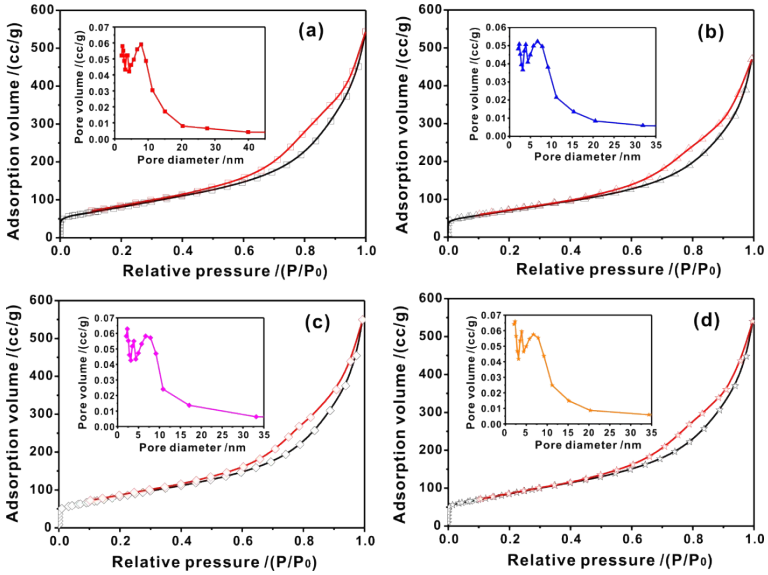

Fig. S1 N_2 adsorption and desorption isotherms of (a) TiNTs, (b) Pd/TiNTs without calcination, (c) kv-PdO/TiNTs and (d) Pd/TiNTs catalysts with their pore-size distributions (inset).

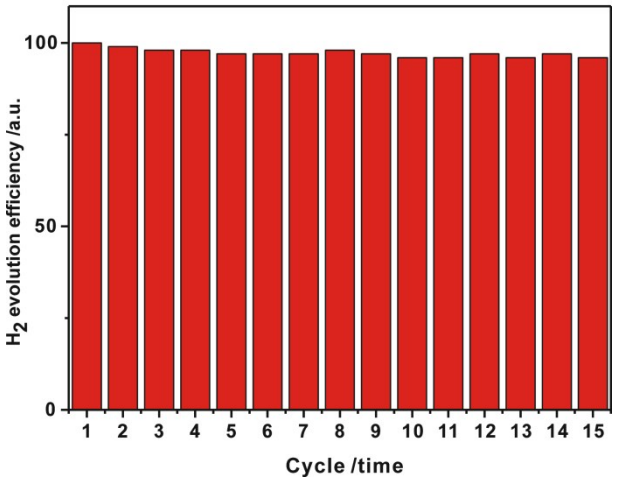

Fig. S2 H_2 evolution from HCOONa aqueous solution (1 M) cyclic experiment catalyzed by PdO/TiNTs (1.0 wt%) catalysts.

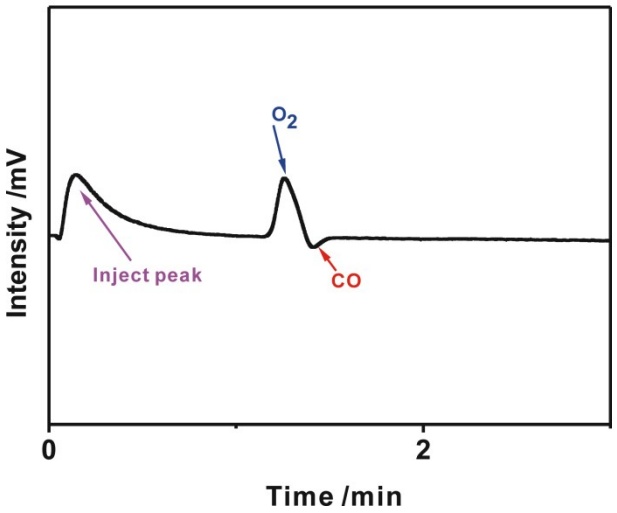

Fig. S3 GC-TCD spectrum of formate acid solution (1 M) catalyzed by kv-PdO/TiNTs (1.0 wt%) catalysts.

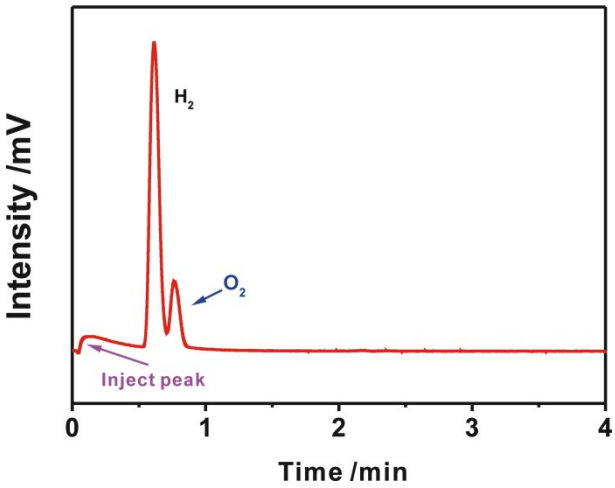

Fig. S4 GC-TCD spectrum of HCOONa solution (1 M) catalyzed by kv-PdO/TiNTs (1.0 wt%) catalysts.

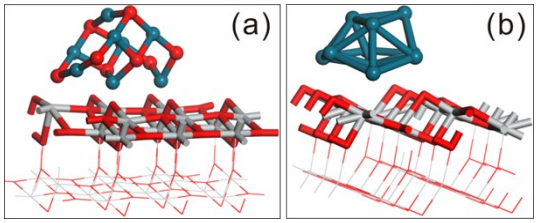

Fig. S5 $(PdO)_8/(TiO_2)_{24}$ and $Pd_{10}/(TiO_2)_{24}$ unit cells

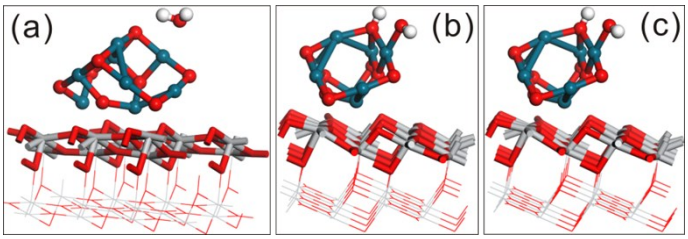

Fig. S6 (a) $(PdO)_8/(TiO_2)_{24}$–H_2O [#1], (b) TS [#2], and (c) $(PdO)_8/(TiO_2)_{24}$–H-HO [#3].

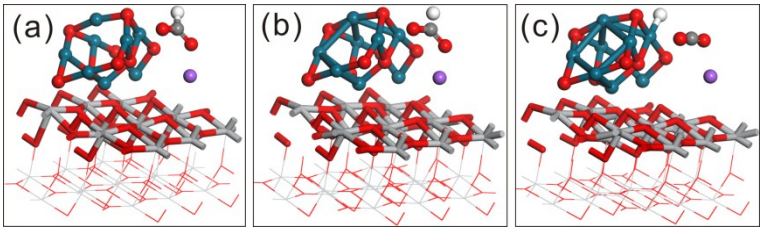

Fig. S7 (a) $(PdO)_8/(TiO_2)_{24}$–HCOONa [#4], (b) TS [#5], and (c) $(PdO)_8/(TiO_2)_{24}$–(Pd)H-COONa [#6].

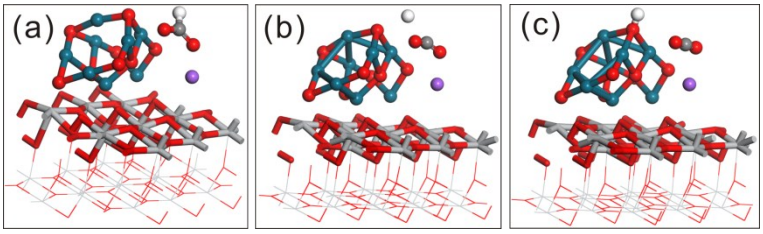

Fig. S8 (a) $(PdO)_8/(TiO_2)_{24}$–HCOONa [#4'], (b) TS [#5'], and (c) $(PdO)_8/(TiO_2)_{24}$–(O)H-COONa [#6'].

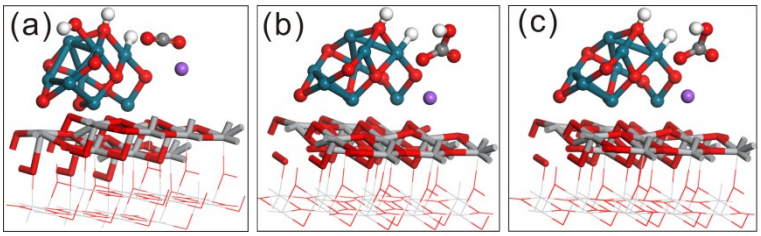

Fig. S9 (a) HO-H-$(PdO)_8$-(Pd)H-COONa-$(TiO_2)_{24}$ [#7], (b) TS [#8], and (c) H-$(PdO)_8/(TiO_2)_{24}$–(Pd)H-$NaHCO_3$ [#9].

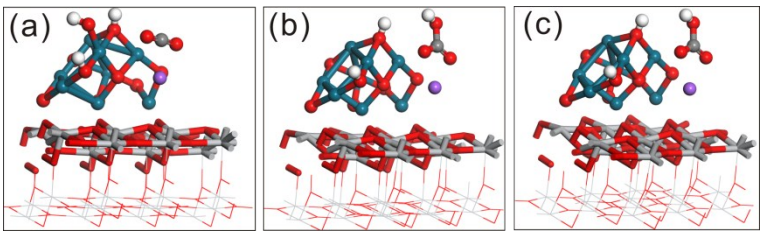

Fig. S10 (a) HO-H-$(PdO)_8$-(O)H-COONa-$(TiO_2)_{24}$ [#7'], (b) TS [#8'], and (c) H-$(PdO)_8/(TiO_2)_{24}$–(O)H-

$NaHCO_3$ [#9′].

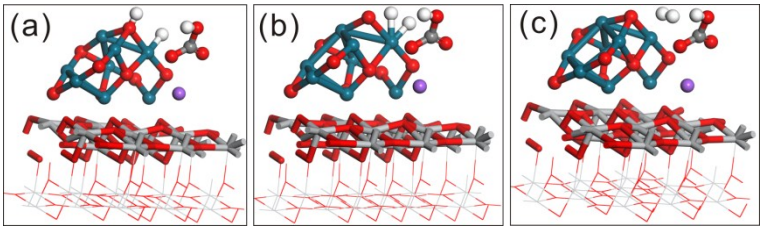

Fig. S11 (a) H-$(PdO)_8$-(Pd)H-$NaHCO_3$-$(TiO_2)_{24}$ [#10], (b) TS [#11], and (c) H_2-$(PdO)_8$-$NaHCO_3$-$(TiO_2)_{24}$ [#12].

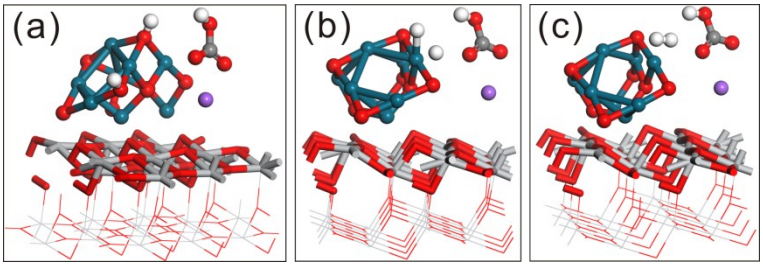

Fig. S12 (a) H-$(PdO)_8$-(O)H-$NaHCO_3$-$(TiO_2)_{24}$ [#10′], (b) TS [#11′], and (c) H_2-$(PdO)_8$-$NaHCO_3$-$(TiO_2)_{24}$ [#12′].

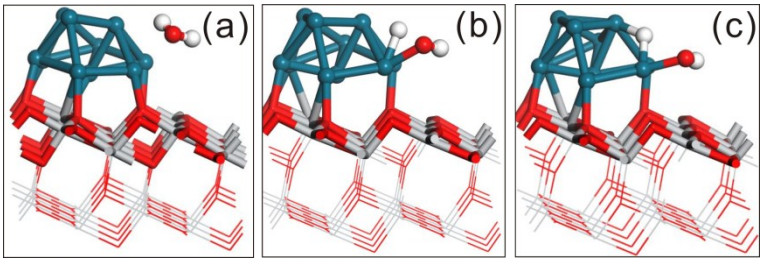

Fig. S13 (a) $Pd_{10}/(TiO_2)_{24}$–H_2O [#1], (b) TS [#2], and (c) $Pd_{10}/(TiO_2)_{24}$–H-HO [#3].

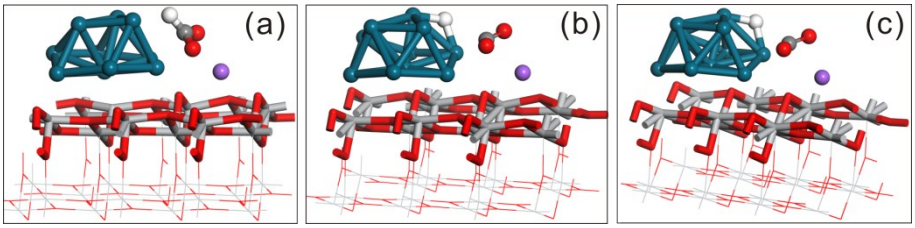

Fig. S14 (a) $Pd_{10}/(TiO_2)_{24}$–HCOONa [#4], (b) TS [#5], and (c) $Pd_{10}/(TiO_2)_{24}$–H-COONa [#6].

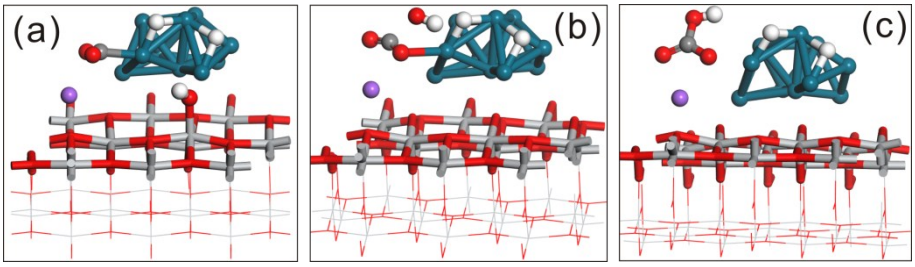

Fig. S15 (a) HO-H-$(Pd)_{10}$-H-COONa-$(TiO_2)_{24}$ [#7], (b) TS [#8], and (c) H-$Pd_{10}/(TiO_2)_{24}$-H-$NaHCO_3$ [#9].

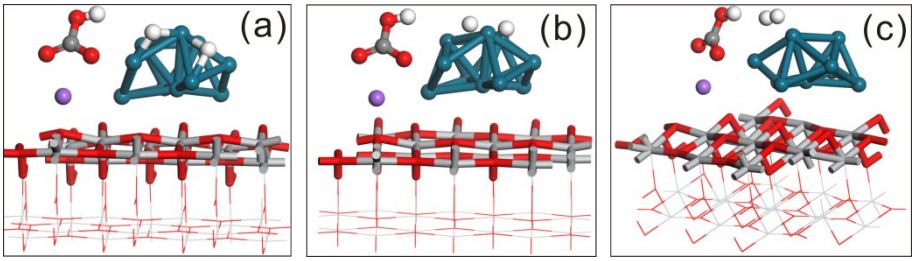

Fig. S16 (a) H-$(Pd)_{10}$-H-$NaHCO_3$-$(TiO_2)_{24}$ [#10], (b) TS [#11], and (c) H_2-$(Pd)_{10}$-$NaHCO_3$-$(TiO_2)_{24}$ [#12].

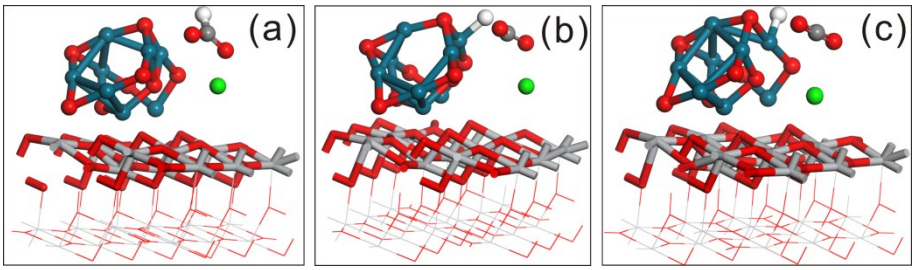

Fig. S17 (a) $(PdO)_8/(TiO_2)_{24}$–HCOOK [#4], (b) TS [#5], and (c) $(PdO)_8/(TiO_2)_{24}$–(Pd)H-COOK [#6].

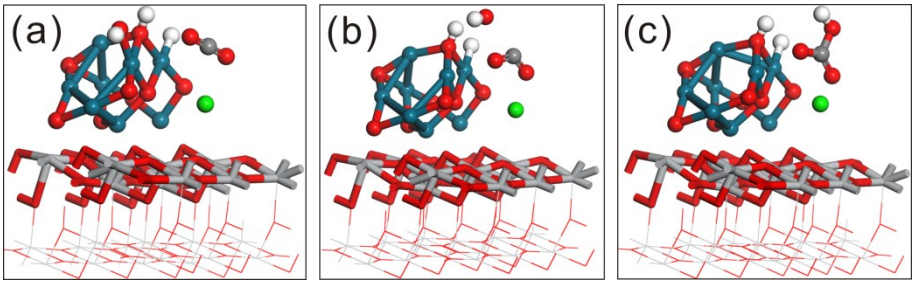

Fig. S18 (a) HO-H-$(PdO)_8$-(Pd)H-COOK-$(TiO_2)_{24}$ [#7], (b) TS [#8], and (c) H-$(PdO)_8/(TiO_2)_{24}$–(Pd)H-$KHCO_3$ [#9].

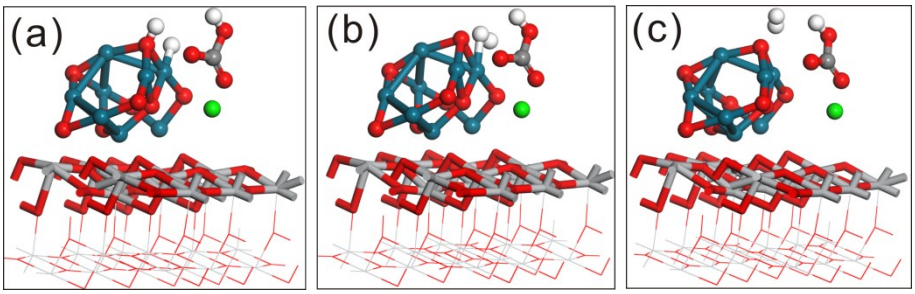

Fig. S19 (a) H-$(PdO)_8$-(Pd)H-$KHCO_3$-$(TiO_2)_{24}$ [#10], (b) TS [#11], and (c) H_2-$(PdO)_8$-$KHCO_3$-$(TiO_2)_{24}$ [#12].

Table S1 Energies of molecules (radicals) and energy change along reactions over $(PdO)_8/(TiO_2)_{24}$ catalyst with Pd as the active site for H abstraction.

	E (eV)	ΔE(eV)	ΔE(kJ/mol)	Relative energy (eV)	Relative energy (kJ/mol)
PdO-TiO_2-H_2O	-69876.228			-1.108	-104.7
TS	-69875.976	0.252	23.81	-0.856	-80.9
PdO-TiO_2-H-OH	-69875.976			-0.856	-80.9
PdO-TiO_2-HCOONa	-71759.241			-4.567	-431.9
TS	-71759.240	0.001	0.09	-4.566	-431.9
PdO-TiO_2-H-COONa	-71759.374			-4.700	-444.19
PdO-TiO_2-H-OH-H-COONa	-72228.725			-5.333	-503.99
TS	-72228.361	0.364	34.39	-5.333	-503.99
PdO-TiO_2-H-H-$NaHCO_3$	-72228.371			-4.979	-470.5
TS	-72226.357	2.014	190.30	-2.965	-280.2
PdO-TiO_2-H_2-$NaHCO_3$	-72227.876			-4.484	-423.7

Table S2 Energies of molecules (radicals) and energy change along reactions over $(PdO)_8/(TiO_2)_{24}$ catalyst with O as the active site for H abstraction.

	E (eV)	ΔE(eV)	ΔE(kJ/mol)	Relative energy (eV)	Relative energy (kJ/mol)
HCOONa	-2348.272				
H_2O	-468.718				
PdO-TiO_2	-69406.402				
PdO-TiO_2-HCOONa	-71759.240			-4.566	-431.5
TS	-71756.804	2.436	230.19	-2.130	-201.3
PdO-TiO_2-H-COONa	-71760.215			-5.541	-523.6
PdO-TiO_2-H-OH-H-COONa	-72230.325			-6.933	-655.1
TS	-72230.134	0.191	18.05	-6.742	-637.0
PdO-TiO_2-H-H-$NaHCO_3$	-72230.134			-6.742	-637.0
TS	-72226.914	3.22	304.26	-3.522	-332.8
PdO-TiO_2-H_2-$NaHCO_3$	-72227.876			-4.48	-423.7

Table S3 Energies of molecules (radicals) and energy change along reactions over $Pd_{10}/(TiO_2)_{24}$.

	E (eV)	ΔE(eV)	ΔE(kJ/mol)	Relative energy (eV)	Relative energy (kJ/mol)
HCOONa	-2348.272				
H_2O	-468.718				
Pd-TiO_2	-67515.902				
Pd-TiO_2-H_2O	-67985.359			-0.739	-69.8
TS	-67984.597	0.762	72.00	0.023	2.2
Pd-TiO_2-H-OH	-67984.951			-0.331	-31.3
Pd-TiO_2-HCOONa	-69868.445			-4.270	-403.5
TS	-69868.405	1.096	103.56	-4.230	-399.7
Pd-TiO_2-H-COONa	-69869.066			-4.892	-462.2
Pd-TiO_2-H-OH-H-COONa	-70339.226			-6.334	-598.5
TS	-70334.72	4.506	425.77	-1.828	-172.7
Pd-TiO_2-H-H-$NaHCO_3$	-70338.354			-5.461	-516.0
TS	-70338.186	2.129	205.14	-5.293	-500.13
Pd-TiO_2-H_2-$NaHCO_3$	-70338.443			-5.550	-524.42

Table S4 Energies of molecules (radicals) and energy change along reactions over $(PdO)_8/(TiO_2)_{24}$ catalyst with HCOOK as the substrate.

	E (eV)	ΔE(eV)	ΔE(kJ/mol)	Relative energy (eV)	Relative energy (kJ/mol)
HCOOK	-1824.197				
H_2O	-468.718				
PdO-TiO_2	-69406.402				
PdO-TiO_2-HCOOK	-71232.186			-1.587	-150.0
TS	-71231.360	0.826	78.05	-0.761	-71.9
PdO-TiO_2-H-COOK	-71232.748			-2.149	-203.0
PdO-TiO_2-H-OH-H-COOK	-71701.948			-2.631	-248.6
TS	-71697.793	4.155	392.60	1.524	144.0
PdO-TiO_2-H-H-$KHCO_3$	-71701.702			-2.385	-225.4
TS	-71700.06	1.642	155.15	-0.743	-70.2
PdO-TiO_2-H_2-$KHCO_3$	-71700.835			-1.518	-143.4

Table S5 Deuterated Isotopic tracer technique studies of the formate sodium solution decomposition over kv-PdO/TiNTs.

Entry	Reactants	H_2/μmol in 1 h	H/D
1	HCOONa +H_2O	431	-
2	DCOONa +D_2O	36	11.9
3	DCOONa +H_2O	67	6.5
4	HCOONa +D_2O	124	3.5

Reaction conditions: formate sodium solution concentration: 0.2 M; reaction temperature: 25 ^oC.

Table S6 kv-PdO/TiNTs catalyzed gas evolution in different catalytic systems.

Entry[a]	H_2/μmol in 1 h	H_2/μmol in 2 h	CO_2
HCOONa	550	960	–
HCOONa/Dyes	Trace	230	Trace
Dyes	–	–	–

[a]Dyes = AR1, MO or AO7; The concentration of HCOONa is 1 M; the concentration of Dyes is 1×10^{-4} M.

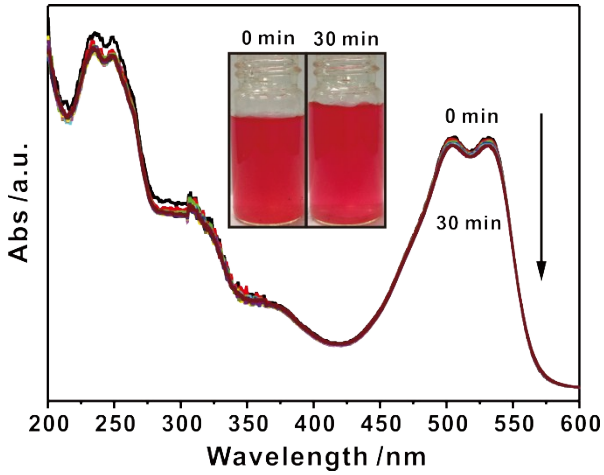

Fig. S20 Concentration changes of AR1 in catalytic system of AR1 solution (10 μM) + kv-PdO/TiNTs; inset shows the visual color change as a function of reaction time.

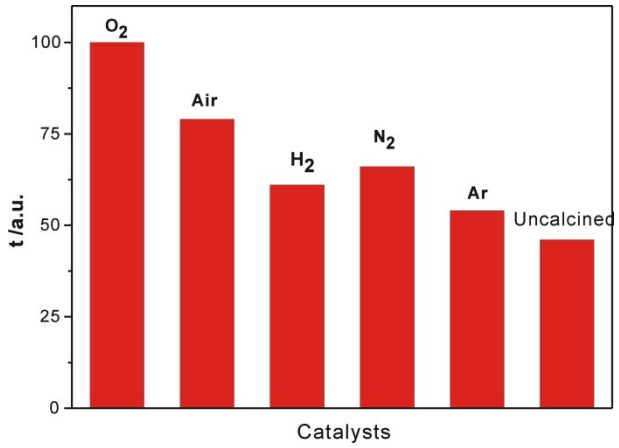

Fig. S21 MO degradation efficiency of Pd-based catalysts calcined under different atmosphere.