

*Supporting Information*

**Enhanced HClO production from chloride by dual cocatalyst  
loaded WO<sub>3</sub> under visible light**

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**Table S1.** Results of some blank tests for the photocatalytic production of HClO under difference conditions.

Entry	Conditions	$C_{\text{HClO}}/\mu\text{M}$
1	standard conditions <sup>a</sup>	37.3
2	without irradiation	0.0
3	without photocatalyst	0.1
4	without NaCl	0.0
5	without O <sub>2</sub> <sup>b</sup>	1.9

<sup>a</sup> Photocatalyst: Pt-Mn/WO<sub>3</sub>, 100 mg; reaction solution: 0.5 M NaCl, 100 mL; O<sub>2</sub> flow rate: 1 mL min<sup>-1</sup>; light source: 300 W Xe lamp with 420 nm cut-off filter; temperature: 303 K; photoirradiation time: 1 h. <sup>b</sup> N<sub>2</sub> was bubbled in the reaction solution instead of O<sub>2</sub>.

**Table S2.** Comparison between the calculated Mn/WO<sub>3</sub> weight ratios and those measured by spectroscopy method.

Calculated Mn amount (wt%) <sup>a</sup>	Tested Mn amount (wt%) <sup>b</sup>
0.0	0.00
0.1	0.04
0.5	0.08
1.0	0.11
2.0	0.15
5.0.	0.19

<sup>a</sup> The amount of Mn calculated using the amount of added Mn(NO<sub>3</sub>)<sub>2</sub> precursor.  
<sup>b</sup> The actually detected Mn amount on the surface of Pt-Mn/WO<sub>3</sub>.

**Table S3.** The actual loading amount of Pt and Mn species, dispersion ratio of Pt on WO<sub>3</sub> surface, and formation rate of HClO on different Pt-Mn/WO<sub>3</sub>.

Sample	Pt amount (wt%)	Mn amount (wt%)	Pt/W <sup>c</sup>	C <sub>HClO</sub> /μM
Pt-Mn/WO <sub>3</sub> _one-step	0.99	0.11	0.013	36.3
Pt-Mn/WO <sub>3</sub> _two-step <sup>a</sup>	1.04	0.12	0.016	16.4
Mn-Pt/WO <sub>3</sub> _two-step <sup>b</sup>	0.94	0.13	0.018	13.1

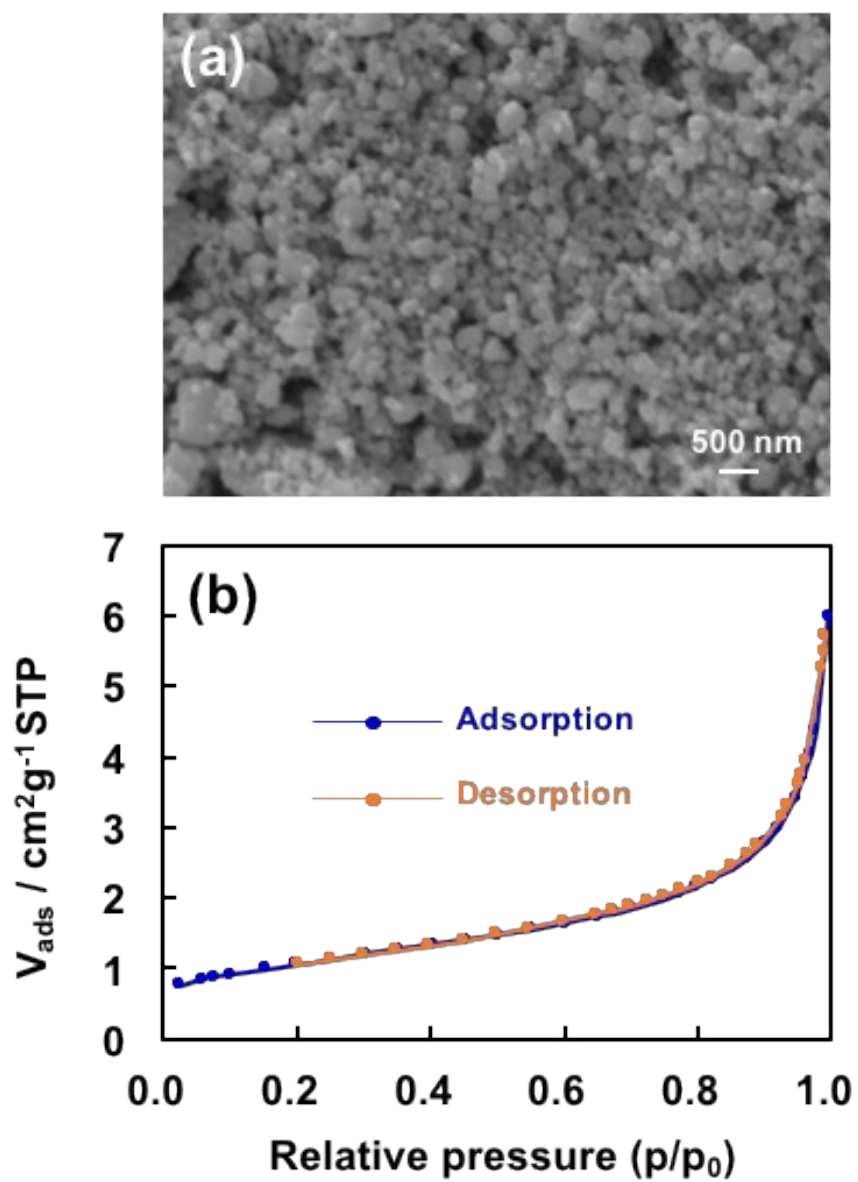
<sup>a</sup> Pt was loaded on WO<sub>3</sub> in first step during the preparation of Pt-Mn/WO<sub>3</sub> using two-step method.

<sup>b</sup> Mn was loaded on WO<sub>3</sub> in first step during the preparation of Pt-Mn/WO<sub>3</sub> using two-step method.

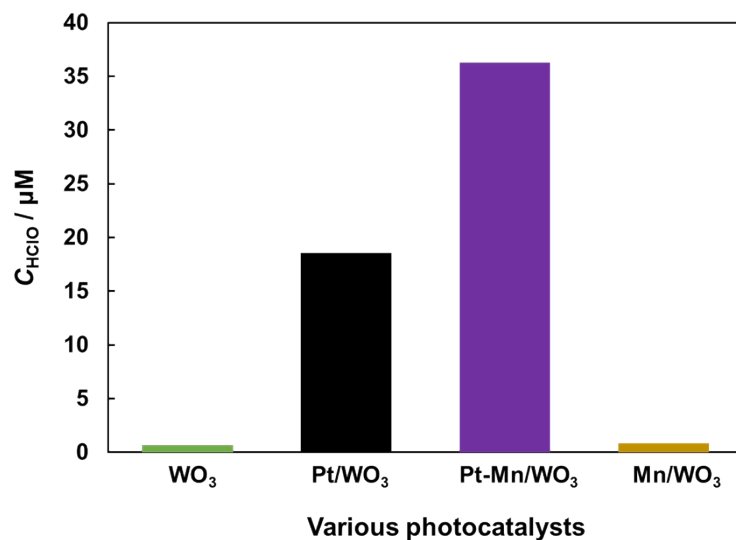
<sup>c</sup> Ratio of Pt 4f peak area to W 4f peak area detected by XPS.

**Table S4.** The actual loading amount of Pt and Mn species, and the recycle test for production of HClO during the photocatalytic oxidation of Cl<sup>-</sup> over Pt-Mn/WO<sub>3</sub> under visible light irradiation for 1 h.

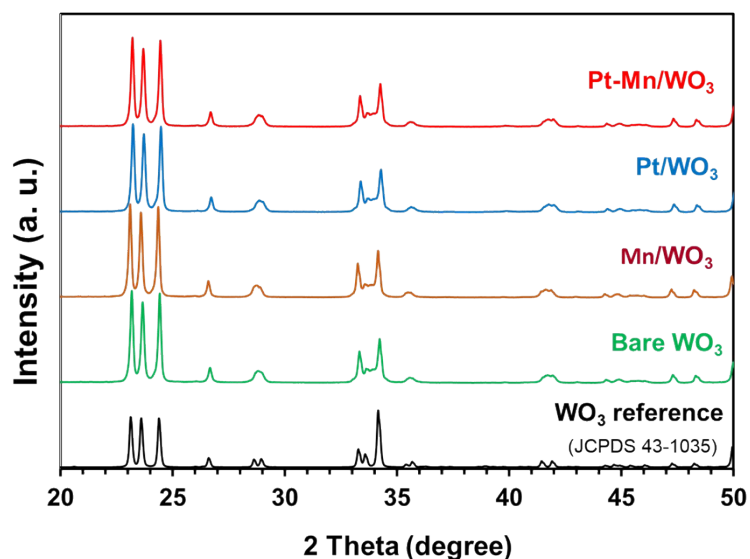
Recycle test / Turn	Pt amount (wt%)	Mn amount (wt%)	C <sub>HClO</sub> /μM
1	0.99	0.11	37.9
2	0.94	0.08	33.8
3	0.90	0.06	29.1



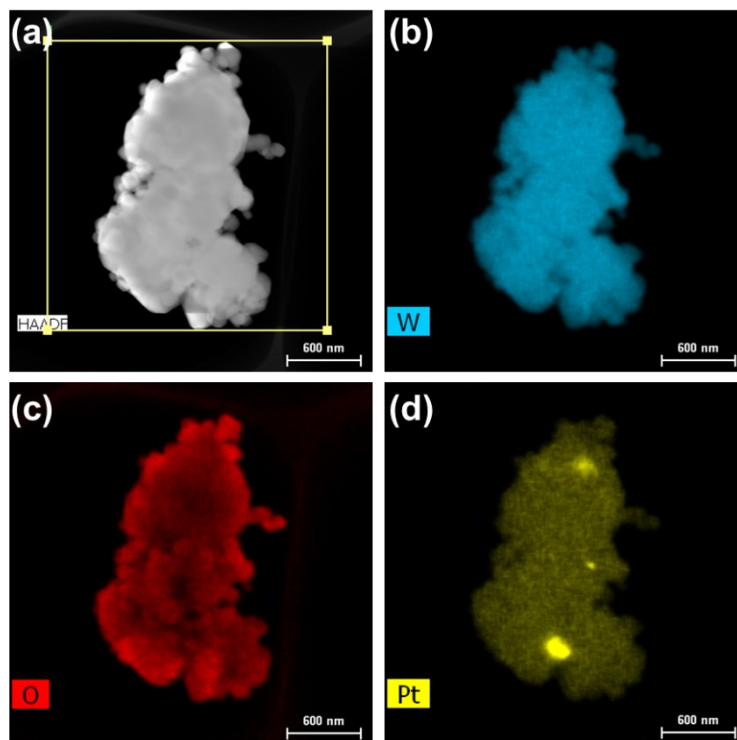
**Fig. S1.** SEM image (a) and  $\text{N}_2$  adsorption/desorption isotherms and pore size distribution curves (b) of as-prepared  $\text{WO}_3$ .



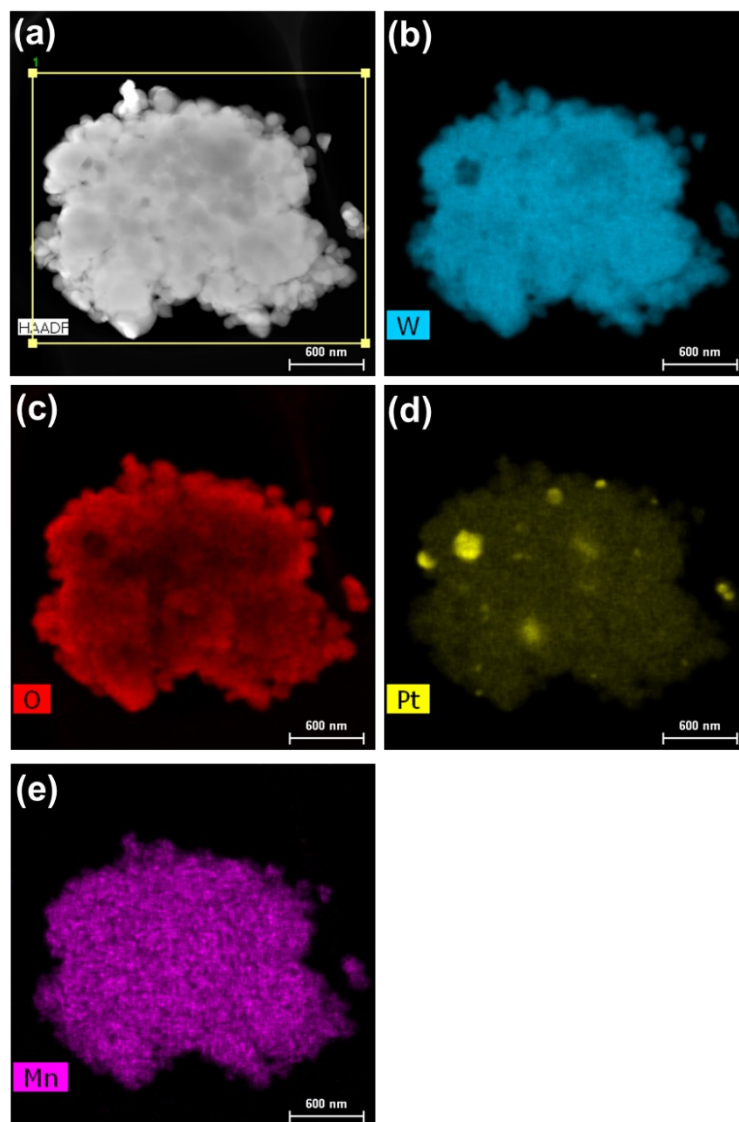
**Fig. S2.** HClO concentration ( $C_{\text{HClO}}$ ) produced by the oxidation of  $\text{Cl}^-$  over bare  $\text{WO}_3$ ,  $\text{Pt}/\text{WO}_3$ ,  $\text{Pt-Mn}/\text{WO}_3$ , and  $\text{Mn}/\text{WO}_3$  under visible light irradiation. Photocatalyst: 100 mg; reaction solution: 0.5 M NaCl, 100 mL;  $\text{O}_2$  flow rate:  $1 \text{ mL min}^{-1}$ ; light source: 300 W Xe lamp with 420 nm cut-off filter; temperature: 303 K, photoirradiation time: 1 h.



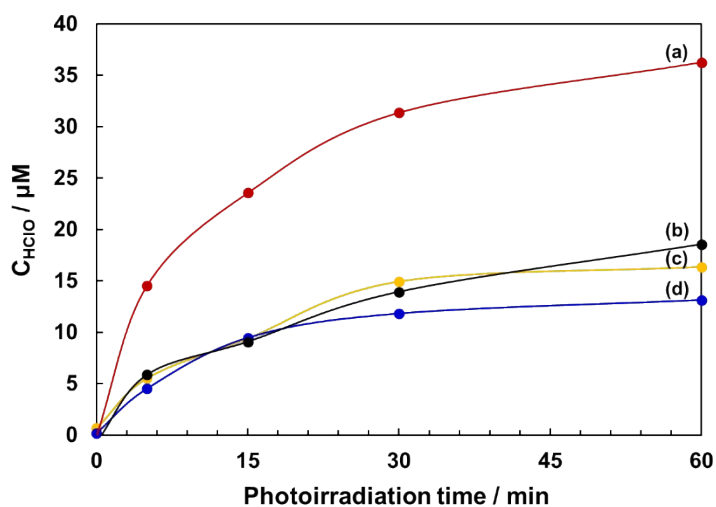
**Fig. S3.** XRD patterns of bare  $\text{WO}_3$  and different cocatalyst loaded  $\text{WO}_3$ .



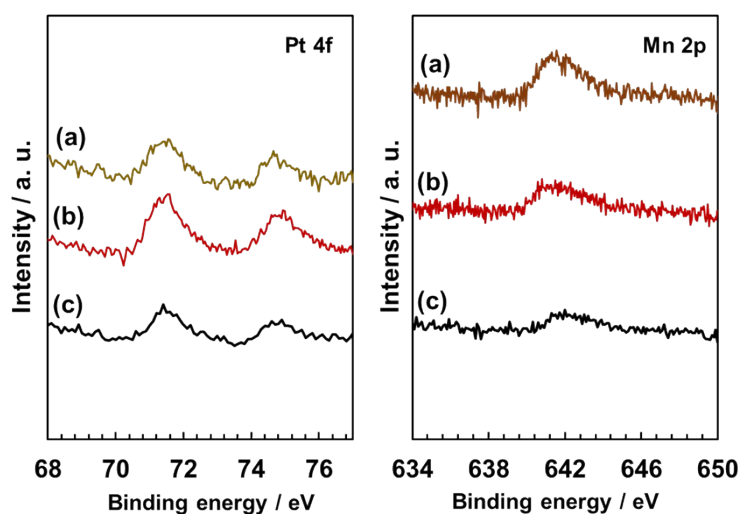
**Fig. S4.** (a) HAADF image and the related element mapping of (b) W, (c) O, and (d) Pt of Pt(1.0)/WO<sub>3</sub>.



**Fig. S5.** (a) HAADF image and the related element mapping of (b) W, (c) O, (d) Pt, and (e) Mn of Pt(1.0)-Mn(0.4)/WO<sub>3</sub>.



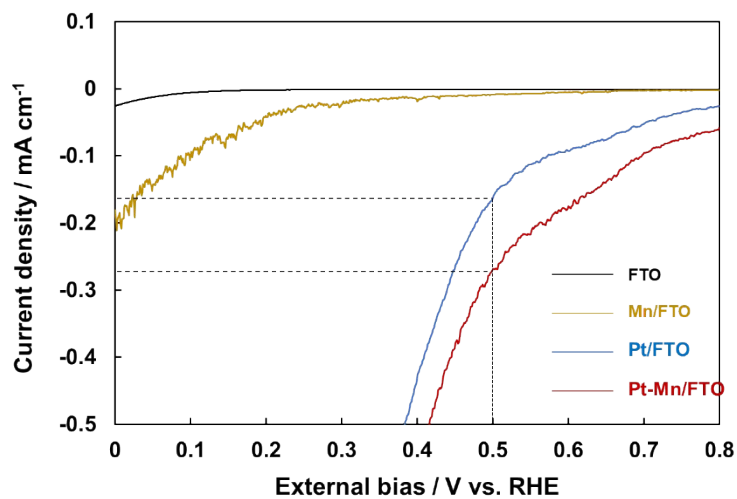
**Fig. S6.** Time course of HClO concentration ( $C_{\text{HClO}}$ ) produced by the oxidation of  $\text{Cl}^-$  under visible light irradiation over (a) Pt(0.99)-Mn(0.12)/ $\text{WO}_3$  prepared by one step method; (b) Pt(1.03)/ $\text{WO}_3$ ; (c) Pt(0.94)-Mn(0.09)/ $\text{WO}_3$  prepared by two step, Mn was photo-deposited in the first step; and (d) Pt(1.04)-Mn(0.12)/ $\text{WO}_3$  prepared by two step, Pt was photo-deposited in the first step. Photocatalyst: 100 mg; reaction solution: 0.5 M NaCl, 100 mL;  $\text{O}_2$  flow rate:  $1 \text{ mL min}^{-1}$ ; light source: 300 W Xe lamp with 420 nm cut-off filter; temperature: 303 K.



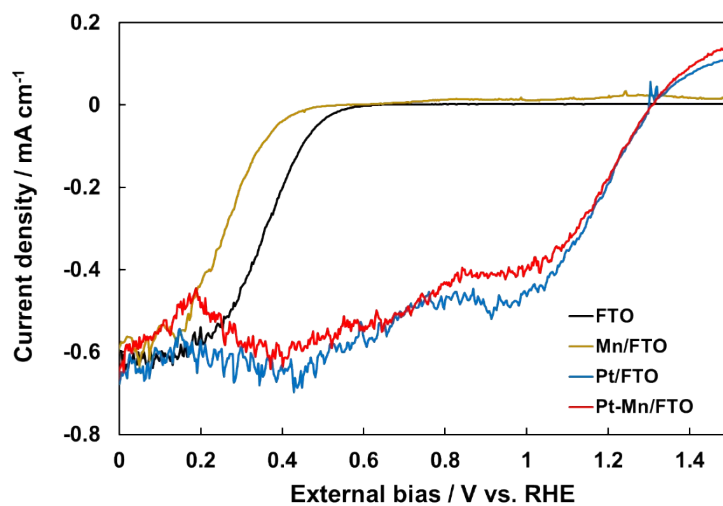
**Fig. S7.** Pt 4f and Mn 2p XPS spectra of (a) Pt(1.0)-Mn(0.39)/ $\text{WO}_3$  prepared by two step



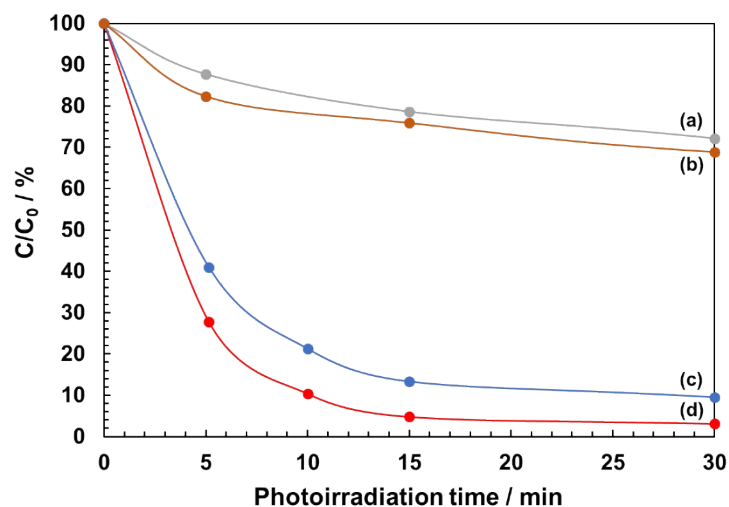
method, Pt was photo-deposited in the first step; (b) Pt(1.0)-Mn(0.27)/WO<sub>3</sub> prepared by two step, Mn was photo-deposited in the first step; (c) Pt(1.0)-Mn(0.19)/WO<sub>3</sub> prepared by one step method.



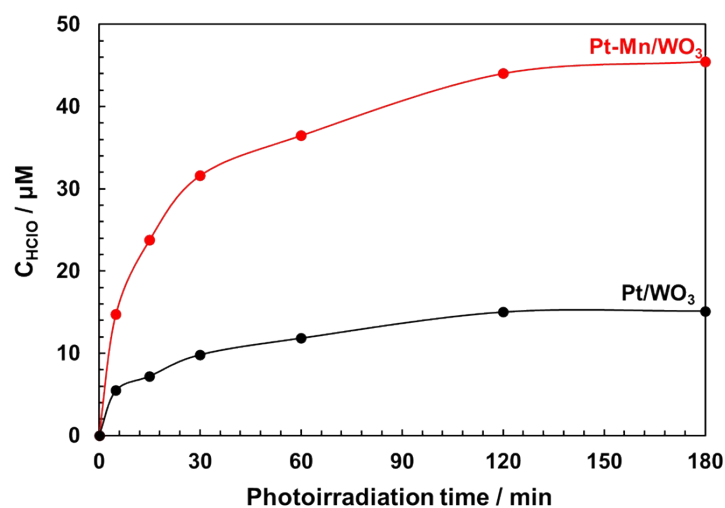
**Fig. S8.** Current-voltage (*I-V*) curves for ORR under O<sub>2</sub> flow over various metal/FTO electrodes using a three-electrode system in a 0.5 M NaCl solution (pH = 5.8).



**Fig. S9.** Current-voltage (*I-V*) curves for HClO reduction reaction under N<sub>2</sub> flow over various metal/FTO electrodes using a three-electrode system in a 0.5 M NaCl solution. 100 μM of HClO was initially added in the NaCl electrolyte.

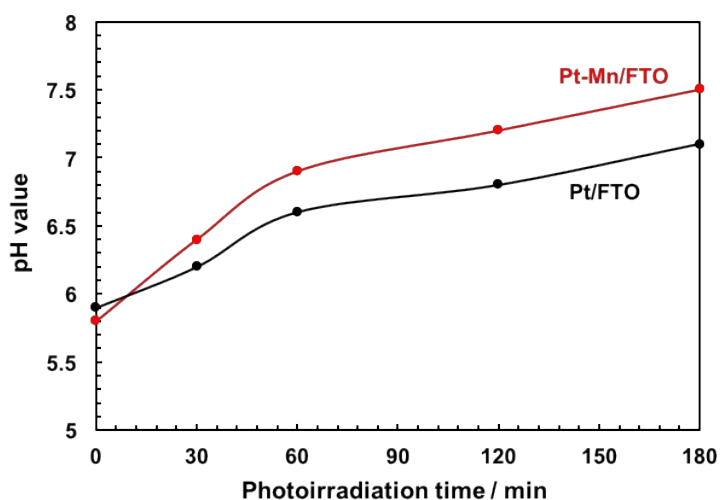


**Fig. S10.** Time course of the decomposition rate of H<sub>2</sub>O<sub>2</sub> over (a) bare WO<sub>3</sub>, (b) MnO<sub>x</sub>/WO<sub>3</sub>, (c) Pt/WO<sub>3</sub>, and (d) Pt-Mn/WO<sub>3</sub> under the photoirradiation of visible light. Photocatalyst: 50 mg; reaction solution: phosphate buffer (pH = 6.2), 50 mL; O<sub>2</sub> flow rate: 1 mL min<sup>-1</sup>; light source: 300 W Xe lamp with 420 nm cut-off filter; temperature: 237K, the initial concentration of H<sub>2</sub>O<sub>2</sub> was about 60 μM.



**Fig. S11.** Time course of HClO produced ( $C_{\text{HClO}}$ ) during the photocatalytic oxidation of Cl<sup>-</sup>

over Pt-Mn/WO<sub>3</sub> and Pt/WO<sub>3</sub> with flowing O<sub>2</sub> under visible light. Photocatalyst: 100 mg; reaction solution: 0.5 M NaCl, 100 mL; O<sub>2</sub> flow rate: 1 mL min<sup>-1</sup>; light source: 300 W xeon lamp with 420 nm cut-off filter; temperature: 303 K.



**Fig. S12.** The change of pH during the photocatalytic oxidation of Cl<sup>-</sup> over Pt-Mn/WO<sub>3</sub> and Pt/WO<sub>3</sub> under visible light irradiation for 180 min. Photocatalyst: 100 mg; reaction solution: 0.5 M NaCl, 100 mL; O<sub>2</sub> flow rate: 1 mL min<sup>-1</sup>; light source: 300 W xeon lamp with 420 nm cut-off filter; temperature: 303 K.