

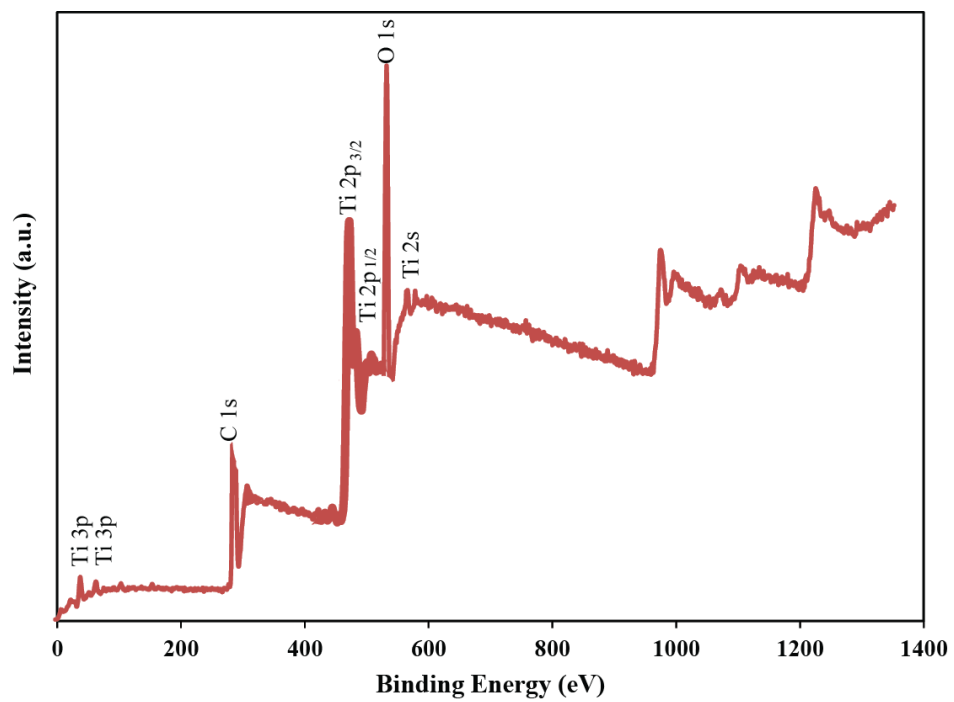
**Supporting Information:**

**Detection of Oxygen Vacancies in Oxides by Defect-Dependent  
Cataluminescence**

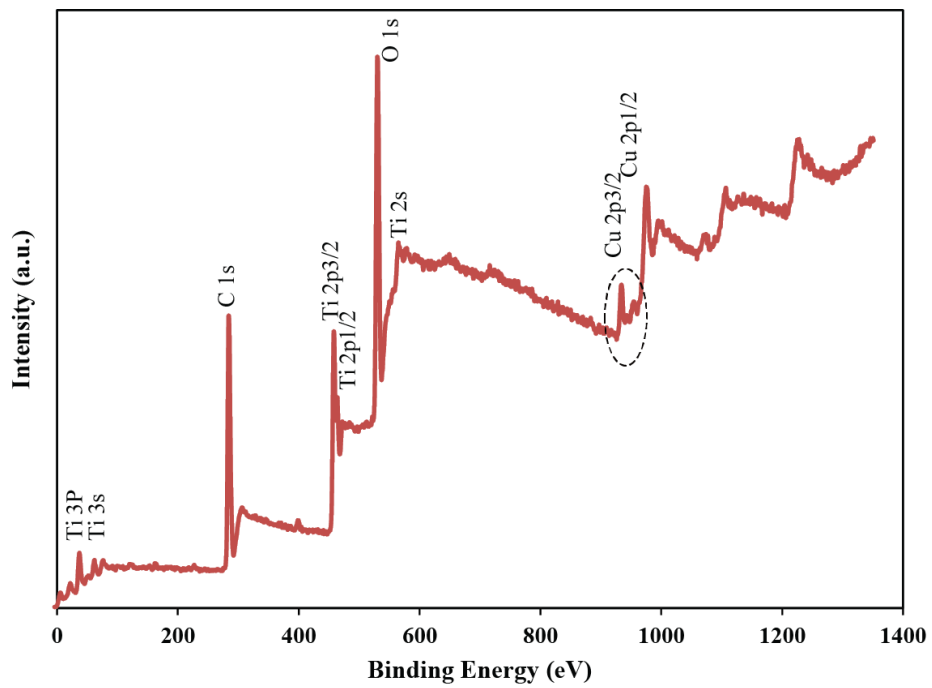
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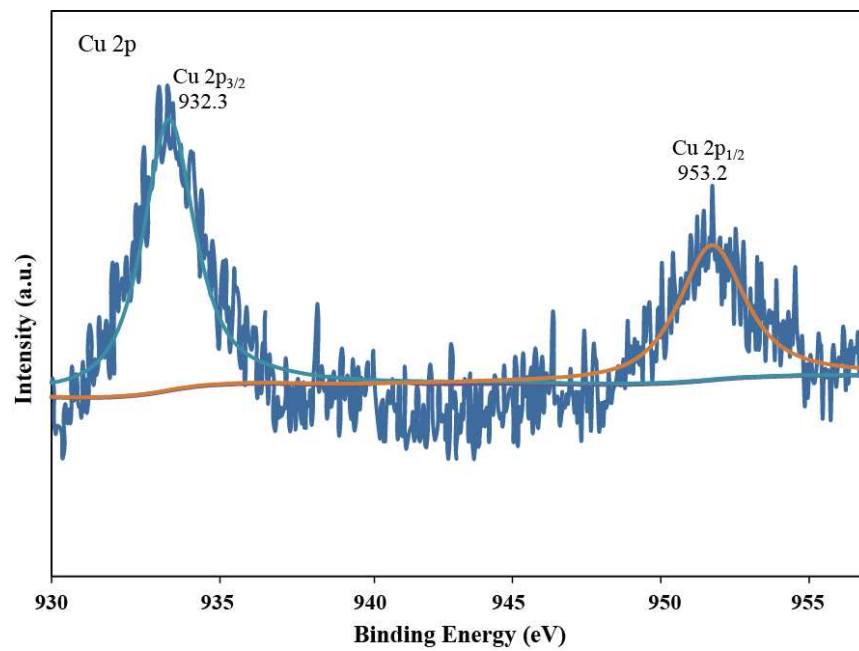
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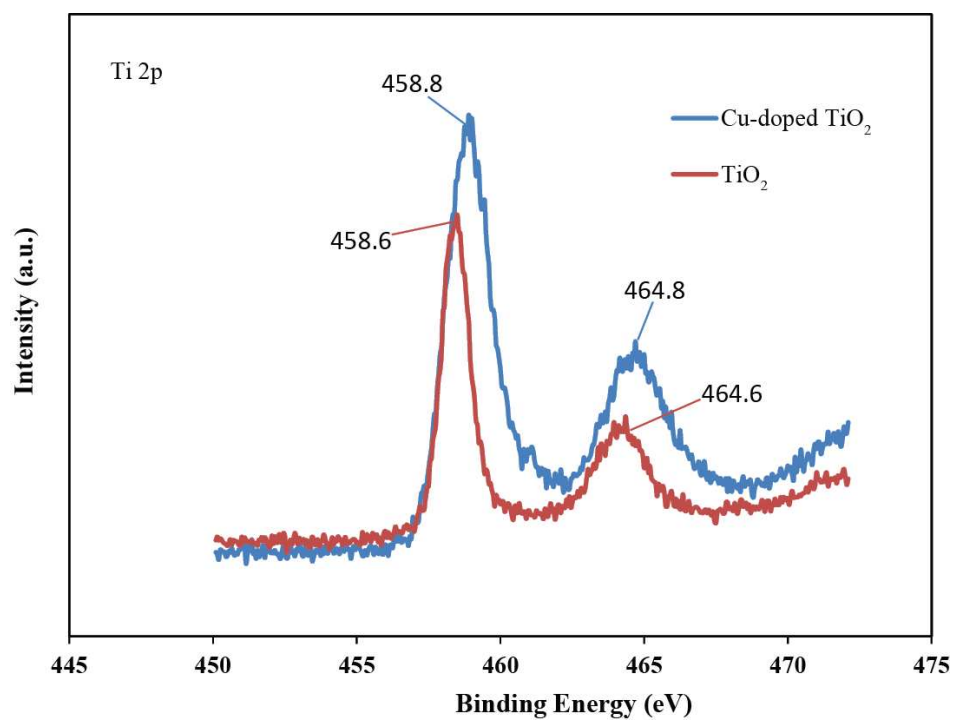
**Figure S1.** XPS survey spectrum of synthesized TiO<sub>2</sub> nanoparticles.



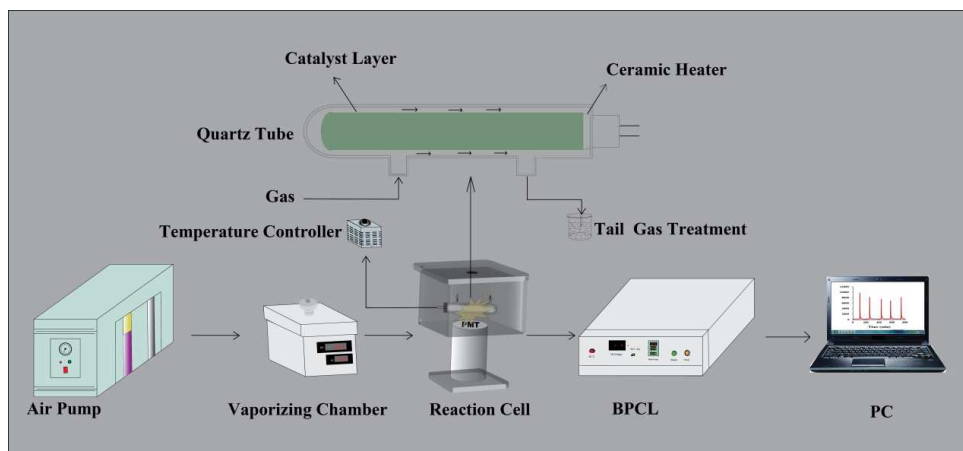
**Figure S2.** XPS survey spectrum of synthesized 1.5 wt% Cu-doped TiO<sub>2</sub> nanoparticles.



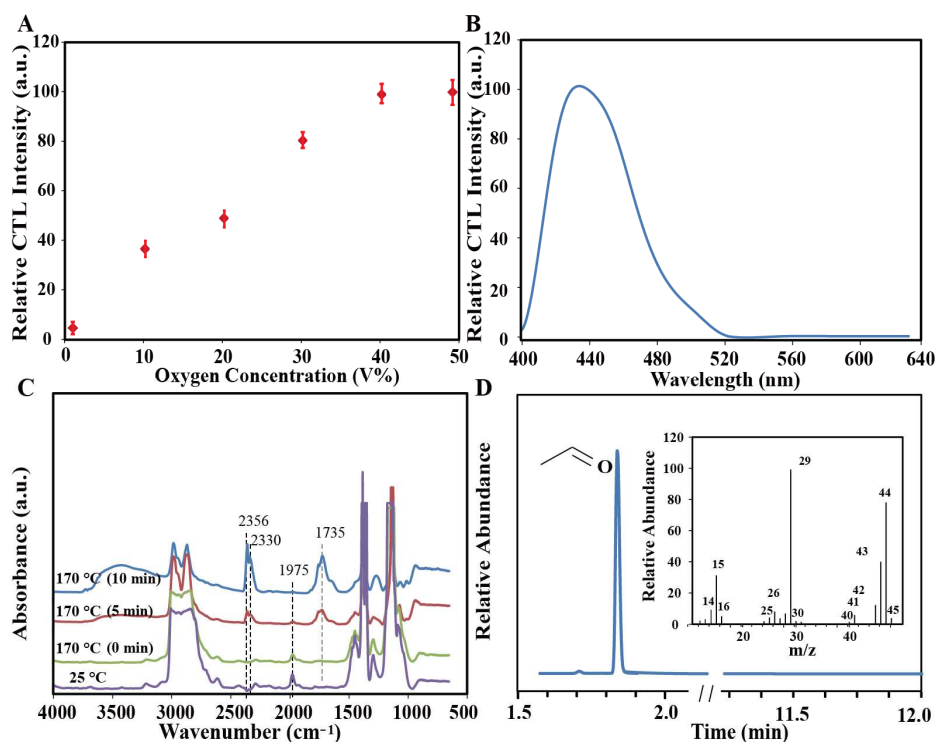
**Figure S3.** Cu 2p spectrum of 1.5 wt% Cu-doped TiO<sub>2</sub> nanoparticles.



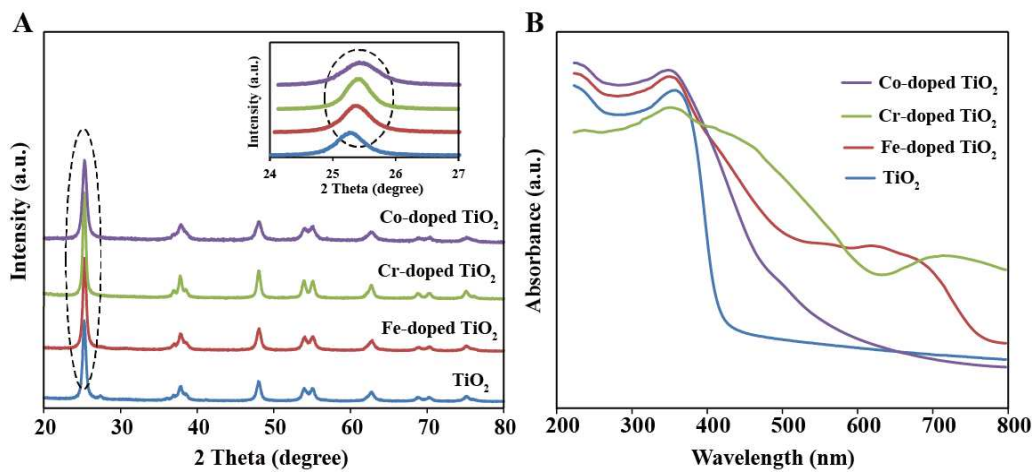
**Figure S4.** XPS spectra of Ti 2p of TiO<sub>2</sub> and the 1.5 wt% Cu-doped TiO<sub>2</sub> nanoparticles.



**Figure S5.** Schematic diagram of the CTL configuration system.

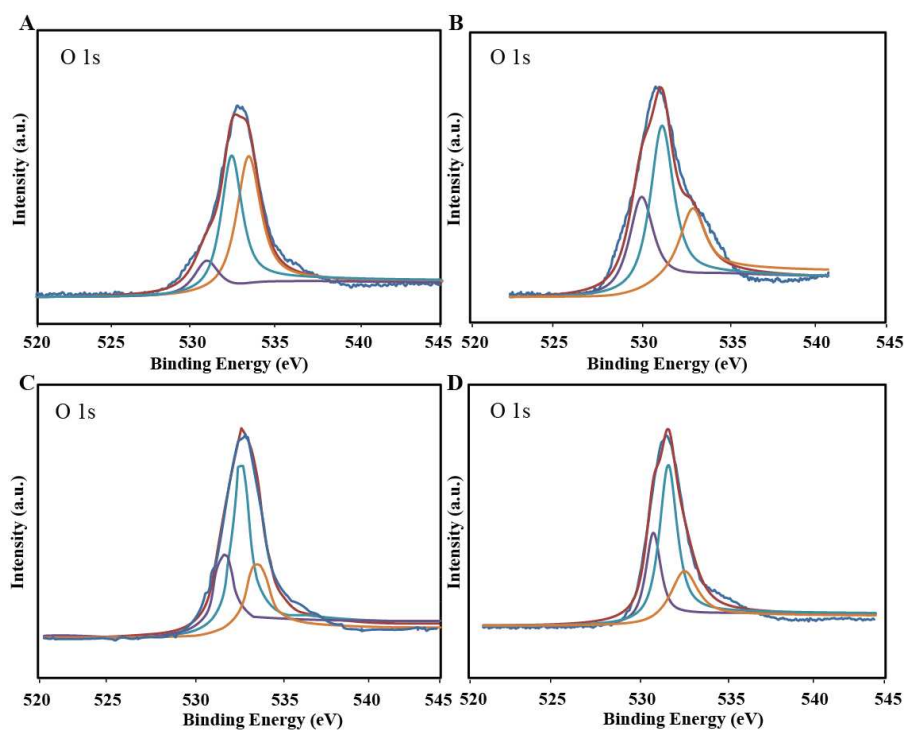


**Figure S6.** (A) Effect of oxygen concentration on the CTL signals of diethyl ether on the surface of 1.5 wt% Cu-doped TiO<sub>2</sub> nanoparticles. Air flow rate, 250 mL min<sup>-1</sup>; working temperature, 170 °C; diethyl ether concentration, 200 mM. (B) CTL spectrum of diethyl ether on the surface of 1.5 wt% Cu-doped TiO<sub>2</sub> nanoparticles. Air flow rate, 250 mL min<sup>-1</sup>; working temperature, 170 °C; diethyl ether concentration, 200 mM. (C) In situ FTIR spectra of diethyl ether oxide reaction on the surface of 1.5 wt% Cu-doped TiO<sub>2</sub> nanoparticles at different reaction temperatures and reaction times. (D) GC/MS chromatograms of diethyl ether CTL reaction on the surface of 1.5 wt% Cu-doped TiO<sub>2</sub> nanoparticles.

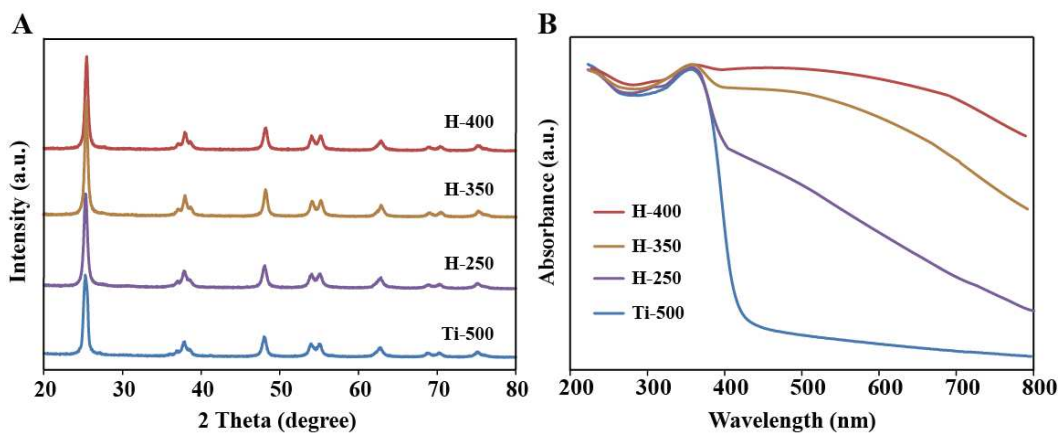


**Figure S7.** (A) XRD and (B) UV-vis diffuse reflectance spectra of TiO<sub>2</sub> and 1.0 wt% Fe, Cr, Co ion-doped TiO<sub>2</sub> nanoparticles.

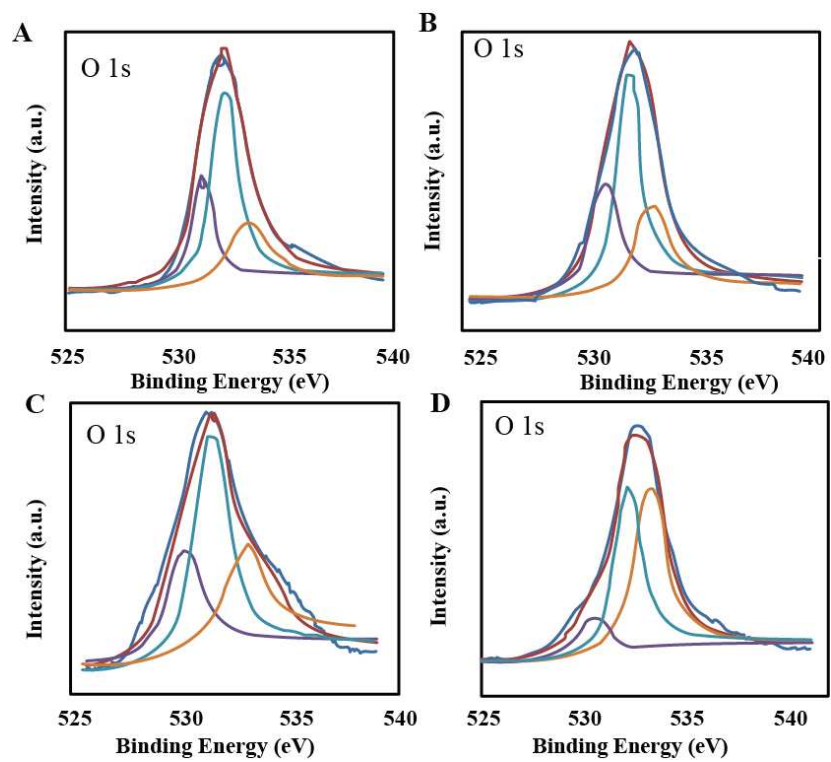




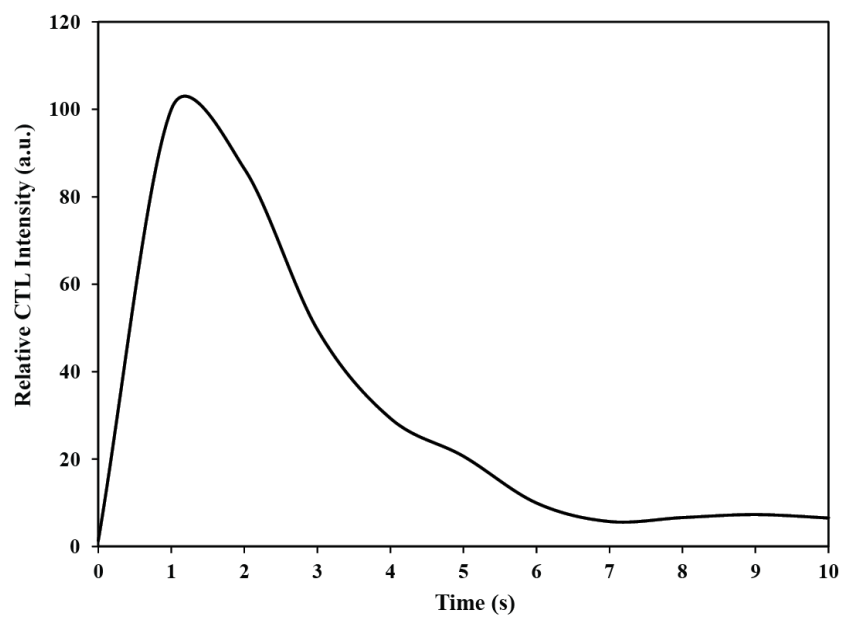
**Figure S8.** XPS spectra of O 1s on the surface of 1.0 wt% (A) Cu-doped TiO<sub>2</sub>, (B) Co-doped TiO<sub>2</sub>, (C) Fe-doped TiO<sub>2</sub> and (D) Cr-doped TiO<sub>2</sub> nanoparticles.



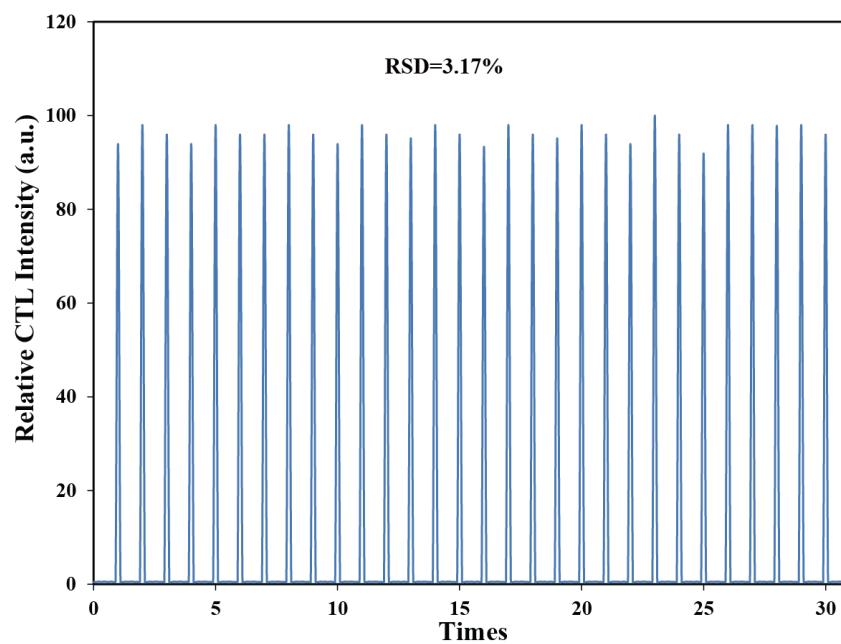
**Figure S9.** (A) XRD and (B) UV-vis diffuse reflectance spectra of Ti-500 and hydrogen treated TiO<sub>2</sub> nanoparticles with different temperatures.



**Figure S10.** XPS spectra of O 1s in (A) Ti-500 (B) H-250 (C) H-350 (D) H-400.



**Figure S11.** CTL response profile of 10 mM diethyl ether on the surface of TiO<sub>2</sub> nanoparticles. Working temperature, 170 °C; flow rate of carrier gas, 250 mL min<sup>-1</sup>.



**Figure S12.** Relative CTL intensity of the repeated injections of 100 mM diethyl ether vapor on the surface of TiO<sub>2</sub> nanoparticles. Working temperature, 170 °C; air flow rate, 250 mL min<sup>-1</sup>.

**Table S1.** Average crystallite sizes,  $d_{101}$  lattice spacing, actual values of Cu doping content and surface areas for Cu-doped TiO<sub>2</sub> nanoparticles.

Samples/Cu (wt%)	Crystalline sizes (nm)	$d_{101}$ (Å)	ICP-OES/Cu (wt%)	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )
0.0	16.14	3.5236	0.00	36.00
0.5	15.40	3.5228	0.45	—
1.0	15.36	3.5208	0.88	—
1.5	15.30	3.5182	1.31	31.24
2.0	14.94	3.5109	1.78	—
2.5	15.15	3.5106	2.25	—

**Table S2.** XPS results of different chemical states of O and Ti elements at the surface of pure TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub> nanoparticles.

Samples	Binding Energy (eV)				O <sub>L</sub> (%)	O <sub>-OH</sub> (%)	O <sub>S</sub> (%)	Evaluated Oxygen Vacancies (%)
	O1s (O <sub>L</sub> )	O1s (O <sub>-OH</sub> )	O1s (O <sub>S</sub> )	Ti2p <sub>3/2</sub>				
TiO <sub>2</sub>	530.2	532.0	533.4	458.6	42.6	39.3	18.1	19.8
1.5Cu/TiO <sub>2</sub>	530.0	532.1	533.4	458.8	35.8	36.5	27.7	30.0
2.0Cu/TiO <sub>2</sub>	530.1	532.0	533.5	458.7	36.9	36.3	26.8	27.6
2.5Cu/TiO <sub>2</sub>	530.3	532.1	533.2	458.8	38.2	38.4	23.4	25.8

The approximate formula was used to calculate the percentage of oxygen vacancies (V<sub>O</sub>):  
 $V_O\% = \{[(\text{the atomic number ratio of Ti} \times 4) - (\text{the atomic number ratio of O}_L \times 2)] / 2\} \times 100$ .

#### References:

- (1) Wagner, C. D.; Moulder, J. F.; Davis, L. E.; Riggs, W. M. *Perkin-Elmer Corporation: Eden Prairie, MN*, **1979**.
- (2) You, M.; Kim, T. G.; Sung, Y. M. *Growth Des.* **2010**, *10*, 983–987.
- (3) Xin, B. F.; Wang, P.; Ding, D. D.; Liu, J.; Ren, Z. Y.; Fu, H. *Appl. Surf. Sci.* **2008**, *254*, 2569–2574.

**Table S3.** XPS results of different chemical states of O and Ti elements at the surface of 1.0 wt% transition metal ion-doped TiO<sub>2</sub>.

Sample	Binding Energy (eV)				O <sub>L</sub> (%)	O <sub>-OH</sub> (%)	O <sub>S</sub> (%)	Evaluated Oxygen Vacancies (%)
	O1s (O <sub>L</sub> )	O1s (O <sub>-OH</sub> )	O1s (O <sub>S</sub> )	Ti2p <sub>3/2</sub>				
Cu/TiO <sub>2</sub>	530.9	532.2	533.1	458.8	27.9	46.8	25.3	28.4
Co/TiO <sub>2</sub>	529.9	532.4	533.1	458.7	30.8	45.3	23.9	26.1
Fe/TiO <sub>2</sub>	530.8	532.0	533.6	458.7	35.1	45.1	19.8	22.8
Cr/TiO <sub>2</sub>	530.7	531.9	533.1	458.6	40.2	47.6	18.2	20.5



**Table S4.** XPS results of different chemical states of O and Ti elements at the surface of Ti-500 and hydrogen treated TiO<sub>2</sub> nanoparticles with different temperatures.

Sample	Binding Energy (eV)				O <sub>L</sub> (%)	O <sub>-OH</sub> (%)	O <sub>S</sub> (%)	Evaluated Oxygen Vacancies (%)
	O1s (O <sub>L</sub> )	O1s (O <sub>-OH</sub> )	O1s (O <sub>S</sub> )	Ti2p <sub>3/2</sub>				
Ti-500	523.0	532.1	533.3	458.6	42.7	38.1	19.2	18.9
H-250	530.0	532.1	533.6	458.5	40.9	35.0	24.1	23.7
H-350	530.3	531.5	533.0	458.5	34.5	39.3	26.2	27.0
H-400	530.3	531.0	533.8	458.5	32.8	37.3	29.9	29.2