Electronic Supplementary Information

A Zn_4O-containing doubly interpenetrated porous metal organic framework for photocatalytic decomposition of methyl orange

Madhab C. Das,[a,#] Hui Xu,[b,#] Zhiyu Wang,[b] Gadipelli Srinivas,[c] Wei Zhou,[c] Yan-Feng Yue,[d] Vladimir N. Nesterov,[d] Guodong Qian,*[b] Banglin Chen*[a]

[a]*Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698 (USA), Fax: (+1) 210-458-7428, E-mail: banglin.chen@utsa.edu*
[b]*State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027 (China) E-mail: gdqian@zju.edu.cn*
[c]*NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6102 and Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742*
[d]*Department of Chemistry, University of North Texas, 1155 Union Circle #305070, Denton, TX 76203-5017(USA).*

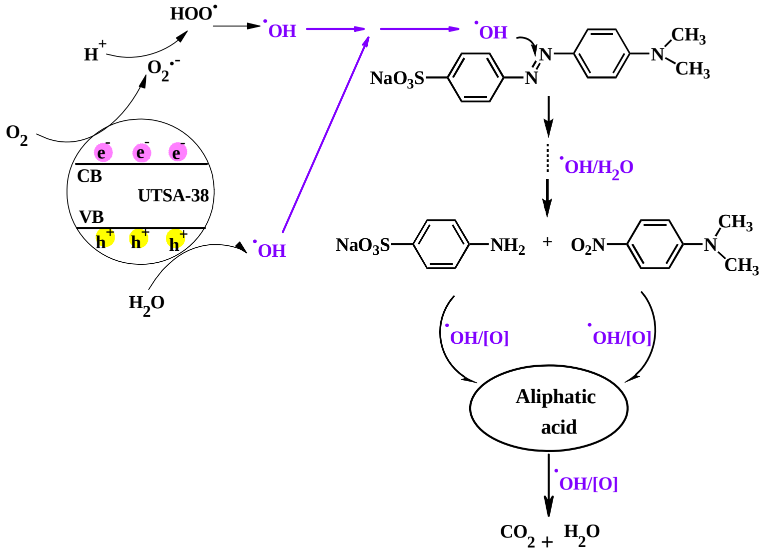
Photocatalytic Experiments:

Photocatalytic reactions for decomposition of methyl orange were carried out in a beaker with 8 cm in diameter and 10 cm in height. A PLS-SXE-300 lamp was used as the UV resource. Typically, 0.2 g of UTSA-**38** was dispersed into 50 ml of 20 mg/L methyl orange aqueous solution in a water bath. The suspensions were magnetically stirred for 30 min in the dark. At regular irradiation time intervals, 2ml solution was sampled, filtered and diluted to 3 times volume. The photographs were taken under the same condition except that 4ml solution was sampled and filtered each time. The diffuse reflective spectra (DRS) of the sample powder and the UV-Vis absorption spectra of methyl orange aqueous solutions were measured by a Hitachi U-4100 spectrophotometer.

The relationship between A and C: $A=0.0027+0.076C$ (A: absorbance, for methyl orange, A (464 nm) is used in this relationship; C: mg/L; this relationship stands when C below or equals to 20 mg/L)

The rate of degradation: $(C_0-C)/C_0$ (C_0: original concentration of methyl orange; C: the concentration of methyl orange after degradation).

Mechanism of Photocatalysis:



Scheme S1. Main pathways proposed for methyl organe photodegraded by UTSA-**38** under UV-visible or visible light irradiation

Single-Crystal X-ray structure determination:

Crystal structure determination was carried out using a Bruker SMART APEX2 CCD-based X-ray diffractometer equipped with a low temperature device and Mo-target X-ray tube (wavelength = 0.71073 Å). Measurements were taken at 100(2) K. Data collection, indexing, and initial cell refinements were carried out using APEX2[1], frame integration and final cell refinements were done using SAINT[2]. The molecular structure of the compound was determined using direct methods and Fourier techniques, and was refined by full-matrix least-squares. An absorption correction, including face indexed absorption correction, was applied using the program SADABS[3]. All non-hydrogen atoms were refined anisotropically. There are large pores in the crystal structure of the compound, which are occupied by heavily disordered solvent molecules and because to locate, identify and refine their positions were unsuccessful. Therefore, the X-ray data were treated by PLATON/SQUEEZE[4] program that calculated a solvent-accessible volume, which was removed from subsequent structure factor calculations (potential solvent area is 2827.4 Å^3 per unit cell volume or 44.5%). After such correction, the structure was refined using the new data. The final chemical formula in the cif file does not contain the solvent. The largest residual electron density for the structure (3.869 e/ Å^3) was located close to (less than 1.0 Å from) the zinc atom and was most likely due to imperfect absorption corrections frequently encountered in heavy-metal atom structures. All hydrogen atoms in the structure were positioned geometrically and refined as riding atoms. Structure solution, refinement, graphics and generation of publication materials were performed using SHELXTL software.[5]

Table S1. Virial graph analyses data for UTSA-**38a** and its CO_2/CH_4, C_2H_2/CH_4, C_2H_4/CH_4, and C_2H_6/CH_4 separation selectivity.

Adsorbate	T/K	K_H/mol g^{-1} Pa^{-1}	A_0/ln(mol g^{-1} Pa^{-1})	A_1 / g mol^{-1}	R^2	S_{ij}*	$Q_{st,n=0}$/kJ mol^{-1}
CH_4	273	8.559E-9	-8.523±0.002	-73.367±8.575	0.993	–	18.9
	295	4.811E-9	-9.144±0.003	-56.258±12.105	0.978	–	
CO_2	273	3.059E-8	-6.830±0.006	-187.428±4.623	0.995	3.6	28.1
	295	1.610E-8	-7.752±0.001	-126.773±0.852	0.999	3.3	
C_2H_2	273	5.583E-8	-6.565±0.001	-217.737±6.292	0.999	6.5	24.7
	295	2.688E-8	-7.374±0.001	-41.736±3.308	0.997	5.6	
C_2H_4	273	4.164E-8	-6.787±0.007	-98.520±10.772	0.999	4.9	29.4
	295	3.061E-8	-7.749±0.001	-43.065±0.625	0.999	6.4	
C_2H_6	273	4.872E-8	-16.488±0.008	-412.664±16.822	0.999	5.7	24.4
	295	4.834E-8	-17.287±0.005	-37.771±1.968	0.999	10.1	

* The Henry's Law selectivity for gas component *i* over CH_4 at the speculated temperature is calculated based on equation: $S_{ij} = K_H(i)/K_H(CH_4)$.

Virial Graph Analyses: Isotherm data were analyzed using following virial equation:

$$\ln(n/P) = A_0 + A_1 \cdot n + A_2 \cdot n^2 + \ldots.$$

where P is pressure, n is amount adsorbed, and A_0, A_1, and so on are virial coefficients. A_0 is related to adsorbate–adsorbent interactions, whereas A_1 describes adsorbate···adsorbate interactions.

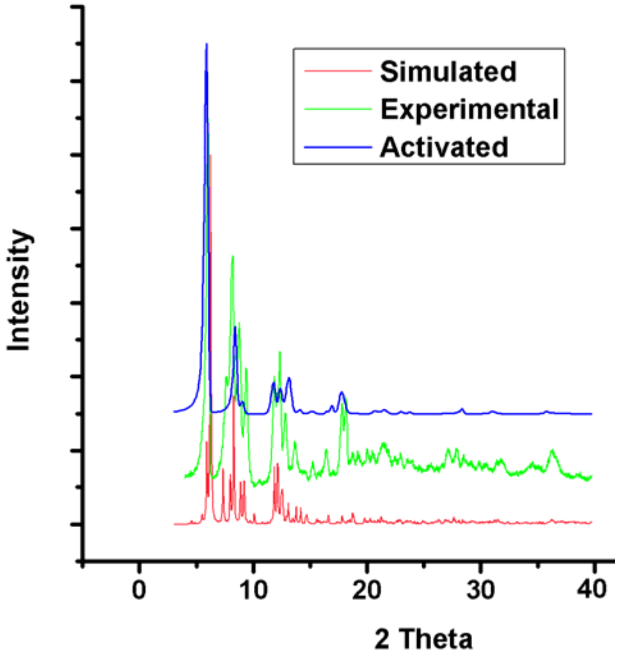


Fig.S1 PXRD patterns UTSA-**38** **(**pink, as-synthesized; green, experimental; blue, activated).

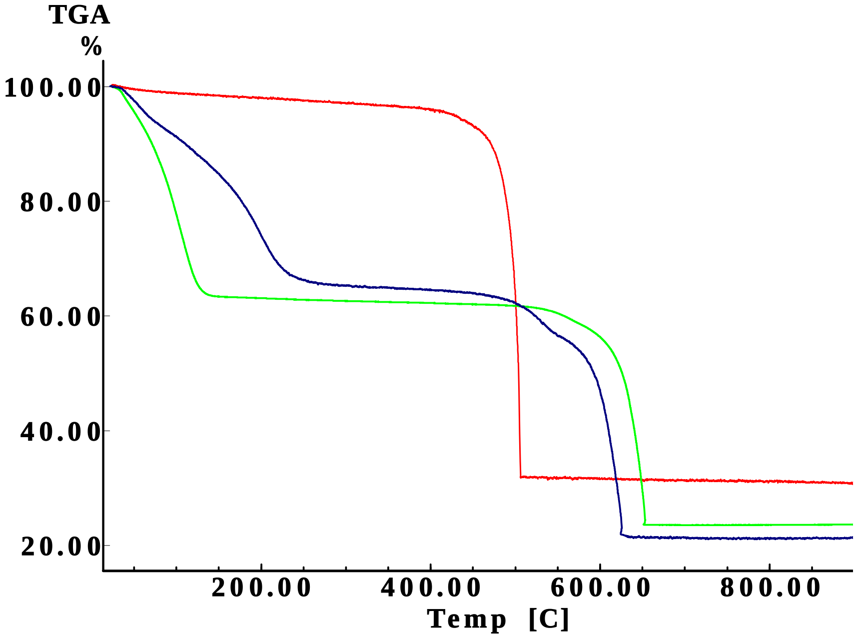


Fig.S2 TGA curves of as-synthesized (blue), chloroform-exchanged (green) and activated (red) UTSA-**38**.

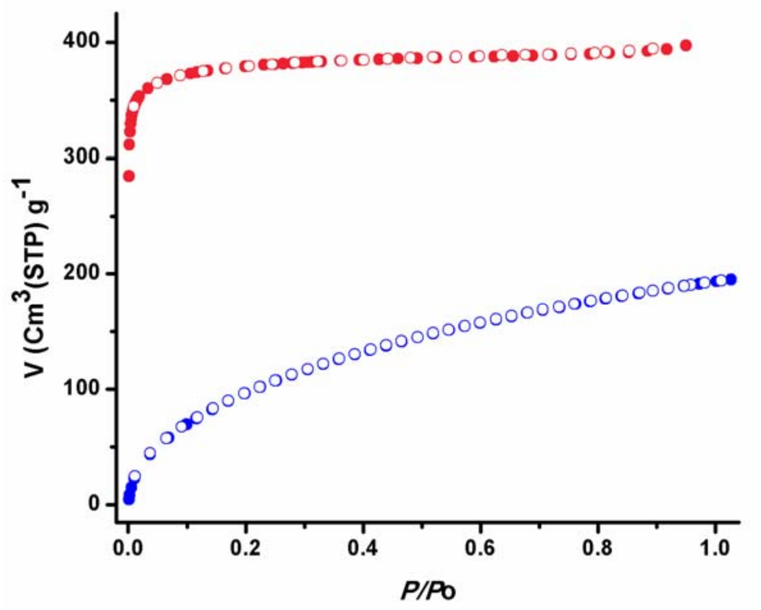


Fig.S3 Nitrogen (pink) and hydrogen (blue) sorption isotherms (closed circle, adsorption; open circle, desorption) of UTSA-**38a** at 77 K.

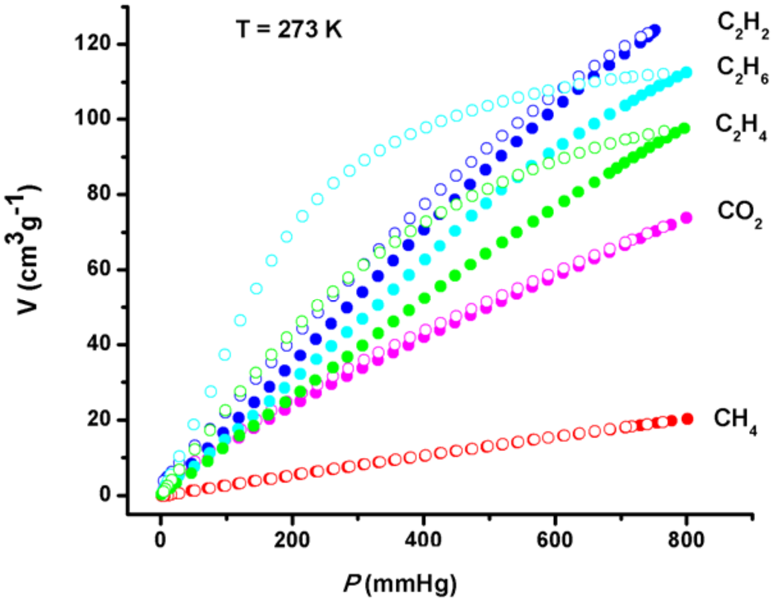


Fig.S4 Methane, carbon dioxide, acetylene, ethylene and ethane sorption isotherms (closed circle, adsorption; open circle, desorption) of UTSA-**38a** at 273 K (left) and 295 K (right). Color code: methane, red; carbon dioxide, pink; acetylene, blue; ethylene, green; ethane, cyan.

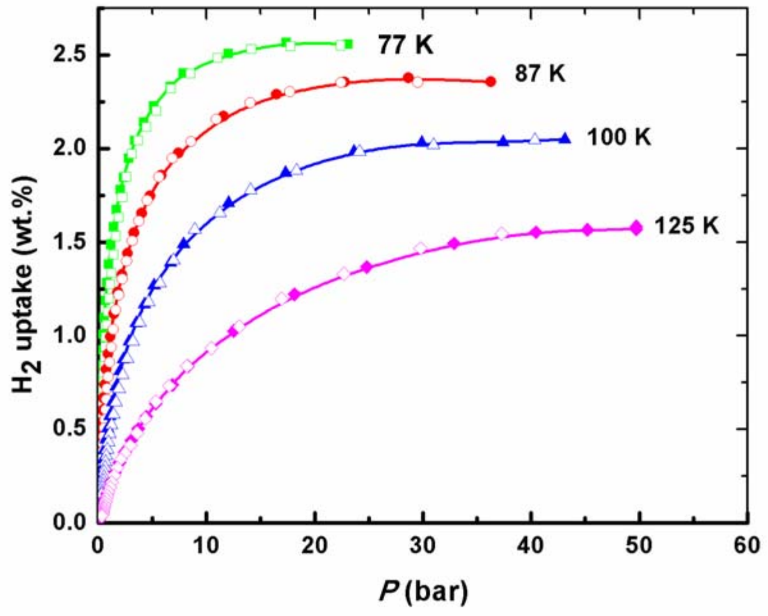


Fig.S5 High pressure hydrogen sorption isotherms (closed symbol, adsorption; open symbol, desorption)on UTSA-**38a** at various temperatures (green at 77 K, red at 87 K, blue at 100 K, pink at 125 K).

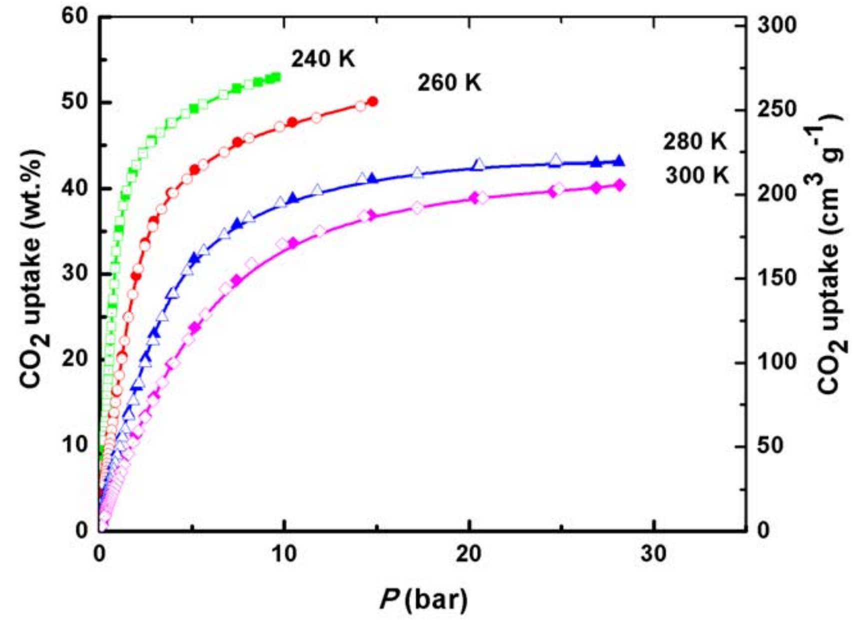


Fig.S6 High pressure carbon dioxide sorption isotherms (closed symbol, adsorption; open symbol, desorption) on UTSA-**38a** at various temperatures (green at 240 K, red at 260 K, blue at 280 K, pink at 300 K).

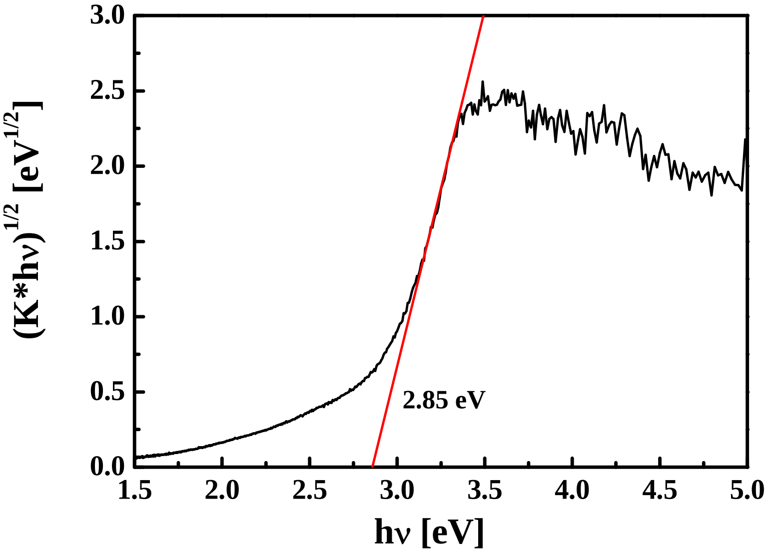


Fig.S7 Calculation of band gap in UTSA-**38** of 2.85 eV.

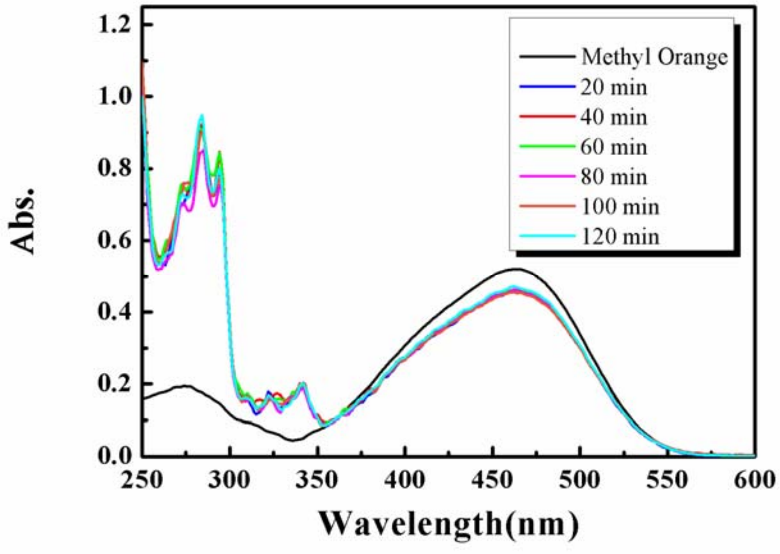


Fig.S8 UV-Vis absorption spectra of methyl orange solution in presence of UTSA-**38** carried out in dark for different time periods.

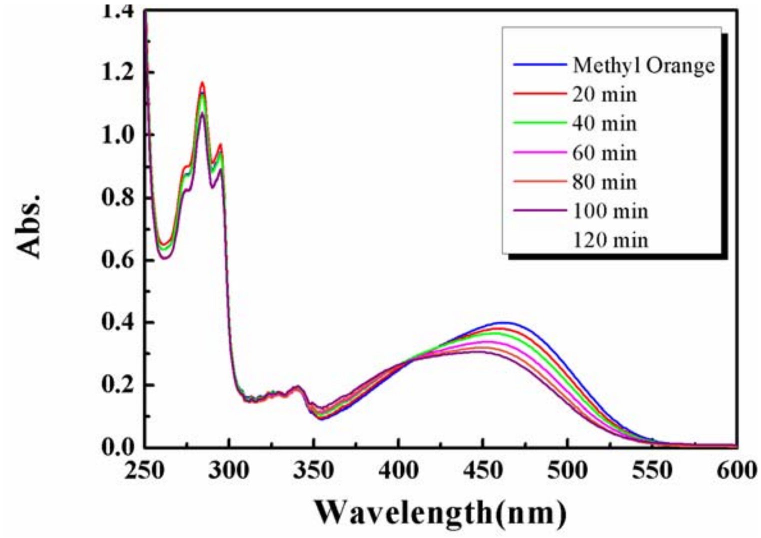


Fig.S9 UV-Vis absorption spectra of methyl orange solution degraded by UTSA-**38** after visible light irradiation for different time periods.

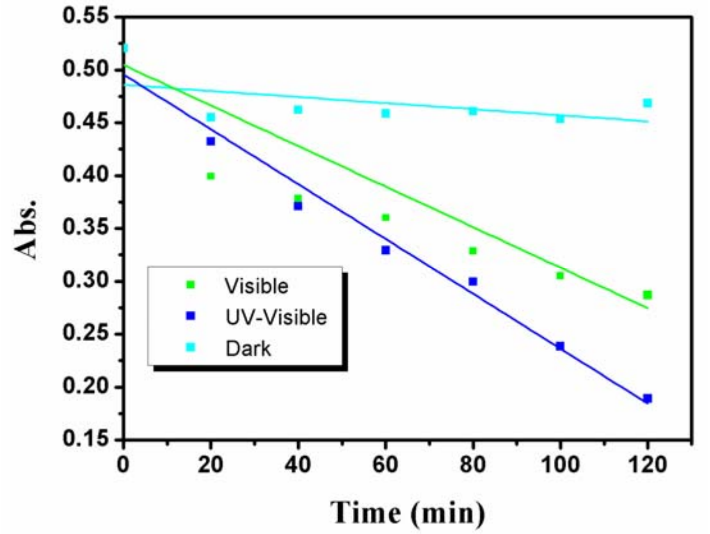


Fig.S10 Curves of absorbance of the methyl orange solution degraded by UTSA-**38** as a function of irradiation time under UV-visible light, visible light and dark.

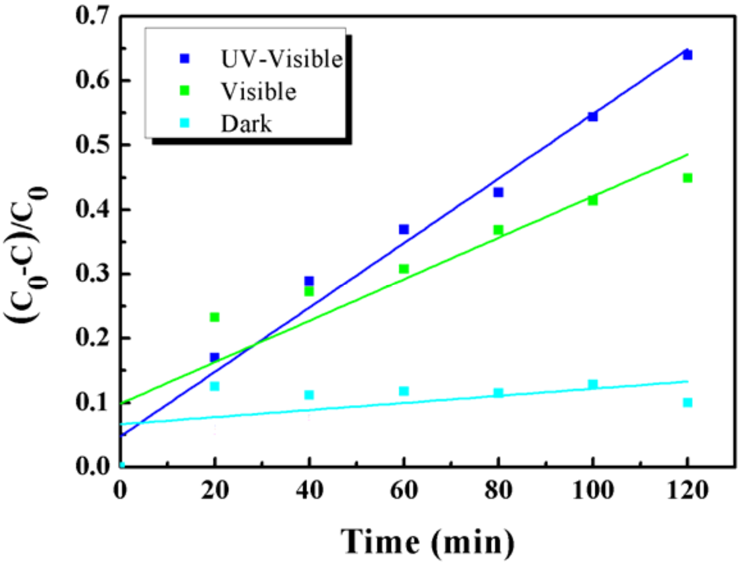


Fig.S11 Curves of degradation rate for the methyl orange solution degraded by UTSA-**38a** as a function of irradiation time under UV-visible, visible light and in the dark.

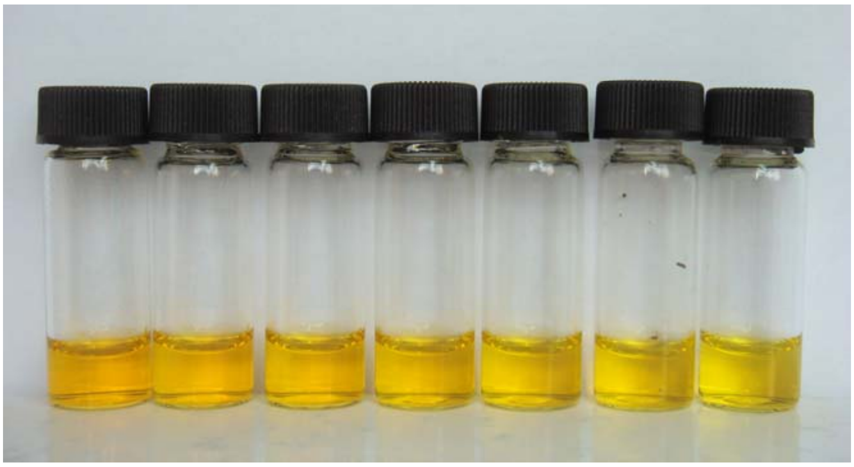


Fig.S12 Photograph showing the photocatalytic degradation under visible light for 0 min, 20 min, 40 min, 60 min, 80 min, 100 min and 120 min (from left to right respectively).

References

1. *Bruker APEX2*; Bruker AXS Inc.: Madison, WI, 2007.
2. *Bruker SAINT*; Bruker AXS Inc.: Madison, WI, 2007.

3. *Bruker SADABS*; Bruker AXS Inc.: Madison, WI, 2007.
4. A. L. Spek, *PLATON – a multipurpose crystallographic tool*, Utrecht University, Utrecht, The Netherlands, 2006.
5. G.M. Sheldrick, *SHELXTL, v. 2008/3*; Bruker Analytical X-ray: Madison, WI, 2008.