Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supplementary Material

for

Correction and new understanding of reactivity for illuminated tungsten trioxide under dark: Antecedents and consequences of photo-storage electrons triggering Fenton reactions

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1. Experimental Procedures

1.1. Quantitative experiments on stored electrons in LP-t min samples.

$KMnO_4$ as a selective probe reagent for the stored electrons (W(V)) trapping through Eq. (1) or (2):

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + \quad 4H_2O \qquad (1)$$

$$MnO_4^- + 5W(V) + 8H^+ \rightarrow Mn^{2+} + 5W(VI) + 4H_2O \qquad (2)$$

Firstly, $KMnO_4$ solution with different concentrations (5, 50, 100, 120, 150, 200 ppm) were prepared at pH of 1 (The solvent was the 0.05 M/L H_2SO_4 solution). Then, the reduction experiments of $KMnO_4$ were carried out following certain steps: 20 mg of LP-t min was added into 30 ml $KMnO_4$ solution with certain concentration under stirring conditions in dark. After 2 h, 3 mL of suspension were withdrawn, centrifuged and the supernatant was analyzed for evolution in concentration of $KMnO_4$ spectrophotometrically at λ_{max} of 525 nm. Finally, based on the consumption amount of $KMnO_4$, the content (mmol/g) of W(V) in LP-t min sample is calculated to obtain the concentration (mmol/g) of stored electrons in the catalyst.

1.2. The oxidation experiments of I^- for different catalysts.

I_3^- as a selective probe reagent for existence of reactive oxygen species (H_2O_2, •OH, $•O_2^-$, O_2) through Eq. (3) and (4)

$$I^- + \text{reactive oxygen species } (H_2O_2, •OH, •O_2^-, O_2) + H^+ \rightarrow I_2 + H_2O \qquad (3)$$

$$I_2 + I^- \rightarrow I_3^- \qquad (4)$$

150 μL of 10 wt. % H_2O_2 was poured into 30 ml deionized water under magnetic stirring. After 10 min, 30 mg catalyst was added into above solution. After 1 h of continuous stirring, 5 mL of suspension were withdrawn, centrifuged and the supernatant was obtained. Subsequently, 10 μL of $(NH_4)_2MoO_4$ solution with concentration of 10 μM/L and 0.5 ml of KI solution with concentration of 100 mM/L were added into the supernatant. The solution was stirred for 5 minutes and then analyzed for evolution in concentration of I_3^- spectrophotometrically at λ (λ_1 = 287 nm, λ_2 = 350 nm).

1.3. Theoretical calculation details.

In this work, the adsorption process of H_2O_2 on the (001) surface of h-WO_3 hydrate were studied in the CASTEP module. The Perdew-Burke-Ernzerhof (PBE) functional based on the generalized-gradient approximation (GGA) was used to described the exchange and correlation interactions between atoms. The cutoff energy of the plane wave was 300 eV and the tolerance for accepting convergence of the total energy per atom was 10^{-5} eV $atom^{-1}$. Moreover, the Brillouin zone was sampled using a suitable Γ point. The adsorption binding energy E_{ads} was calculated according to Eq. (5).

$$E_{ads} = E_{total} - E_{adsorbate} - E_{adsorbent} \quad (5)$$

where E_{total}, $E_{adsorbate}$ and $E_{adsorbent}$ correspond to the total energies of the system, antibiotics, and adsorbents, respectively.

Molecular dynamics (MD) simulations were used to study the adsorption behavior of H_2O_2 molecule on the (001) surface of h-WO_3 hydrate. The computational model was composed by the h-WO_3 hydrate (3 ×3) super cell, H_2O_2 solution slab and vacuum slab

(30 Å). Before calculation, the constructed system was geometrically optimized. The condensed phases were simulated using the force field UNIVERSAL. The Ewald summation technique was used to set bonded and unbonded terms as atom-based summations. The Nasal thermostat was used to perform constant temperature molecular dynamics simulations at 298 ± 10 K with a time step of 1.0 fs and a simulation time of 1000 ps.

Quantum chemical calculations were performed using Gaussian 09 program with DFT algorithm to optimize the structure of DNBP at the B3LYP/6-31G (d, p) level. The wave function analysis was carried out using the Multiwfn program to obtain the frontier molecular orbitals (the highest occupied molecular orbits (HOMO), the lowest unoccupied molecular orbits (LUMO), surface electrostatic potential (ESP)) and Fukui indices of DNBP molecule.

2. Results and Discussion

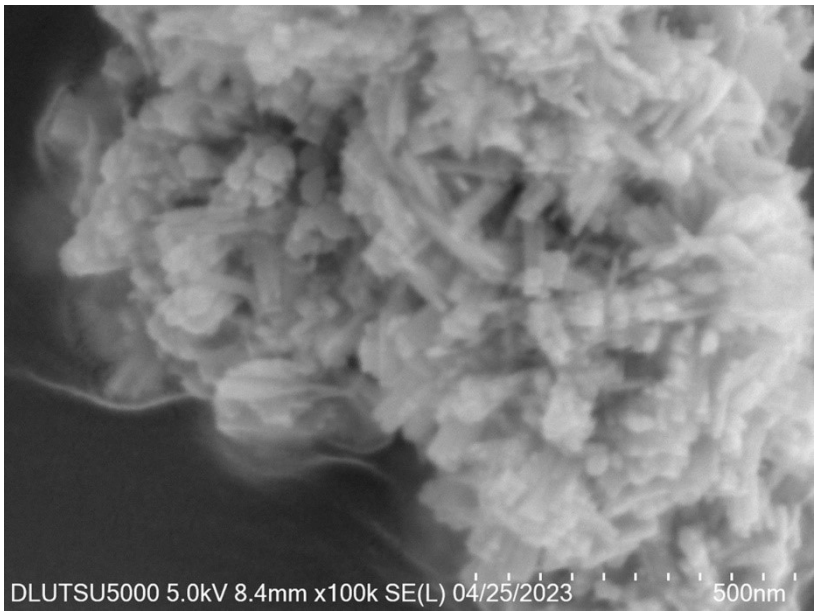


Figure S1. SEM image of h-WO_3•0.46H_2O.

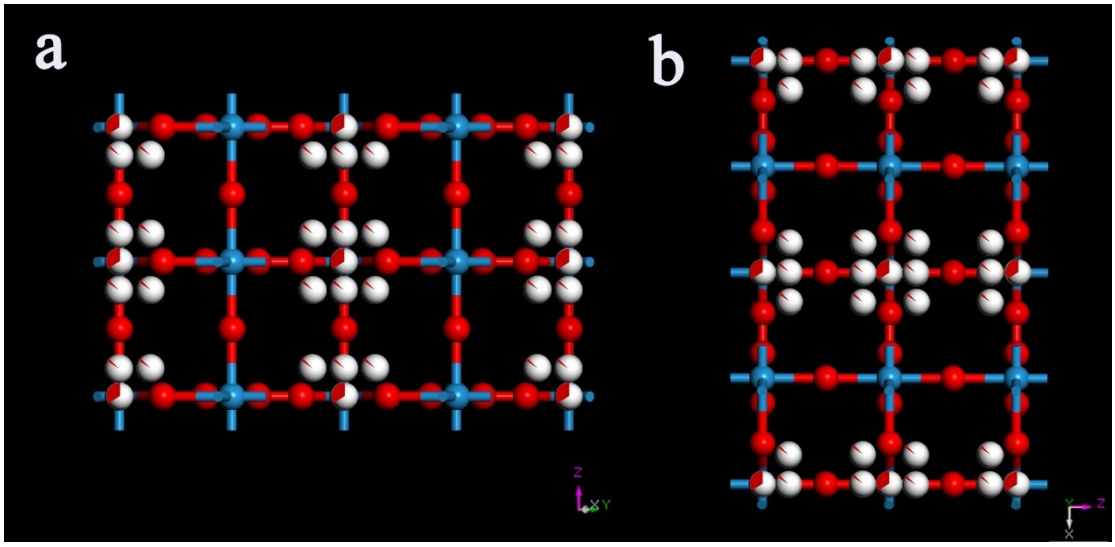


Figure S2. The refined crystal structure unit of h-WO_3•0.46H_2O viewed toward (a) *yz* plane and (b) *xz* plane.

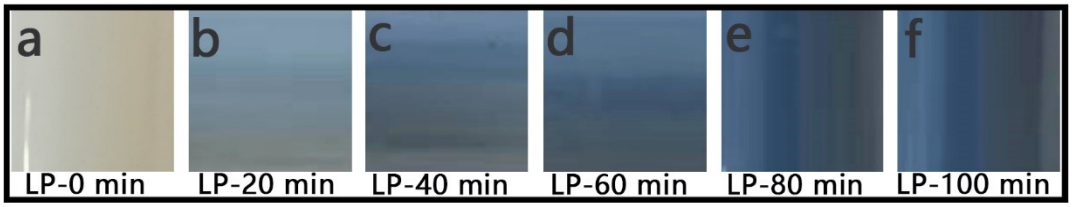
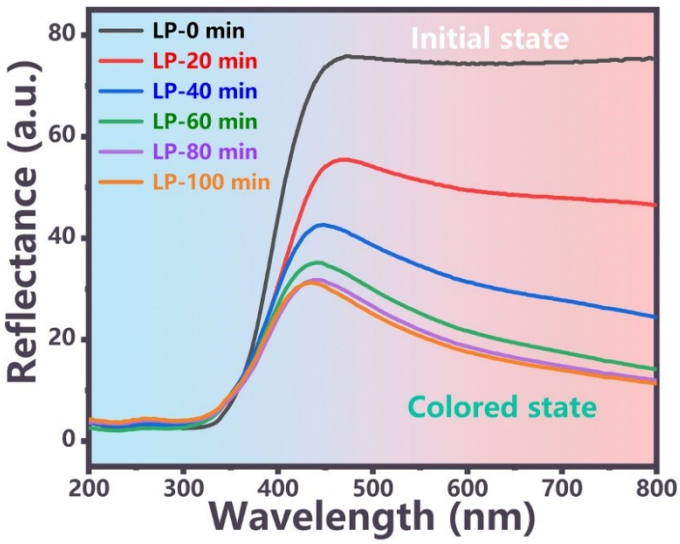


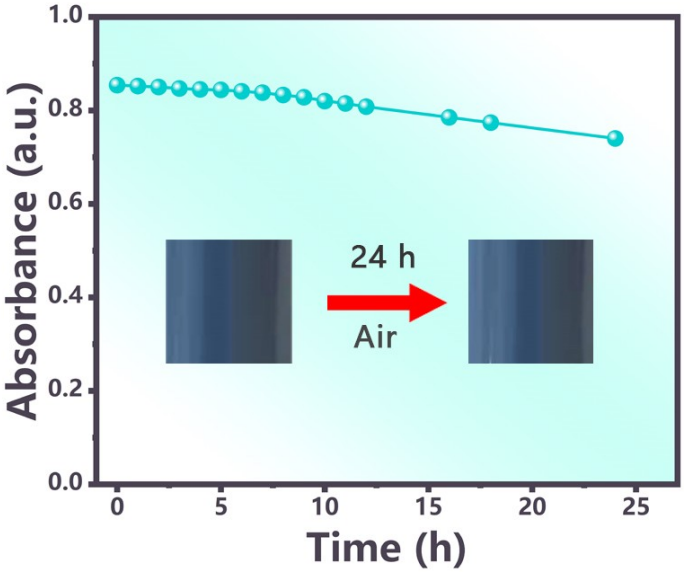
Figure S3. Optical photographs of different illuminated h-WO_3•0.46H_2O samples.



117

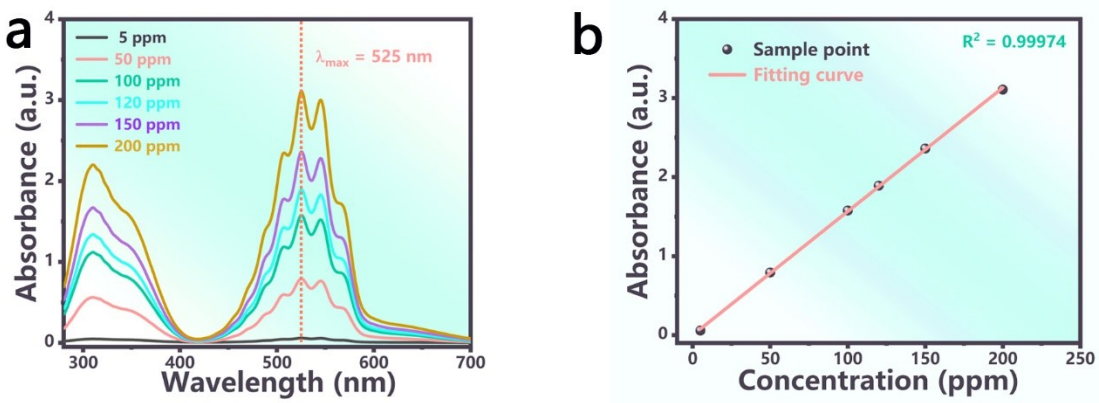
118 **Figure S4**. Reflectance spectra of different illuminated h-WO_3•0.46H_2O samples.

119



120

121 **Figure S5**. Reflectance spectra of different illuminated h-WO_3•0.46H_2O samples.



122

Figure S6. (a) UV–vis absorbance spectra of $KMnO_4$ solution with different concentration and (b) standard curve based on the absorbance at λ_{max} = 525 nm.

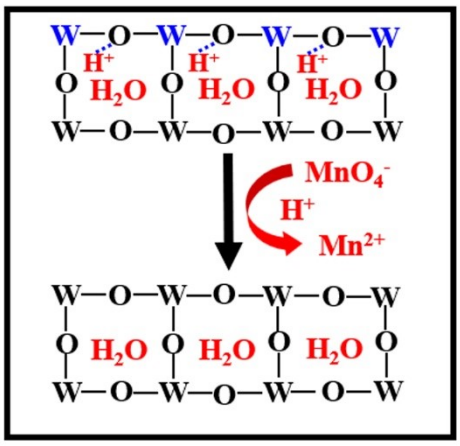


Figure S7. Schematic representation of the reduction process of MnO_4^- among illuminated .h-WO_3•0.46H_2O.

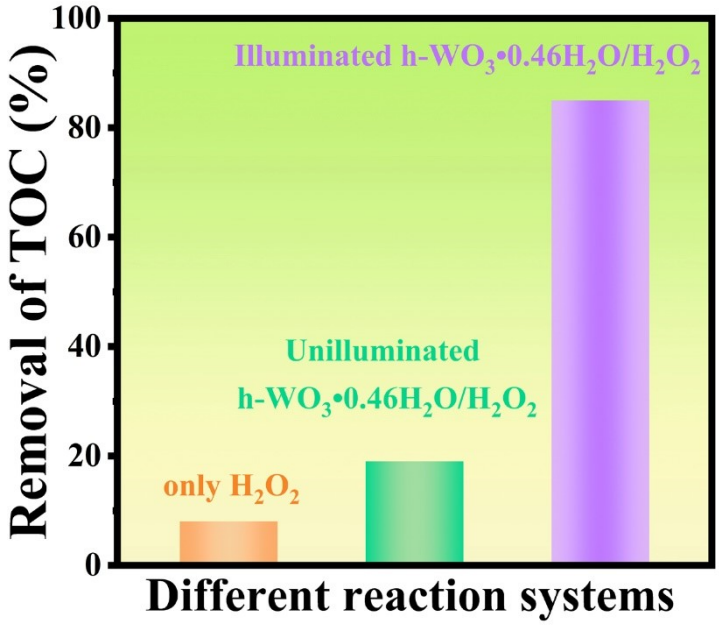
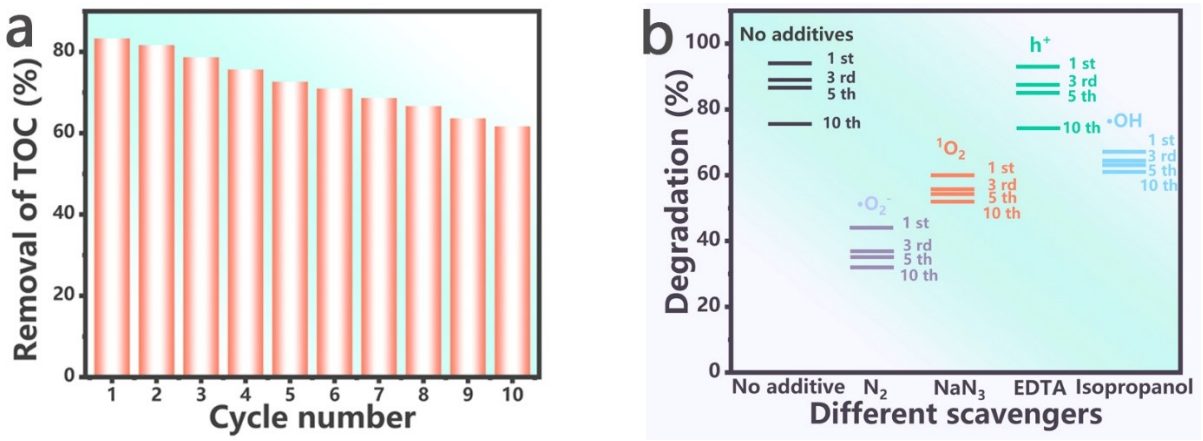


Figure S8. TOC removal for DNBP degradation by different reaction systems.

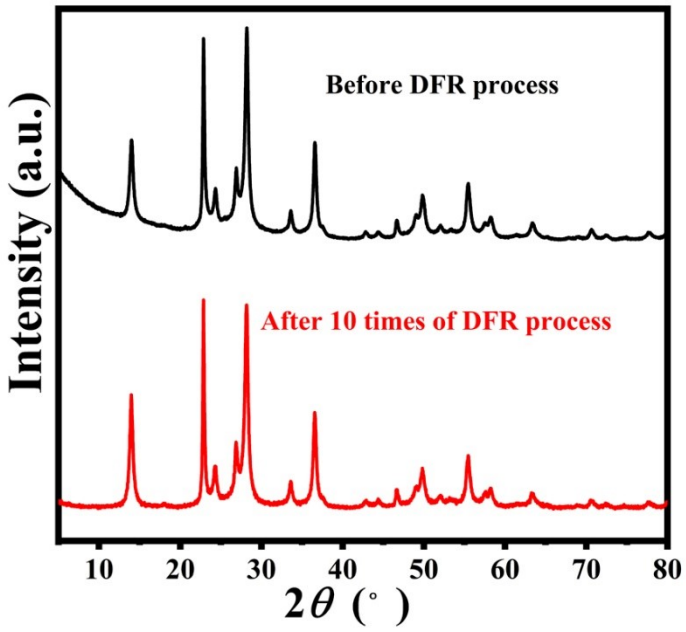


131

132 **Figure S9**. (a) The TOC removal and (b) trapping experiments of reactive species

133 through DNBP degradation process for LP-80 min through different cycle times.

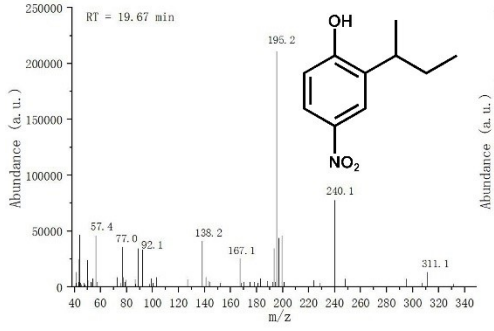
134

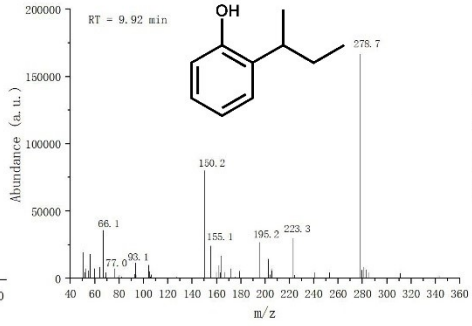


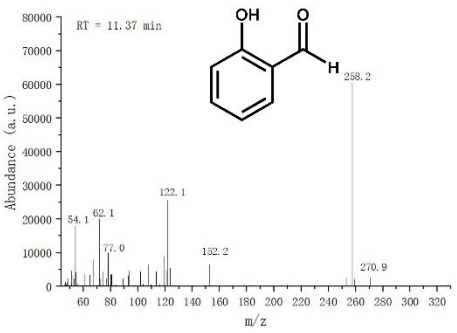
135

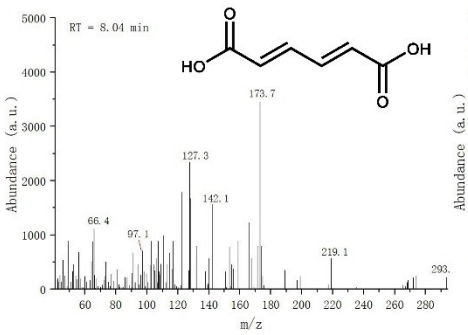
136 **Figure S10**. The XRD pattern of illuminated h-WO_3•0.46H_2O before and after 10 times

137 of DFR process.


RT = 19.67 min
Abundance (a.u.)
m/z
OH
NO2
195.2
240.1
57.4
77.0
92.1
138.2
167.1
311.1


RT = 9.92 min
Abundance (a.u.)
m/z
OH
278.7
150.2
66.1
77.0
93.1
155.1
195.2
223.3


RT = 11.37 min
Abundance (a.u.)
m/z
OH
O
H
258.2
122.1
54.1
62.1
77.0
132.2
270.9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m/z
HO
OH
O
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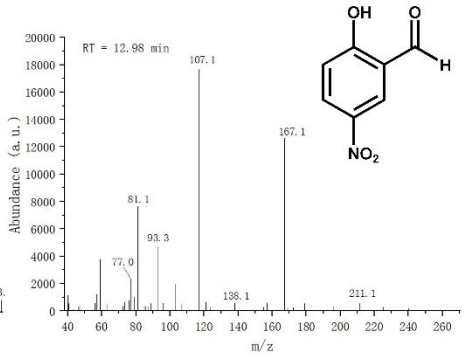
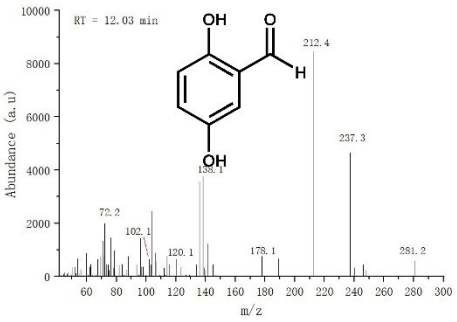
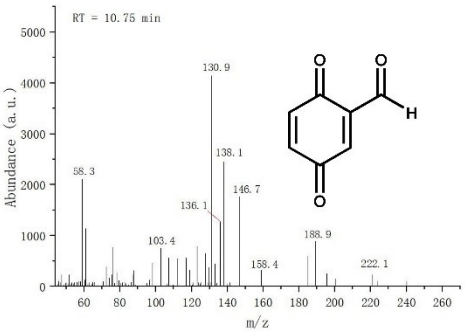
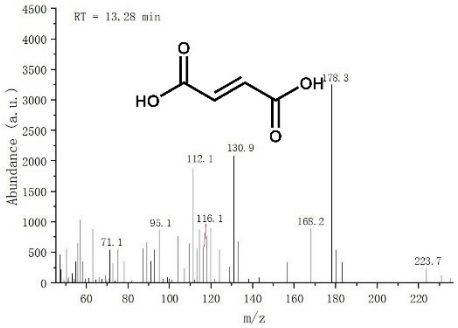
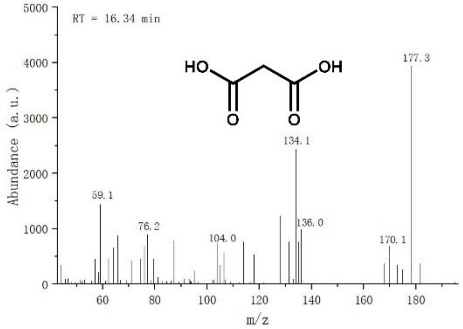
127.3
142.1
66.4
97.1
219.1
293.

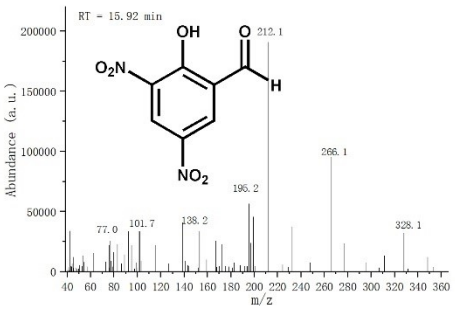

RT = 12.98 min
Abundance (a.u.)
m/z
OH
O
H
NO2
107.1
167.1
81.1
93.3
77.0
138.1
211.1

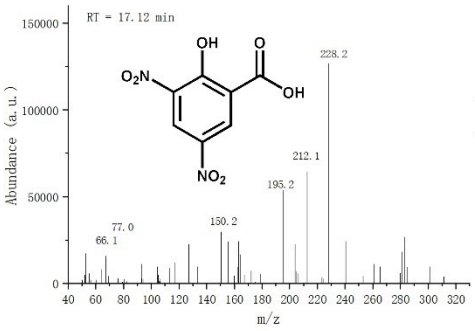

RT = 12.03 min
Abundance (a.u.)
m/z
OH
O
H
OH
212.4
237.3
138.1
72.2
102.1
120.1
178.1
281.2


RT = 10.75 min
Abundance (a.u.)
m/z
O
O
H
130.9
138.1
58.3
146.7
136.1
103.4
188.9
158.4
222.1


RT = 13.28 min
Abundance (a.u.)
m/z
HO
OH
O
178.3
112.1
130.9
95.1
116.1
168.2
71.1
223.7


RT = 16.34 min
Abundance (a.u.)
m/z
HO
OH
O
177.3
134.1
59.1
76.2
104.0
136.0
170.1


RT = 15.92 min
Abundance (a.u.)
m/z
OH
O
212.1
O2N
NO2
H
266.1
196.2
77.0
101.7
138.2
328.1


RT = 17.12 min
Abundance (a.u.)
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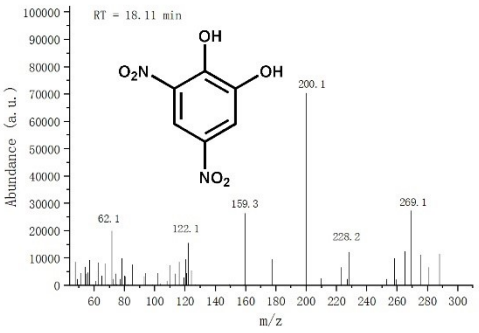
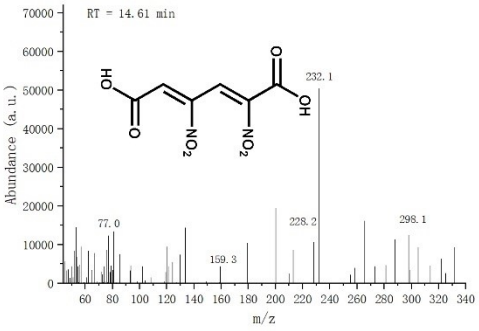
O
228.2
O2N
NO2
OH
212.1
195.2
77.0
66.1
150.2


RT = 18.11 min
Abundance (a.u.)
m/z
OH
O2N
OH
NO2
200.1
159.3
269.1
62.1
122.1
228.2


RT = 14.61 min
Abundance (a.u.)
m/z
OH
O
HO
NO2
NO2
232.1
77.0
228.2
298.1
159.3

138

Figure S11. Mass spectra (MS) of intermediates during the process of DNBP degradation among illuminated h-WO_3•0.46H_2O/H_2O_2 system.

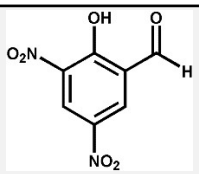
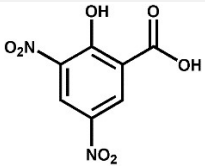
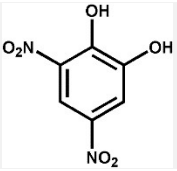
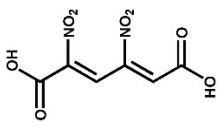
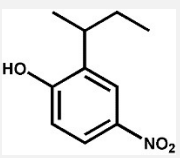
Table S1. Different round-the-clock photocatalysts based on stored electrons in WO_3 for organic contaminants degradation under dark condition.

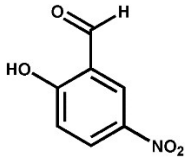
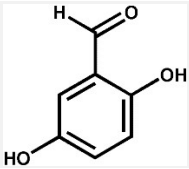
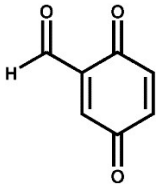
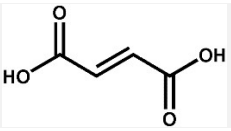
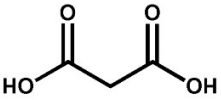
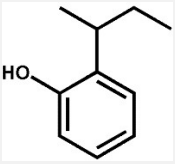
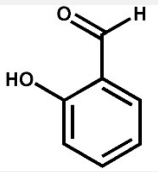
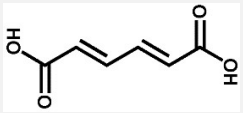
Photocatalysts	Pollutants	Light source	Illumination reaction time (charging)	Dark reaction time (discharging)	Active species in the dark reaction	References
Spray dried TiO_2/WO_3 heterostructure	Methylene blue	UV	40 min	30 min	•OH	[1]
WO_3/TiO_2 hollow microsphere composites	Methyl orange	Vis	40 min	40 min	•OH	[2]
Pt: TiO_2/WO_3 photocatalyst	Methanol	Vis	2 h	6 h	•OH	[3]
Dual-phase TiO_2/WO_3	Methanol	stimulated solar light	2 h	6 h	$•O_2^-$	[4]
$WO_3/g\text{-}C_3N_4$ composite	Rhodamine B	Vis	1 h	8 h	•OH	[5]
Pt-TiO_2/WO_3 hybrid material	Methylene blue	UV/Vis	30 min	60 min	•OH	[6]
n-MoS_2/p-WO_3 based diode catalyst	Methylene blue	-	-	-	•OH	[7]
Mg-ZnO/WO_3 QDs/GO	Rhodamine B	UV/Vis	6 h	2 h	$•O_2^-$	[8]

Table S2. Results of the refinement data of h-$WO_3 \cdot 0.46H_2O$ in the Space Group P6/mmm.

	Atom	x	y	z	Occupancy	B	Site	Symmetry
1	W1	0.50000	0.00000	0.00000	1.000	1.381	3f	mmm
2	O1	0.38380	0.19190	0.00000	1.000	1.164	6l	mm2
3	O2	0.50000	0.00000	0.50000	1.000	1.858	3g	mmm
4	O3	0.00000	0.00000	0.00000	0.402	2.500	1a	6/mmm
5	O4	0.13990	0.13990	0.20979	0.027	4.000	12n	…m

Table S3. Intermediates of DNBP in illuminated h-WO_3•$0.46H_2O/H_2O_2$ system.

The series number of intermediates	Formula	m/z	Structure	Retention time (min)
1	$C_7H_4N_2O_6$	212		15.92
2	$C_7H_4N_2O_7$	228		17.12
3	$C_6H_4N_2O_6$	200		18.11
4	$C_6H_4N_2O_8$	232		14.61
5	$C_{10}H_{13}NO_3$	195		19.67

6	**$C_7H_5NO_4$**	**167**		**12.98**
7	**$C_7H_6O_3$**	**138**		**12.03**
8	**$C_7H_4O_3$**	**136**		**10.75**
9	**$C_4H_4O_4$**	**116**		**13.28**
10	**$C_3H_4O_4$**	**104**		**16.34**
11	**$C_{10}H_{14}O$**	**150**		**9.92**
12	**$C_7H_6O_2$**	**122**		**11.37**
13	**$C_6H_6O_4$**	**142**		**8.04**

3. Reference

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