Supporting Information

A Novel Hexanuclear Titanium(IV)-oxo-iminodiacetate Cluster with Ti_6O_9 Core: Single-Crystal Structure and Photocatalytic Activities.

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Table S1. Crystallographic data and structural refinements for **{Ti_6O_9}** cluster.

	{Ti_6O_9}
Empirical formula	$C_{24}H_{56}Cl_2K_7N_6O_{46}Ti_6$
Formula weight ($g \cdot mol^{-1}$)	1796.75
Temperature (K)	293(2)
Wavelength (Å)	0.71069
crystal system, S. G.	Hexagonal, *P63/mcm*
a (Å)	13.067(5)
b (Å)	13.067(5)
c (Å)	24.283(5)
α (deg)	90
β (deg)	90
γ (deg)	120
volume ($Å^3$)	3591(2)
Completeness	97.8 % % (to θ = 26.37°)
Z	2
Abs coefficient (mm^{-1})	1.217
$d_{(calcd.)}$ ($Mg \cdot m^{-3}$)	1.662
F(000)	1818
Crystal size (mm^3)	0.20×0.18× 0.10
GOF on F^2	1.087
Reflections collected / unique	16061 / 1338 [$R_{(int)}$ = 0.0270]
Final $R_1[I>2\sigma(I)]$[a]	0.0521
wR_2 indices $[I>2\sigma(I)]$[b]	0.1579

[a] $R_1 = \sum(Fo - Fc)/\sum Fo$; [b] $wR_2 = \{\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\}^{1/2}$

Table S2. Selected bond lengths (Å) and angles (º) for **{Ti_6O_9}** cluster.

Ti(1)-O(4)	1.8127(8)	Ti(1)-O(3a)	1.8293(15)	Ti(1)-O(3)	1.8295(13)
Ti(1)-O(1b)	2.096(3)	Ti(1)-O(1)	2.096(3)	Ti(1)-N(1)	2.252(3)
Ti(1)-Ti(1a)	3.3709(18)	Ti(1)-Ti(1c)	3.3709(18)		
O(4)-Ti(1)-O(3a)	103.31(15)	O(4)-Ti(1)-O(3)	103.31(15)	O(3a)-Ti(1)-O(3)	97.2(2)
O(4)-Ti(1)-O(1b)	89.00(14)	O(3a)-Ti(1)-O(1b)	88.19(13	O(3)-Ti(1)-O(1b)	164.93(12)
O(4)-Ti(1)-O(1)	89.00(14)	O(3a)-Ti(1)-O(1)	164.93(12)	O(3)-Ti(1)-O(1)	88.19(13
O(1b)-Ti(1)-O(1)	83.32(16)	O(4)-Ti(1)-N(1)	159.2(2)	O(3a)-Ti(1)-N(1)	90.29(13)
O(3)-Ti(1)-N(1)	90.29(13)	O(1b)-Ti(1)-N(1)	75.57(11)	O(1)-Ti(1)-N(1)	75.57(11)
O(4)-Ti(1)-Ti(1c)	92.53(15)	O(3a)-Ti(1)-Ti(1)	80.14(10)	O(3)-Ti(1)-Ti(1)	22.87(10)
O(1b)-Ti(1)-Ti(1c)	168.27(8)	O(1)-Ti(1)-Ti(1c)	108.33(8)	N(1)-Ti(1)-Ti(1c)	105.44(10)
O(4)-Ti(1)-Ti(1a)	92.53(15)	O(3a)-Ti(1)-Ti(1)	22.87(10	O(3)-Ti(1)-Ti(1a)	80.14(10)
O(1b)-Ti(1)-Ti(1a)	108.33(8)	O(1)-Ti(1)-Ti(1a)	168.27(8)	N(1)-Ti(1)-Ti(1a)	105.44(10)
Ti(1c)-Ti(1)-Ti(1a)	60.0				

Symmetry transformation for **{Ti_6O_9}** cluster: *a, -y,x-y,z; b, x-y,-y,z; c, -x+y,-x,z*

Table S3. Comparisons of the average Ti−O and Ti−Ti bond distances (Å) in the purely titanium(IV)-oxo-carboxylate complexes.

	^{av}Ti−O_{bridg}	^{av}Ti−$O_{carboxy}$	^{av}Ti−N	^{av}Ti−Ti
$(NH_4)_4[Ti_2(O_2)_2(C_6H_4O_7)_2]\cdot 2H_2O$ [11a]	1.871(2)	2.038(2)	/	3.336(1)
$[Ti_4O_4(C_2O_4)_8]\cdot 4C_2N_2H_{10}\cdot 4H_2O$ [11d]	1.812(2)	2.071(2)	/	
$Cs_4[Ti_4O_4(nta)_4]\cdot 6H_2O$ [11b]	1.831(2)	1.981(2)	2.292(2)	
$Cs_2H_2[(Ti_8O_8)(\mu\text{−dptaO})_4]\cdot 12H_2O$ [11c]	1.817(8)	2.029(9)	2.28(1)	/
$[Ti_8O_{10}(OOCR)_{12}]$ [R = $CH(CH_3)_2$, CCl_3] [11f]	1.83	2.06	/	/
$[Ti_8O_8(OOCR)_{16}]$ [R= C_6H_5, $C(CH_3)_3$, CH_3] [11e]	1.8264(2)	2.0539(3)	/	/
$[Ti_8O_{10}(citrate)_4(H_2O)_{12}]$ $14H_2O.3(HoPr^i)$ [11g]	1.894(3)	2.055(3)	/	3.63
$[Ti_8O_8(OH)_4(O_2CC_6H_4CO_2)_6]$	1.915(5)	1.98(1)	/	
$K_7H[Ti_6O_9(ida)_6]Cl_2\cdot 20H_2O$ **{Ti_6O_9}** (This work)	1.8208(10)	2.096(2)	2.252(3))	3.3703(17)

Table S4. Bond valence sums (BVS) for **{Ti_6O_9}** cluster**.**

{Ti_6O_9} cluster							
Ti1	4.0163	O1	2.2178	O2	1.7376	O3	1.9131
O4	1.8997						

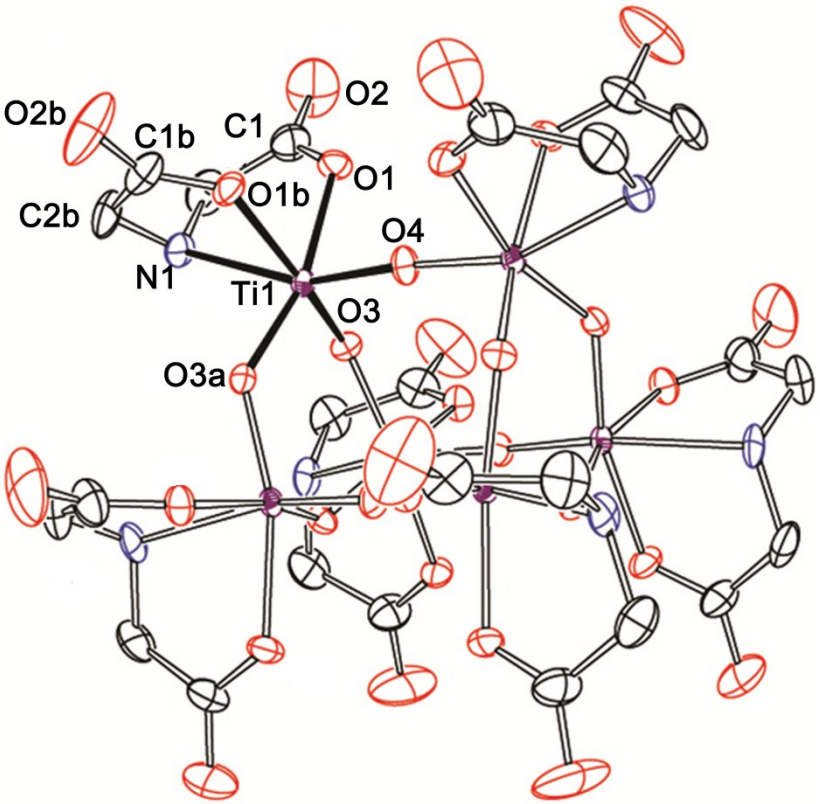

Figure S1. ORETP plot of $[Ti_6O_9(ida)_6]^{6-}$ polyanion with 30% thermal ellipsoids probability. hydrogen atoms have been omitted for clarity. (color code: Ti: pink; O: red; N: blue; C: black; symmetry codes: *a*, *-y, x-y, z*; *b*, *x-y, -y, z*; *c*, *-x+y, -x, z*).

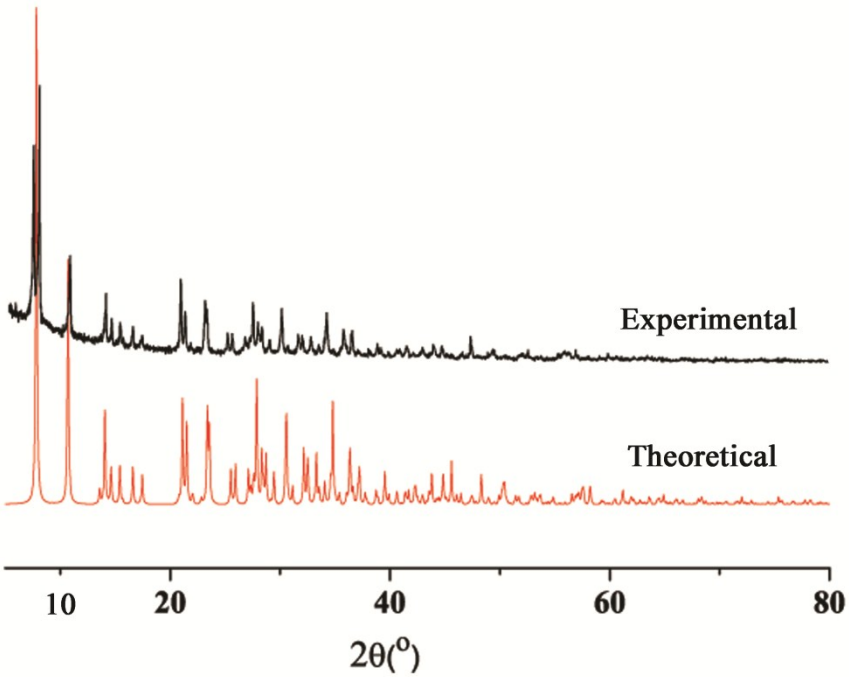

Figure S2. X-ray powder diffraction pattern of bulk **{Ti_6O_9}** cluster vs. the calculated pattern. Peak positions are in good agreement, indicating the phase purity of the compound. Differences in intensity are due to preferred orientation of the powder sample.

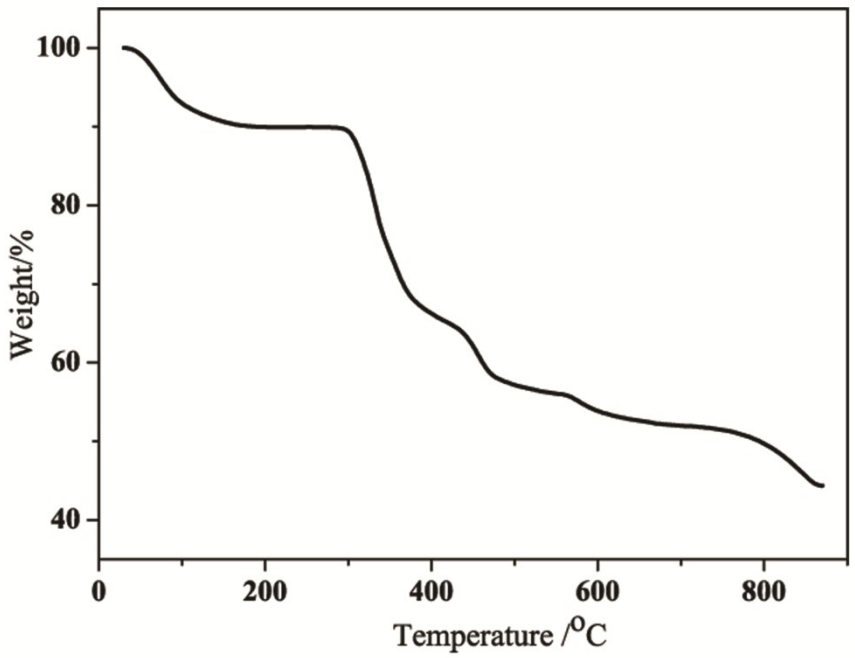

Figure S3. Thermogravimetric curves of **{Ti_6O_9}** compound.

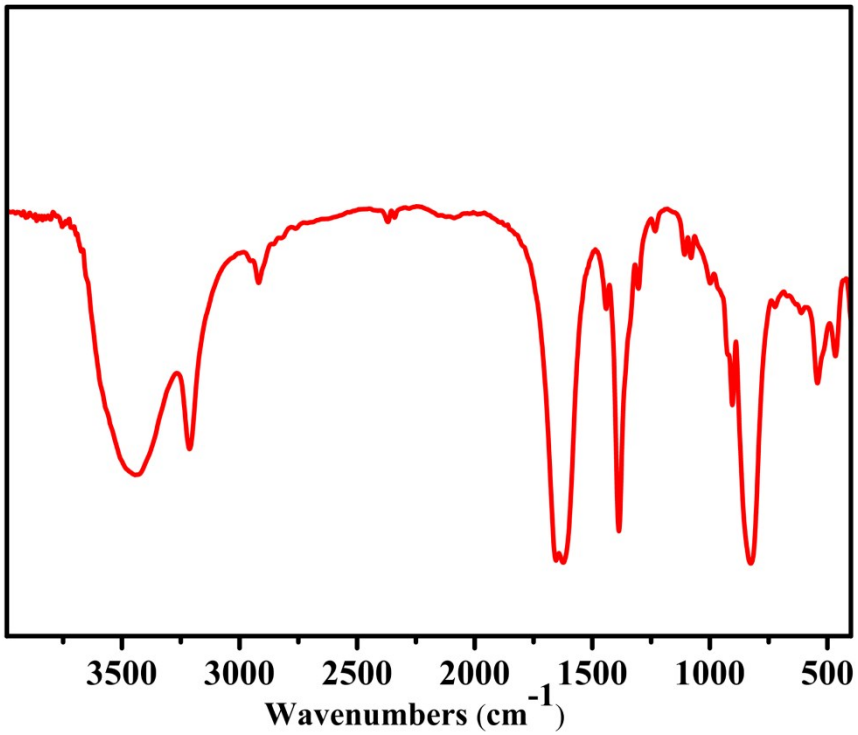

Figure S4. FT-IR spectra of **{Ti_6O_9}** cluster in solid state.

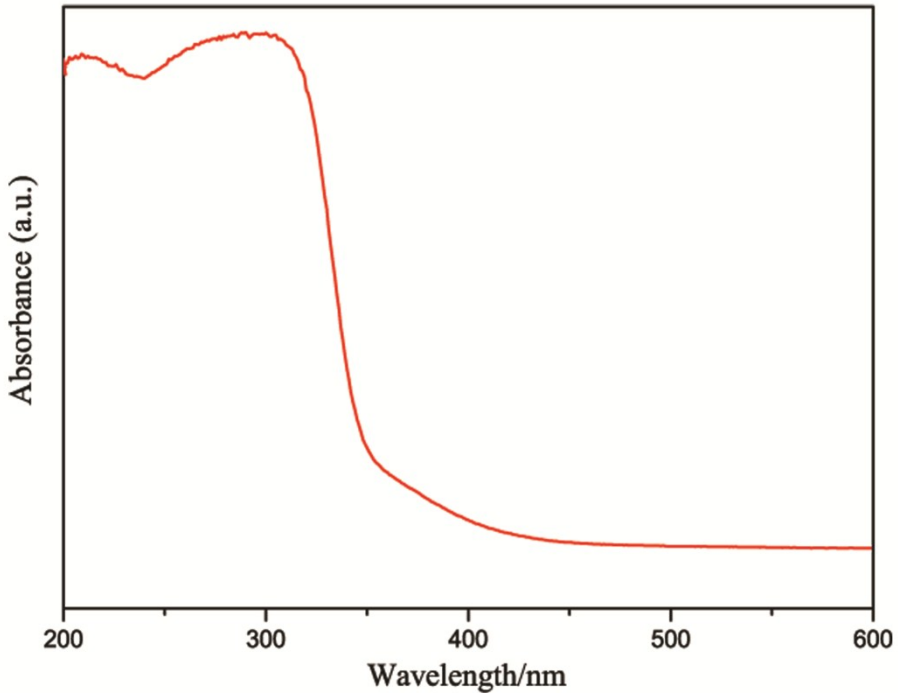

Figure S5. Solid state UV/vis spectra of **{Ti_6O_9}** cluster. (Band gap: E_g (eV) = hc / λ ≈ 1240 / λ_{onset}, h Planck's constant; c the speed of light in vacuum.

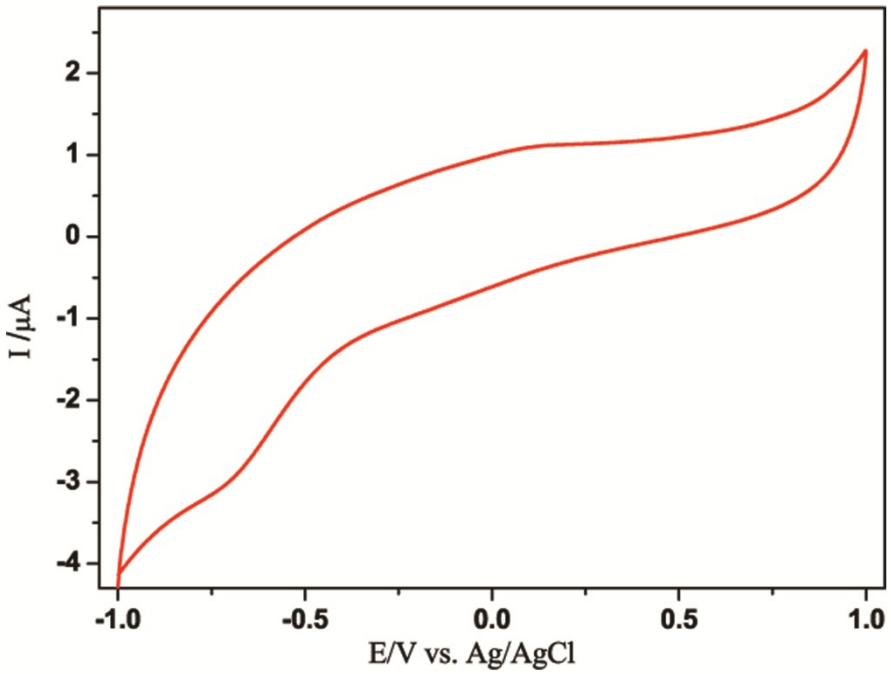

Figure S6. Cyclic voltammograms of 2 mM **{Ti_6O_9}** compound in aqueous solution (scan rate 25 mV/s, GCE working electrode, Ag/AgCl reference electrode).

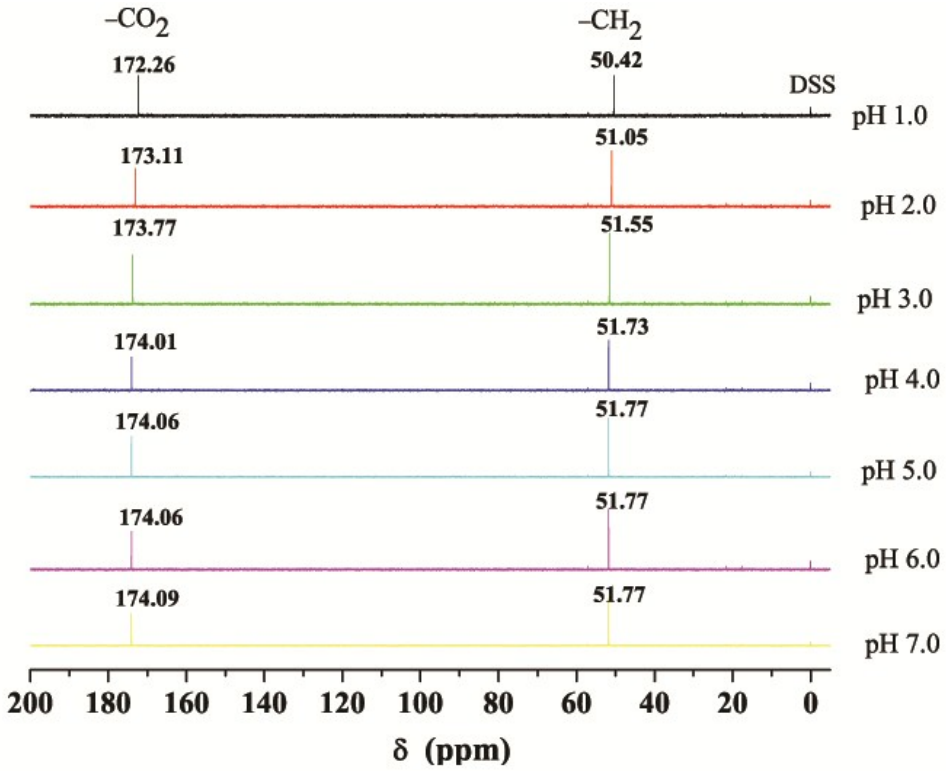

Figure S7. ^{13}C NMR spectra of the solutions of K_2(ida) at various pH values.

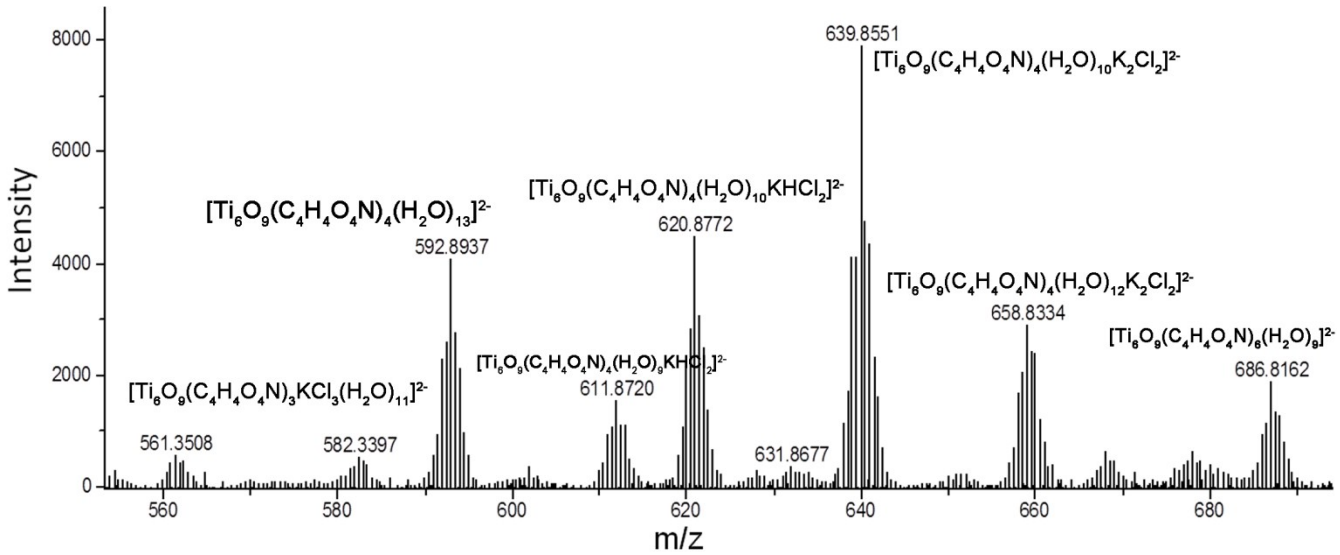

Figure S8. Negative ion electrospray ionization mass spectra (ESI-MS) of **{Ti_6O_9}** cluster in H_2O/MeCN (80:20) solution.

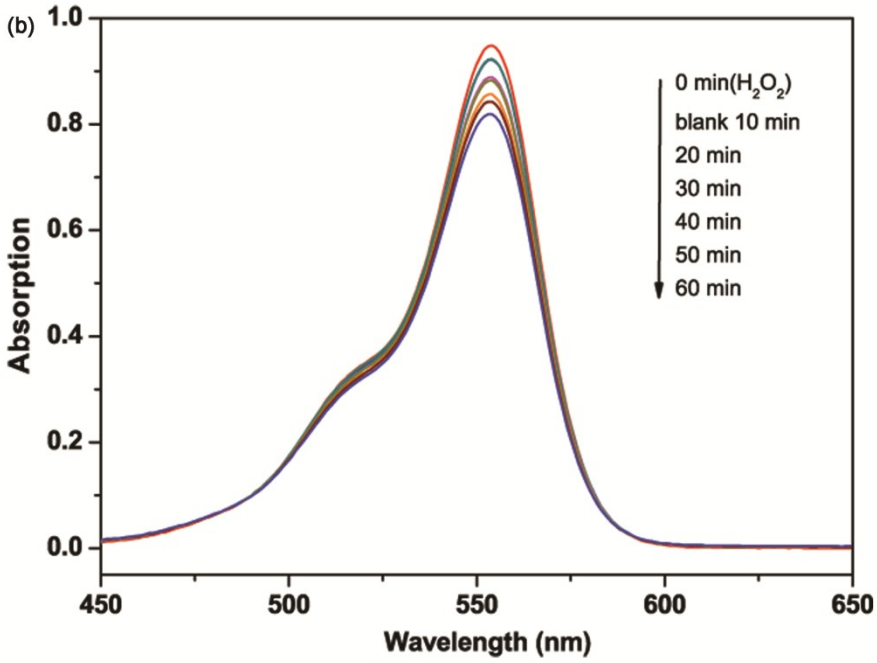

Figure S9. Absorption spectra of RhB during the degradation under visible light only with H_2O_2 (2mL, 20mmol).