Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2019

## **Electronic Supplementary Information**

## Controllable construction of oxygen vacancies by anaerobic catalytic combustion of dichloromethane over metal oxides for enhanced solar-to-hydrogen conversion

Sufen Zhang, Jianni Liu, Xiaoyang Dong, Xiaoxia Jia, Ziwei Gao, and

Quan Gu\*

Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi

Normal University, Xi'an, 710062, China

\*E-mail: guquan@snnu.edu.cn



Figure S1 amount of  $CH_4$  detected by GC during the reaction of  $CH_2Cl_2$  with TiO<sub>2</sub> at 200, 300, and 400 °C.



Figure S2 XRD patterns of TiO<sub>2</sub>, TiO<sub>2</sub>-V, and TiO<sub>2</sub>-T (T=50, 100, 200, 300, and 400).



Figure S3 SEM images of  $TiO_2$  (A),  $TiO_2$ -50 (B),  $TiO_2$ -100 (C),  $TiO_2$ -200 (D),  $TiO_2$ -300 (E), and  $TiO_2$ -400 (F).



Figure S4 Raman spectra of  $TiO_2$ ,  $TiO_2$ -V, and  $TiO_2$ -T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature.



Figure S5 EDX image of TiO<sub>2</sub>-200.



Figure S6 the nitrogen adsorption-desorption isotherms (A) and the corresponding pore-size distribution curves (B) of  $TiO_2$  and  $TiO_2$ -T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature.

sample	Pore volume (ml/g)	Pore size (nm)	$S_{BET} (m^2/g)$
TiO <sub>2</sub>	0.5385	26.46	55.3
TiO <sub>2</sub> -V	0.4499	25.95	56.9
TiO <sub>2</sub> -50	0.4272	26.49	51.3
TiO <sub>2</sub> -100	0.4250	26.31	51.5
TiO <sub>2</sub> -200	0.3938	25.96	49.5
TiO <sub>2</sub> -300	0.4408	25.99	57.3
TiO <sub>2</sub> -400	0.4127	25.81	57.6

Table S1 summary of the physicochemical characteristics of as-prepared samples.



Figure S7 EPR spectra of TiO<sub>2</sub>, TiO<sub>2</sub>-V, and TiO<sub>2</sub>-T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature determined at 140 K under dark and visible light irradiation.



Figure S8 high-resolution C 1s and Cl 2p XPS spectra of  $TiO_2$  and  $TiO_2$ -T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature.



Figure S9 PL spectra of  $TiO_2$ ,  $TiO_2$ -V, and  $TiO_2$ -T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature.



Figure S10 XRD patterns of (A)  $TiO_2(001)$ , (B) rutile  $TiO_2$ , (C)  $MoO_3$ , (D)  $WO_3$ , and (E) ZnO before and after treatment.



Figure S11 (A) Hydrogen evolution amount of Pt supported samples from ethanol solution (10 vol%) under visible light irradiation. (B) Hydrogen evolution amount of TiO<sub>2</sub>, TiO<sub>2</sub>-T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature, TiO<sub>2</sub>-V, and TiO<sub>2</sub>-H from ethanol solution (10 vol%) solar light irradiation. (C) Hydrogen evolution amount of Pt supported samples from ethanol solution (10 vol%) under solar light irradiation.



Figure S12 hydrogen evolution amount of (A)  $TiO_2$ ,  $TiO_2$ -T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature,  $TiO_2$ -V and  $TiO_2$ -H and (B) the corresponding Pt supported samples from EDTA-2Na solution (1.0 mg/ml) under visible light irradiation. Hydrogen evolution amount of (C)  $TiO_2$ ,  $TiO_2$ -T (T=50, 100, 200, 300, and 400) obtained at different reaction temperature,  $TiO_2$ -V and  $TiO_2$ -H and (D) the corresponding Pt supported samples from EDTA-2Na solution (1.0 mg/ml) under solar light irradiation.



Figure S13 cycling test of TiO<sub>2</sub>-200 for photocatalytic H<sub>2</sub> generation form EDTA-2Na solution under visible light irradiation ( $\lambda$ >420 nm).



Figure S14 TEM (A and B) and HRTEM (C) images of Pt nanoparticles supported  $TiO_2$ -200.