Electronic Supplementary Information (ESI)

Vacancies mediated Z-scheme charge transfer in 2D/2D La$_2$Ti$_2$O$_7$/g-C$_3$N$_4$ nanojunction as bifunctional photocatalysts for solar-to-energy conversion

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Experimental

Preparation of catalysts

Oxygen vacancy $La_2Ti_2O_7$ nanosheets (OVLTO) ware prepared by a hydrothermal assisted solid-state reaction. The pristine $La_2Ti_2O_7$ nanosheets ware prepared by a hydrothermal method. 2 g of as-prepared $La_2Ti_2O_7$ powder and 0.5 g of $NaBH_4$ were mixed in an agate mortar and heated to 400 °C under Ar atmosphere at a heating rate of 10 °C min^{-1}, and then held at the 400 °C for 2 h. Finally, the colored LTO sample was obtained by simply washing for several times and dried at 80 °C. g-C_3N_4 was prepared by heating melamine to 550 °C for 4 h. 500 mg of bulk g-C_3N_4 powder was ultrasonically exfoliated into thin nanosheets in 350 mL of water mixed ethyl alcohol for 40 h. To this dispersion, amounts of OVLTO nanosheets was added and then stirred at room temperature for 16 h assisted by 6 h of ultrasonication. OVLTO/CN composites were collected and dried at 60 °C. Nanocomposites with x % (weight ratio) loaded ODLTO were denoted as OVLTO-x/CN.

Characterization

The crystallinity of samples was analyzed by powder X-ray diffraction (XRD) on X'Pert Pro with Cu Kα radiation. The absorption edges and photoluminescence (PL) spectra of samples were tested by a Shimadzu UV 3600 Plus and Shimadzu, RF-5301. The morphologies and high angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) images of the sample were examined by transmission electron microscopy (JEM-2100F and Talos 200s). X-ray photoelectron spectra (Thermo Multi-lab 2000) were recorded on a spectrometer and the C 1s binding energy of adventitious carbon was 284.8 eV. Time-resolved transient PL decay

measurements were carried out by Edinburgh Instruments FLSP920. The excitation wavelength of PL analysis is 312 nm and the emission wavelength of TRPL analysis is 400 nm. Photo electrochemical analysis were tested by an electrochemical workstation (CHI660E) in a typical three-electrode system and the electrolyte was 0.5 M Na_2SO_4.

Photocatalytic H_2 evolution and CO_2 reduction

The photocatalytic hydrogen evolution experiments were taken in a 435 mL sealed quartz three-necked Pyrex flask. Four blue LED (4*3 W, 420 nm) served as the visible-light source. Cocatalyst Pt particles was loaded on serial photocatalysts by the photoreduction method: H_2PtCl_6 aqueous solution was added dropwise into the reactor and was reduced into Pt nanoparticles by irradiating the solution. In a typical progress, 50 mg of photocatalyst was dispersed in 100 mL of TEOA solution (10 vol%) solution. The system was deaerated by N_2 bubbling into the dispersion for 15 minutes to remove the dissolved oxygen in tube. 200 μL of gas was sampled at regular intervals (1 h) through the septum, and gas component was analyzed by a gas chromatograph (GC-2014C, Shimadzu, with Ar as a carrier gas,) equipped with a 5 Å molecular-sieve column and a thermal-conductivity detector. The photocatalytic CO_2 reduction was carried out in a glass vessel with a quartz glass top (Perfectlight, China). The Petri dish with 20 mg catalyst was put on the bottom of vessel. The high-purity CO_2 was used as CO_2 source. Each set of experiment was irradiated by 300 W Xe lamp with 420 nm filter. Furthermore, the gas products were qualitatively analyzed by gas chromatography (GC-7820，Zhongkehuifen) through observing and comparing

the chromatographic peaks with those for the authentic CH_3OH, CH_4, CO. The *in-situ* FT-IR experiment was performed on a Bruke Tensor II FT-IR spectrometer. Firstly, we dropped 50 µL H_2O on the surface of as-prepared samples. Then, the samples were sealed in the specimen chamber. After that, the pure CO_2 was followed into the specimen chamber. and the infrared absorbance spectra were recorded simultaneously. After 30 min later, the specimen chamber loaded with the samples was irradiated from the SiO_2 window with a Xe lamp for another 1 h.

The AQY of CO_2 reduction reaction was measured using LED lamp (420 nm) as light source. The irradiation area was 1 cm^2. The light intensity was 4µW cm^{-2}. The AQY was calculated as AQY=N_e/N_p*100%=(6M_1+2M_2)$N_A hc$/($SEt\lambda$)*100%. (N_e, the number of generated electrons; N_p, the number of photons; M_1 and M_2, the generated CH_3OH and CO molecules, respectively; N_A, the Avogadro constant; h, the Planck constant; c, the speed of light; S, the irradiation area; E, the light intensity; t, the reaction time; λ, the wavelength)

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DFT computational details

Vienna ab initio simulation package (VASP) calculation based on density functional theory (DFT) was used to calculate the electronic structure of perfect

La$_2$Ti$_2$O$_7$ unit cell, La$_2$Ti$_2$O$_7$ with surface oxygen vacancy and single layer g-C$_3$N$_4$ and charge difference distribution of oxygen defective La$_2$Ti$_2$O$_7$/g-C$_3$N$_4$ composite. The exchange-correction function was measured by the Perdew-Burke-Ernzerhof formulation of the generalized gradient approximation. The cutoff energy of atomic wave functions was 400 eV and the k-points 4×4×3 and 3×3×3 are performed in the calculations of two types La$_2$Ti$_2$O$_7$ and g-C$_3$N$_4$, respectively. Besides, work functions of La$_2$Ti$_2$O$_7$ with surface oxygen vacancy and monolayer g-C$_3$N$_4$ calculations in this work were performed by CASTEP code. The ultrasoft pseudopotential was used to investigate the interaction between the ionic core and valence electrons. In addition, the convergence criteria of geometric optimization were synergically achieved by the convergence thresholds of $1.0*10^{-5}$ eV/atom for total energy, 0.03 eV/Å for maximum force, 0.05 GPa for maximum stress, and 0.001 Å for maximum displacement.
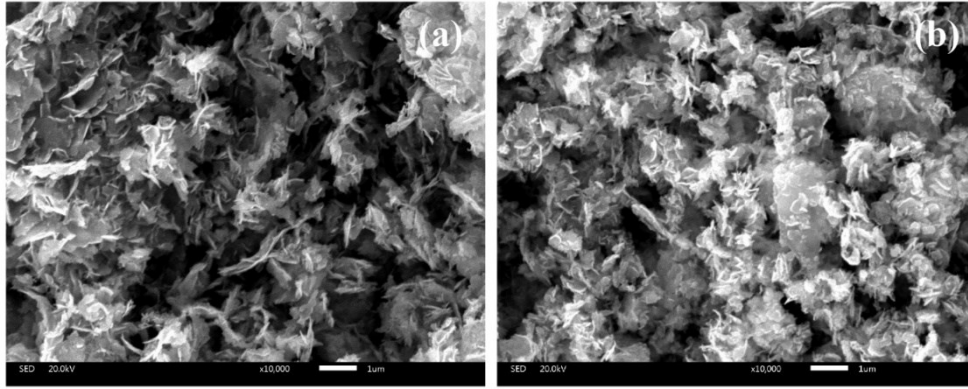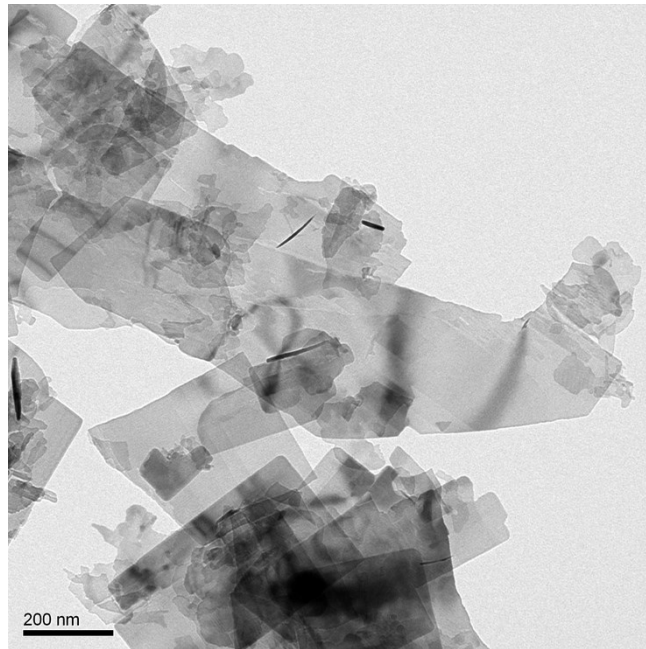
Fig. S1. SEM images of (a) LTO and (b) OVLTO.
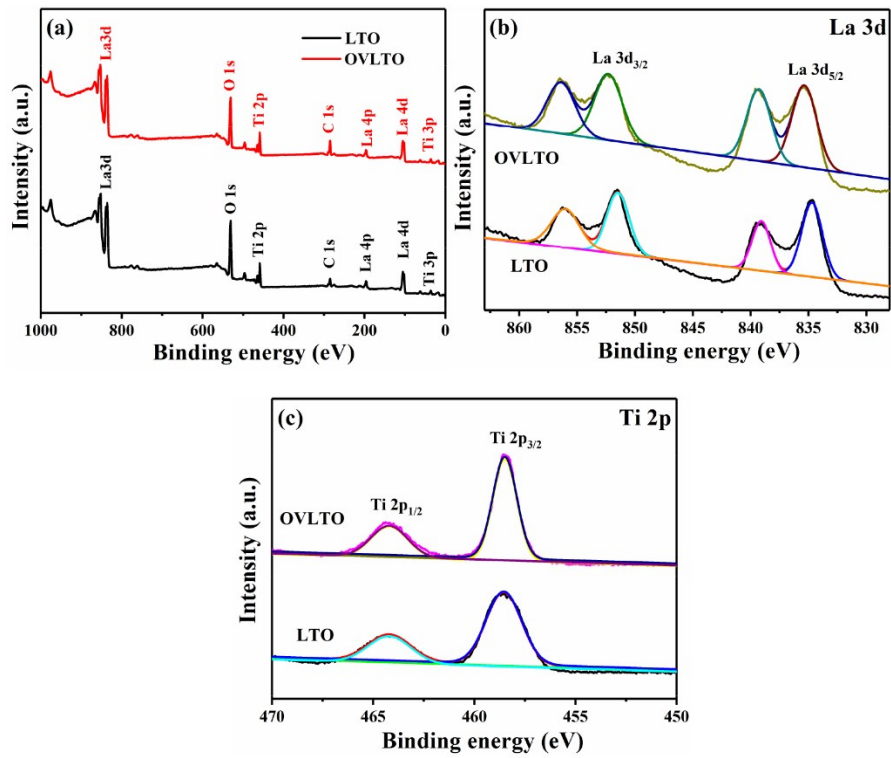

Fig. S2. TEM image of LTO nanosheets.

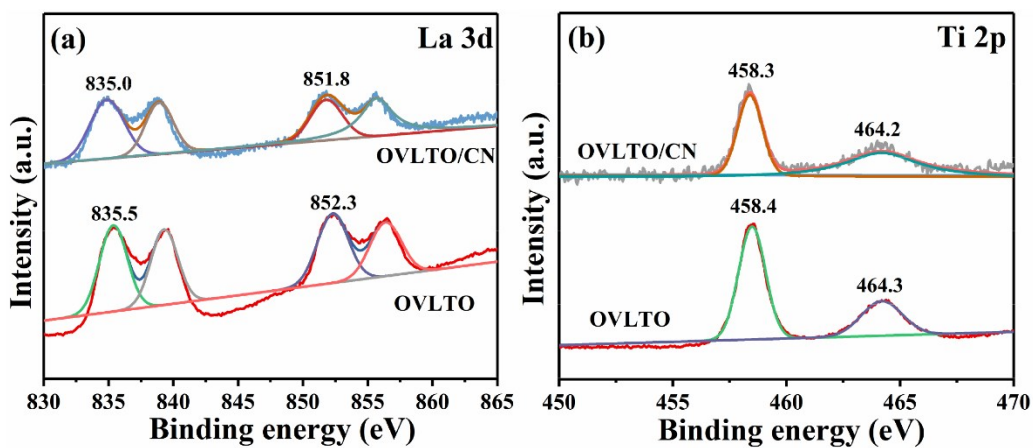**Fig. S3.** (a) XPS Survey spectra, (b) La 3d spectra and (c) Ti 2p spectra of LTO and OVLTO.

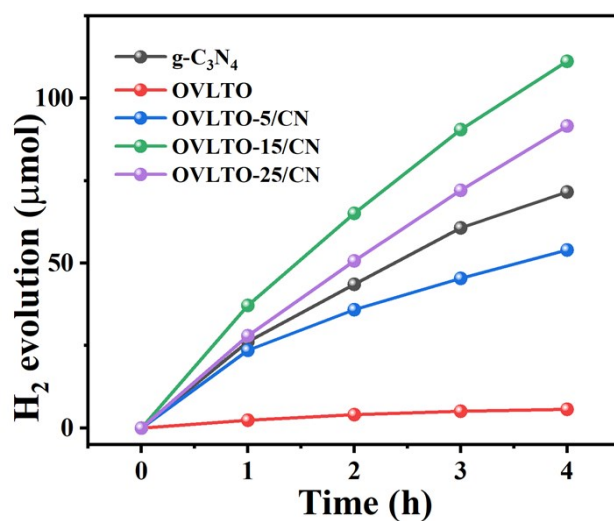**Fig. S4.** (a) XPS La 3d spectra and (b) Ti 2p spectra of OVLTO and OVLTO/CN.

Fig. S5. Time course of H_2 evolution over different samples with CH_3OH as sacrificial agent.

Table S1 Summary of the photocatalytic hydrogen evolution of g-C$_3$N$_4$ based catalysts.

| Catalysts	Light source	Incident light	H$_2$ rate (μmol g^{-1}h^{-1})	AQY	(Ref)
g-C$_3$N$_4$/Bi$_4$NbO$_8$Cl	Xe lamp	$\lambda > 420$ nm	287.71	2.02%, 420 nm	58
FeP/g-C$_3$N$_4$	Xe lamp	$\lambda > 420$ nm	177.9	1.57%, 420 nm	52
CoTiO$_3$/g-C$_3$N$_4$	Xe lamp	$\lambda > 420$ nm	858	3.23%, 420$\pm$20 nm	39
g-C$_3$N$_4$/TiO$_2$	Xe lamp	$\lambda > 420$ nm	513	0.31%, 420 nm	6
g-C$_3$N$_4$/N-La$_2$Ti$_2$O$_7$	Xe lamp	$\lambda > 400$ nm	430	2.1%, 400 nm	20
Modified g-C$_3$N$_4$	Xe lamp	$\lambda > 420$ nm	661	2.88%, 420$\pm$20 nm	54
g-C$_3$N$_4$-Py	Xe lamp	$\lambda > 420$ nm	398	1.18%, 420 nm	53
OVLTO/CN	LED lamp	$\lambda = 420$ nm	1485	3.61%, 420 nm	This work
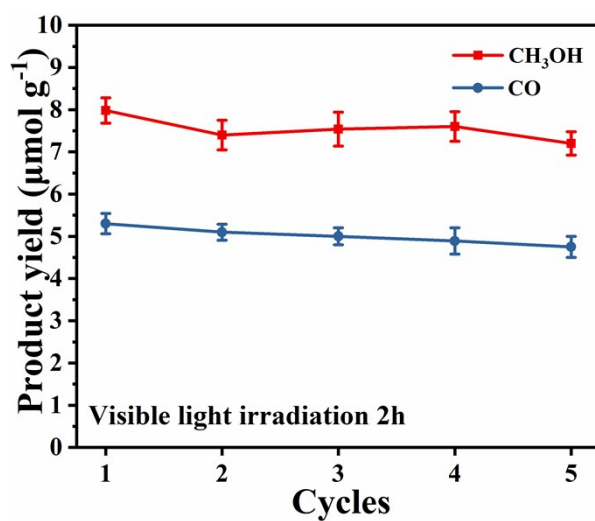
Fig. S6. Photostability test of OVLTO-15/CN sample under visible light irradiation.
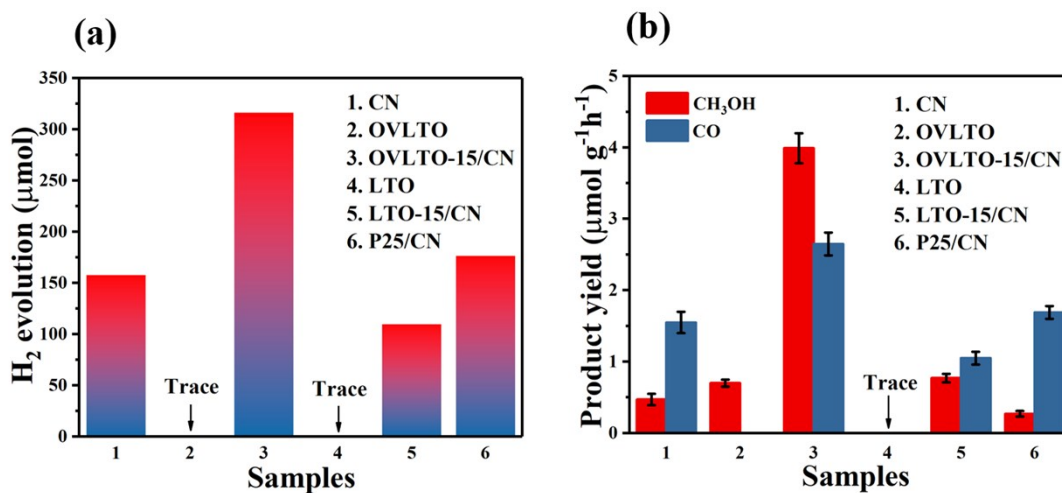
Fig. S7 Photocatalytic (a) H_2 generation and (b) CO_2 reduction over different catalysts.
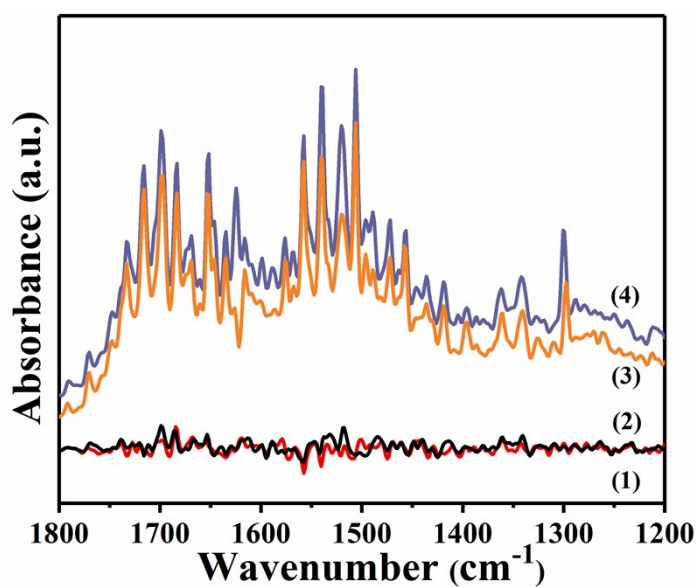

Fig. S8. The *in situ* FTIR spectra of the OVLTO-15/CN sample in different wavenumber ranges: (1) without CO_2 gas, (2) with flowing CO_2 gas for 30 min without irradiation, and (3) irradiation for 15 min and (4) 30 min.
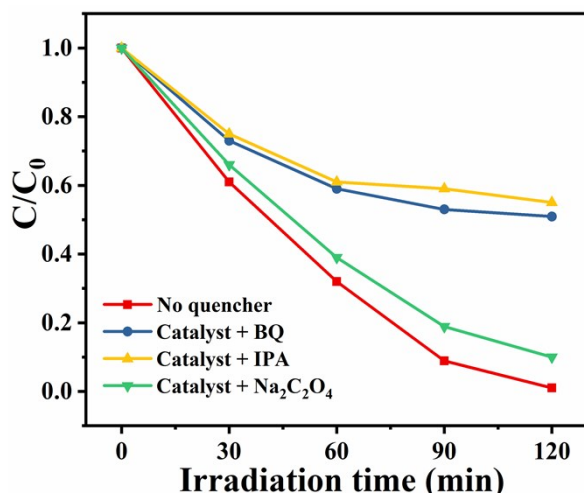
Fig. S9. Photocatalytic degradation of dye over OVLTO-15/CN with different scavengers.

Table S2 PL lifetime τi and corresponding constant Rel. %.

Sample	τ_1 (Rel.%)	τ_2 (Rel.%)	$<\tau>$
CN	2.3 ns (48)	9.6 ns (52)	8.28 ns
OVLTO/CN	2.6 ns (45)	10.5 ns (55)	8.96 ns
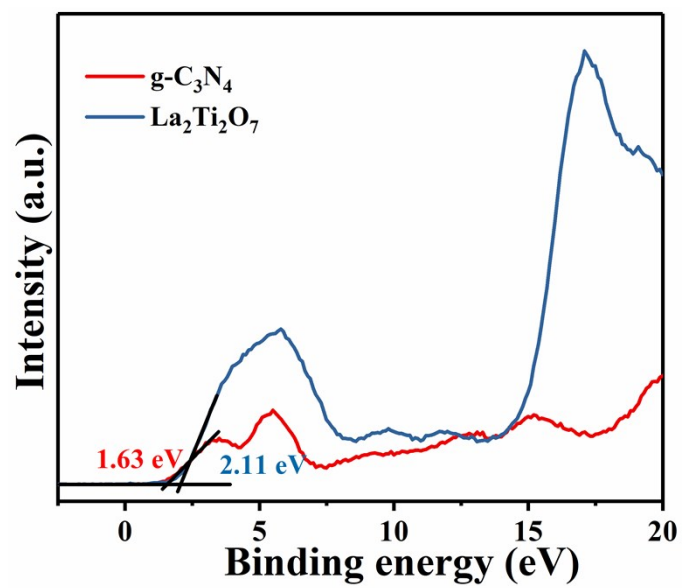
Fig. S10. VB-XPS spectra of g-C$_3$N$_4$ and OVLTO sample.