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Supplementary information

Synergy of vacancy engineering and plasmon modifacation for improving the photocatalytic performance of $La_2Ti_2O_7$ with broad band gap

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1. Materials and characterization

1.1 Materials

2,2,6,6-tetramethylpiperidine (TEMP), tryptophan (TRP), and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were purchased from Aladdin Reagent Co. Ltd (China). Titanium sulfate ($TiSO_4$), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH, 98%), sodium chloride (NaCl, 99.5%), disodium ethylenediaminetetraacetate (EDTA-2Na), silver nitrate ($AgNO_3$, 99.8%), isopropanol (IPA), sodium acetate (NaAc), lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, 99%), acetic acid (HAc) and 1,4-benzoquinone (BQ) were purchased from Sinopharm Chemical Reagent Co. Ltd (China). All the chemicals were analytically pure and used without further purification in this study.

1.2 Characterization

A Bruker AXS D8 Advance X-ray diffractometer (XRD) from Germany was used to analyze the crystal structure of the photocatalysts with a scan range of 2θ= 10-70° and a scan rate of 5° /min. A Raman spectroscopy wasused to investigated interaction forces of the materials. A SEM (Hitachi, S-4800, Japan) was used to observe the microstructure of the material, and the operating voltage was set to 3.0 kV. The structural morphology of the samples was characterized by TEM (Hitachi, JEM-2100 plus, Japan) and the operating voltage was set to 200 kV. The surface chemical state and elemental composition of the samples were accurately characterized by XPS (Kratos, Axis supra, UK). The light absorbing ability of the photocatalysts were characterized using a Shimadzu UV-3600 plus UV/Vis spectrophotometer. Fluorescence spectrometer (Edinburgh, FS5, UK) was used to measure the photoluminescence (PL) property of the photocatalysts, and the excitation wavelength setting 280 nm. The photoelectrochemical properties of the photocatalysts were measured using a CHI 660D electrochemical workstation (China). The prepared samples were used as working electrodes, and the counter and reference electrodes were platinum wire electrodes and Ag/AgCl electrodes, respectively. An ESR spectrometry (Bruker, EMXplus-10/12, Germany) was used to

detect the active substances and oxygen vacancy. The degradation intermediates were investigated by HPLC-MS (Waters, Maldi Synapt MS, UK).

2. Comparative analysis of LTO and OVLTO

The microscopic morphology of the prepared LTO and OV-LTO were observed by scanning electron microscope. As shown in Fig. S1a-b, the prepared OV-LTO retained the 2D lamellar structure after the thermal reduction of sodium borohydride. As shown in Fig. S1c, there was no significant difference in the XRD patterns of LTO and OV-LTO. In order to confirm the successful introduction of oxygen vacancy, electron paramagnetic resonance (EPR) tests were performed on LTO and OV-LTO, and the results were shown in Fig. S1d. It can be clearly seen that the signal of EPR could not be found in LTO. Whereas there was an obvious EPR signal at g =2.004 in OV-LTO, which was the typical signal of oxygen vacancies.

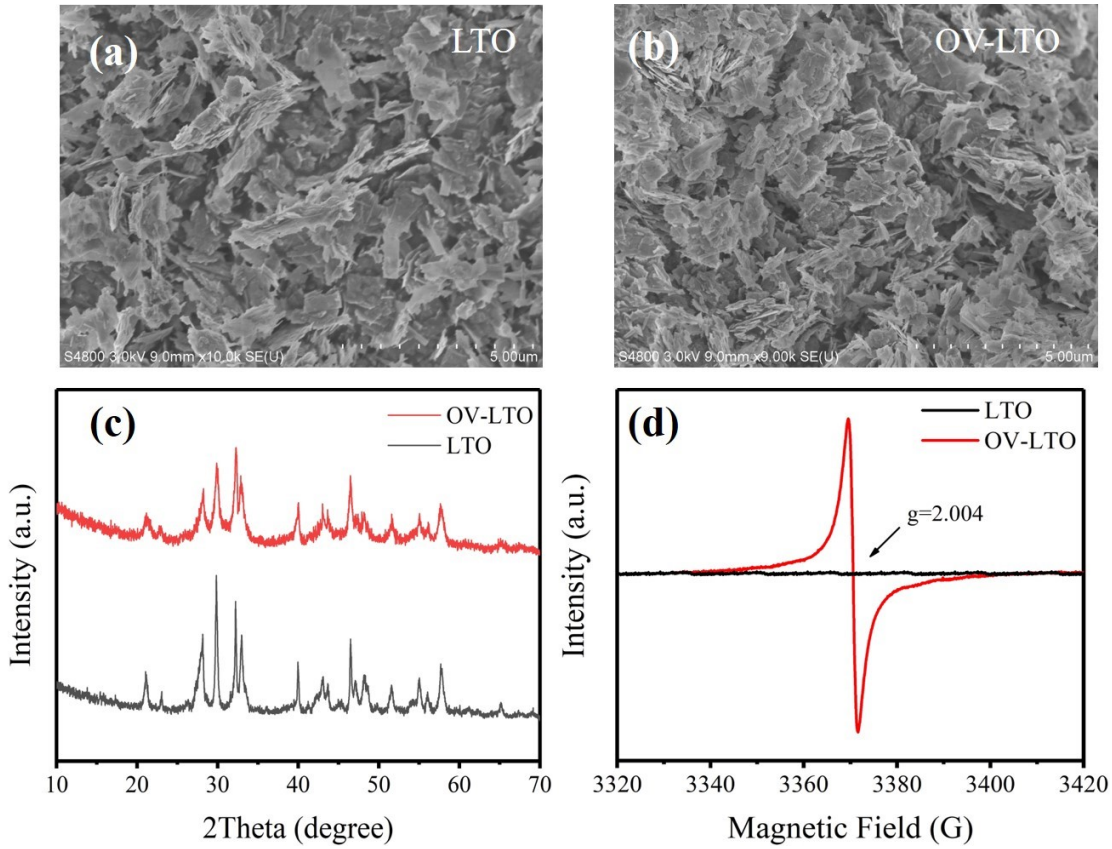
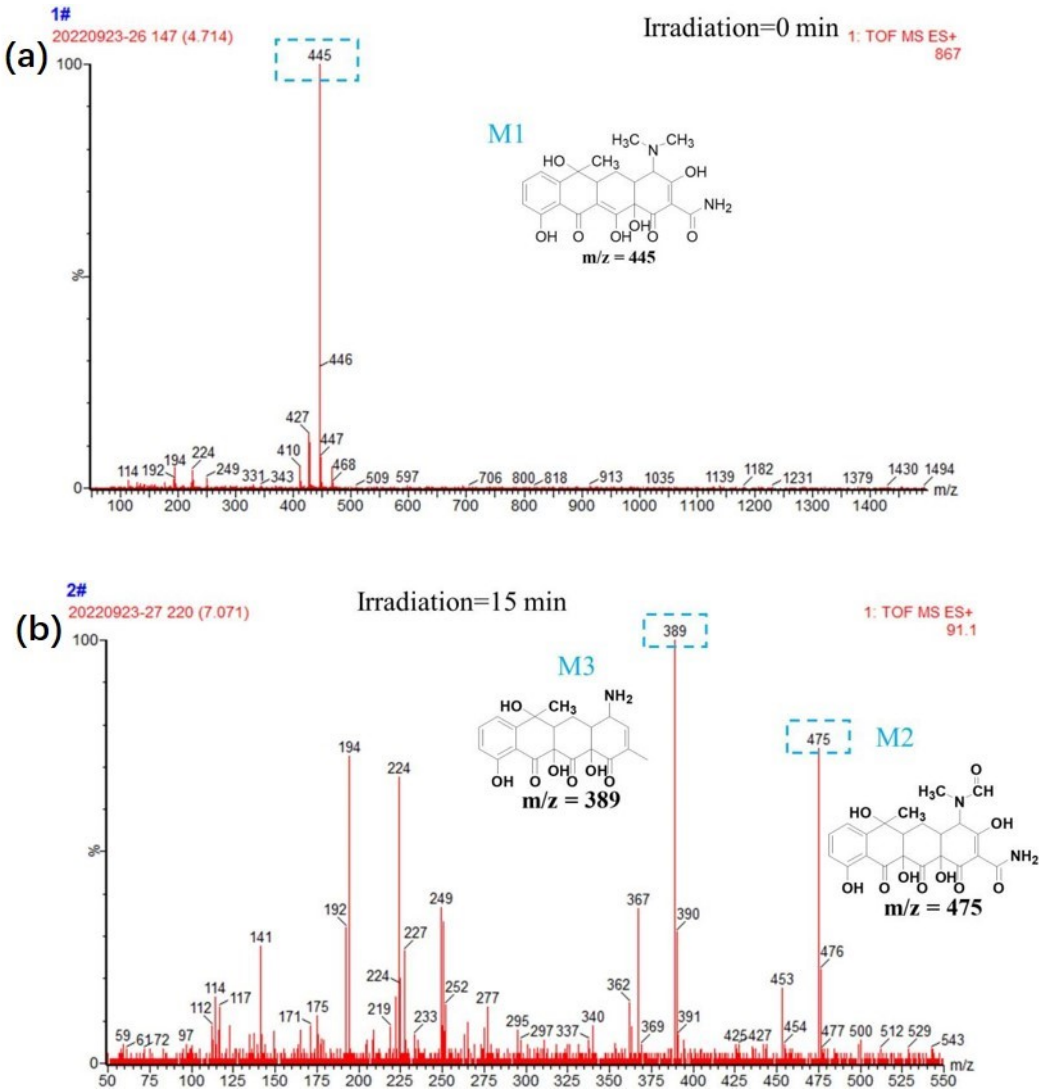
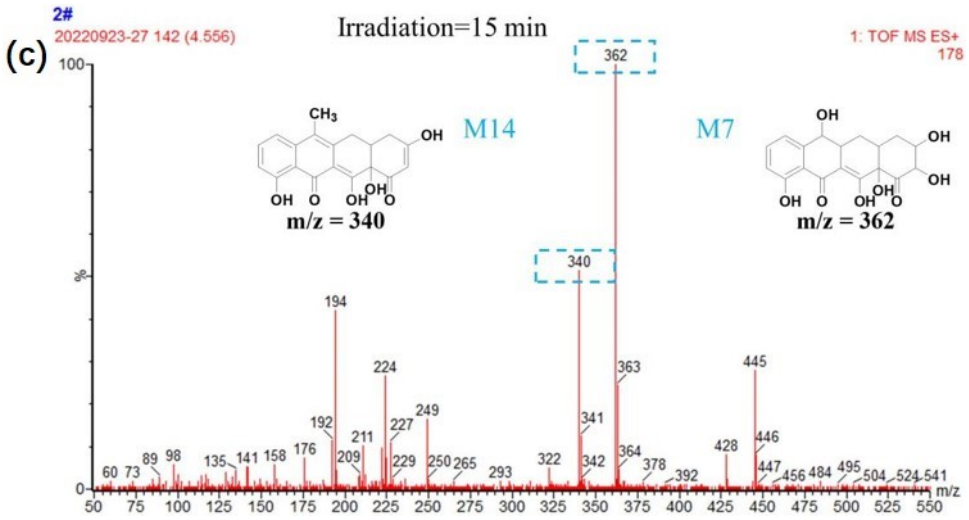


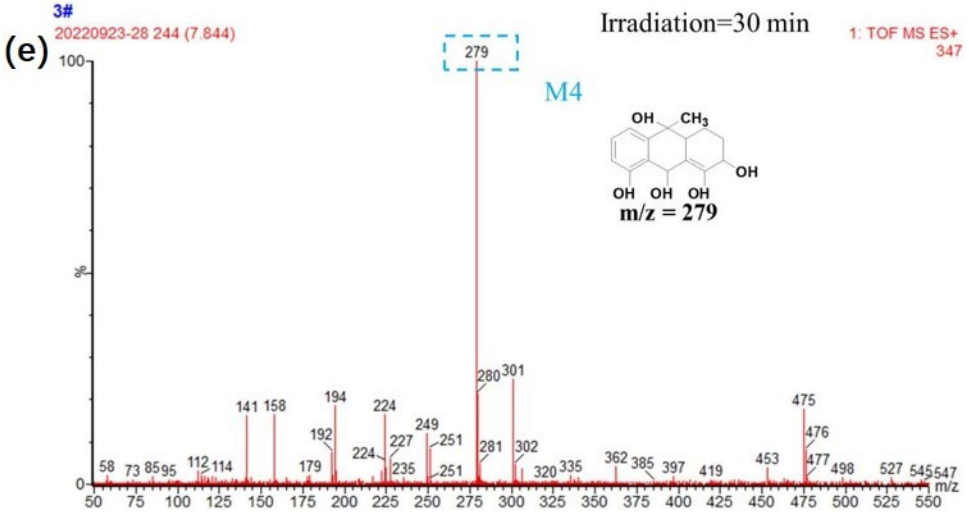
Fig. S1. Characterization of the LTO and OVLTO samples: SEM image of LTO (a) and OV-LTO (b); (c) XRD patterns and (d) ESR spectra of LTO and OV-LTO samples.

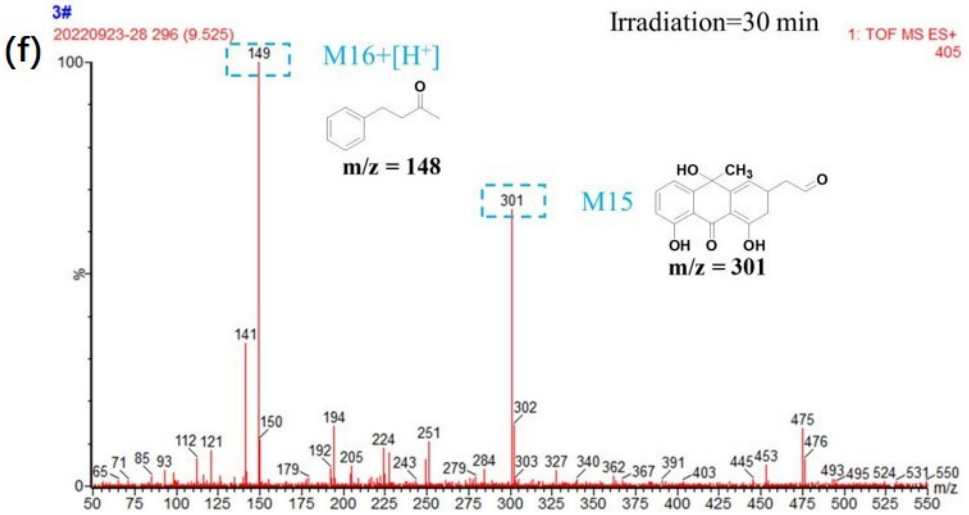
3. Analysis of degradation intermediates

To further investigate the photocatalytic degradation pathway of TC, the reaction intermediates in the degradation process were analyzed by HPLC-MS. As shown in Fig. S2a, the mass peak at m/z 445 (M1) belongs to TC. The main degradation intermediates with m/z 475, 389, 279, 194, 114, 362, 295, 224, 140, 128, 427, 410, 340, 301 and 148 (M2-M16) were shown in Fig. S2b-2i.




(c)
2#
20220923-27 142 (4.556)
Irradiation=15 min
1: TOF MS ES+
178
M14
m/z = 340
M7
m/z = 362
362
340
194
224
363
445
192
227
249
211
341
446
428
209
229
250
265
293
322
342
364
378
392
447
456
484
495
504
524
541
m/z


(e)
3#
20220923-28 244 (7.844)
Irradiation=30 min
1: TOF MS ES+
347
279
M4
m/z = 279
280
301
141
158
194
224
475
192
227
249
251
476
224
281
302
179
235
251
320
335
362
385
397
419
453
477
498
527
545
547
m/z


(f)
3#
20220923-28 296 (9.525)
Irradiation=30 min
1: TOF MS ES+
405
149
M16+[H+]
m/z = 148
301
M15
m/z = 301
141
302
150
194
475
112
121
224
251
476
192
205
243
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403
445
453
493
495
524
531
550
m/z

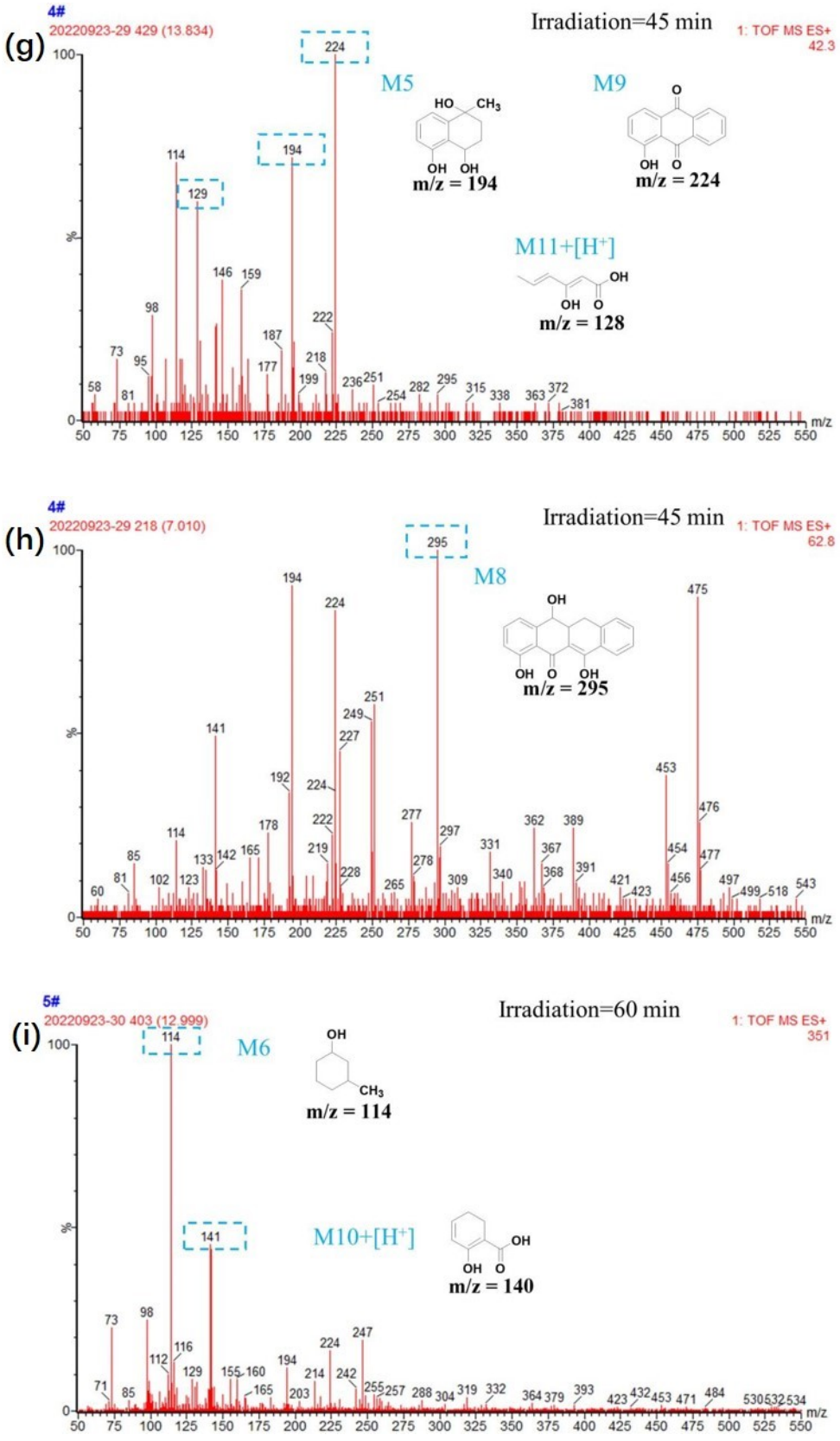

Fig. S2. HPLC-MS spectra of TC at different periods (0~60min) of photocatalytic degradation and analysis of degradation intermediates (a-i, M1-M16).