Supplementary information for

Interface Modification by Defects Engineering for g-C_3N_4/$LaPO_{4-x}$ Core-shell Nanorods towards Efficient CO_2 Photoreduction

Sai Yan [a], Lei Chen [a], Fangyu Peng [a], Yuanyuan Fan [a], Yanlong Yu [a,*], Yue Liu [b,*], and Yaan Cao [c]

[a] Faculty of Mathematics and Physics, Huaiyin Institute of Technology, Huaian, 223003, People's Republic of China.

[b] College of Material Science Engineer, Liaoning Technical University, Fuxin, 123000, People's Republic of China

[c] Key Laboratory of Weak-light Nonlinear Photonics, Ministry of Education, TEDA Applied Physics Institute and School of Physics, Nankai University, Tianjin, 300457, People's Republic of China

Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu Kα, λ=1.54056 Å). High-resolution transmission electron microscopy (HRTEM)images were obtained by a JEOL 3010, for which the samples were prepared by applying a drop of ethanol suspension onto an amorphous carbon-coated copper grid and dried naturally. X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo ESCALAB 250XI spectrometer using an unmonochromated Al Kα (1486.6 eV) X-ray source. The electron spin resonance (ESR) spectra were measured on a Bruker a300 spectrometer at room temperature in air. Diffuse reflectance UV−visible absorption spectra were collected on a UV–visible spectrometer (UV-

1061PC, Shimadzu). Photocurrent measurements were performed on a CS 300 electrochemical workstation (CorrTest, Wuhan, China) in a conversional three electrode configuration with a Pt foil as the counter electrode and a Ag/AgCl (saturated KCl) reference electrode. A 500 W Xe arc lamp severed as a light source. A 1 M Na_2SO_4 aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 10 mg of the prepared photocatalyst was added into 1 mL of ethanol to make slurry under ultrasonic treatment. The slurry was then spread on a 2 × 1 cm^2 FTO glass substrate with an active area of about 1 cm^2 by the doctor-blade method, using adhesive tape as the space. The films were dried in air and annealed at 400 ^oC for 60 min in air. The photo-responses of the samples as light on and off were measured at 0.0 V. The electronic spin resonance (ESR) technique was measured on an electron paramagnetic resonance spectrometer (EMXplus-6/1, Bruker).

Theory Calculation

A model of 72 atoms for (1 0 0) plane of $LaPO_4$ was constructed. The density functional theory (DFT) calculation was performed by using first-principle calculation software package CASTEP. Generalized gradient approximation (GGA)-based density functional theory (DFT) was used to calculate electronic band structure band structure and density of states (DOS) for $LaPO_4$ slab. The plane wave cutoff was set to be 300 eV and the k-point set was 1 × 3 ×1. The valence electronic configurations for La, O and P were $5s^25p^65d^16s^2$, $2s^22p^4$ and $3s^23p^3$, respectively.

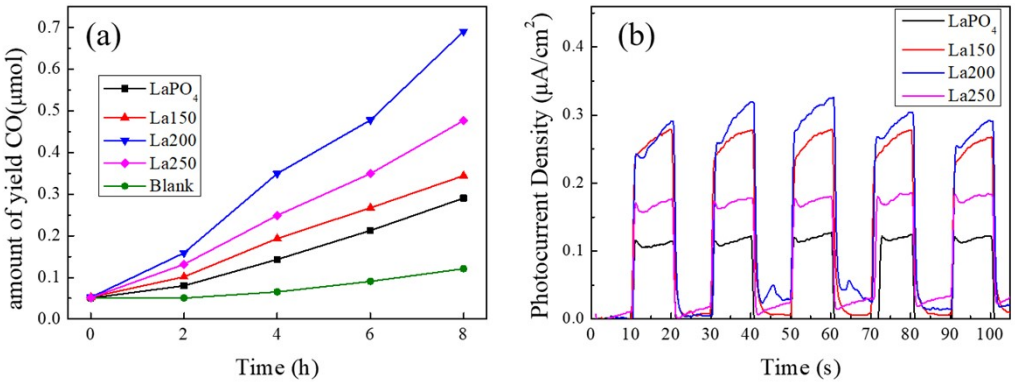

Figure S1. (a) Photocatalytic results on photo-reduction of CO_2 into CO and (b) photocurrent response spectra of $LaPO_4$ and $LaPO_{4-x}$ (La150, La200 and La250) nanorods.

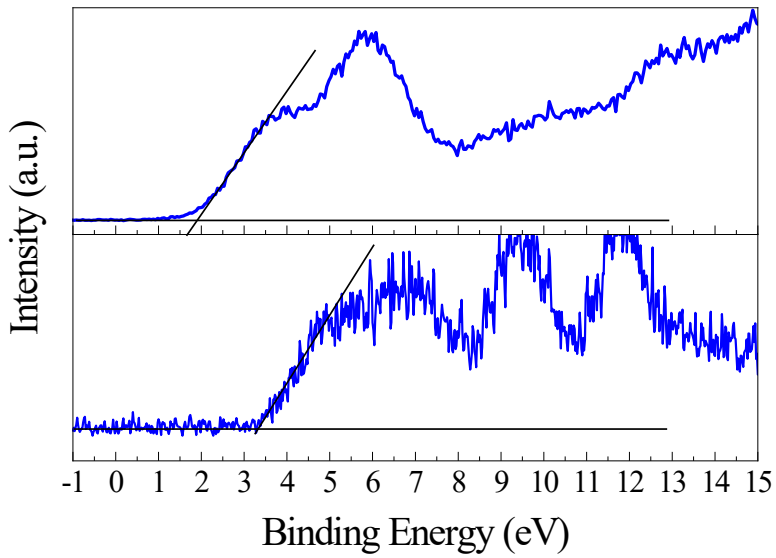

Figure S2. XPS valence band of g-C_3N_4 and La200.

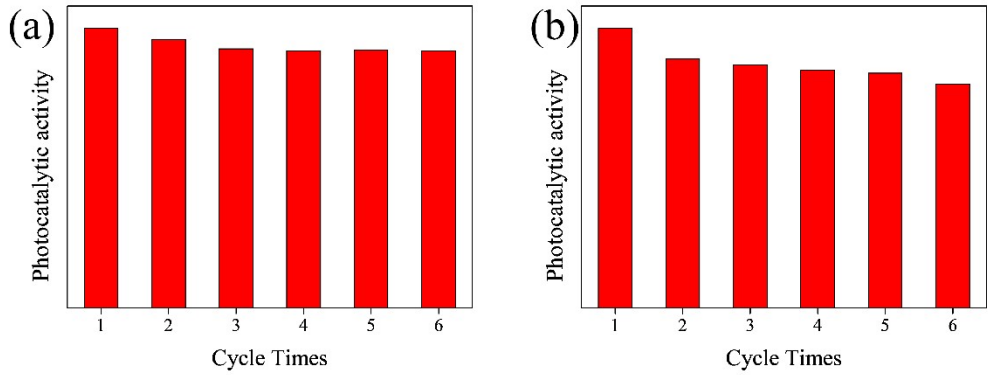

Figure S3. Photocatalytic stability of (a) g-C_3N_4/La200 and (b) La200.

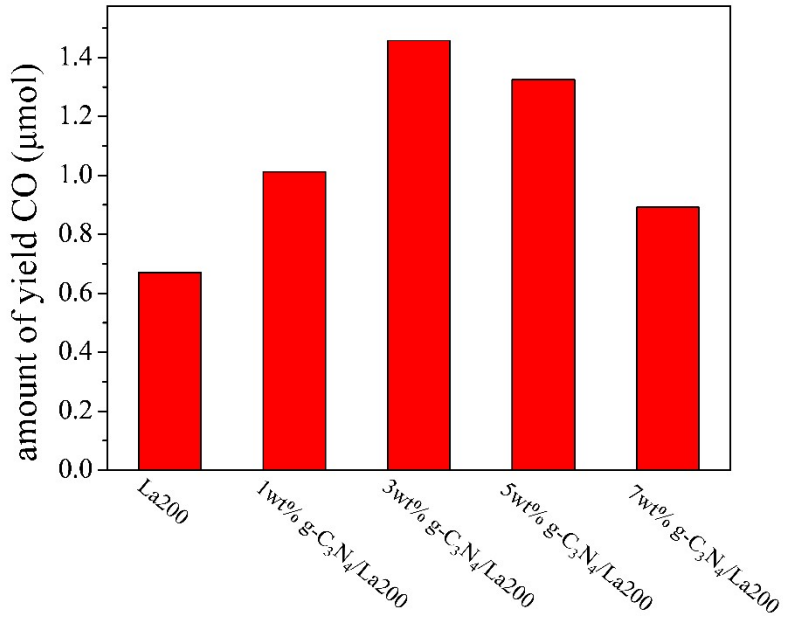

Figure S4. Photocatalytic activity of Xwt% g-C_3N_4/La200.

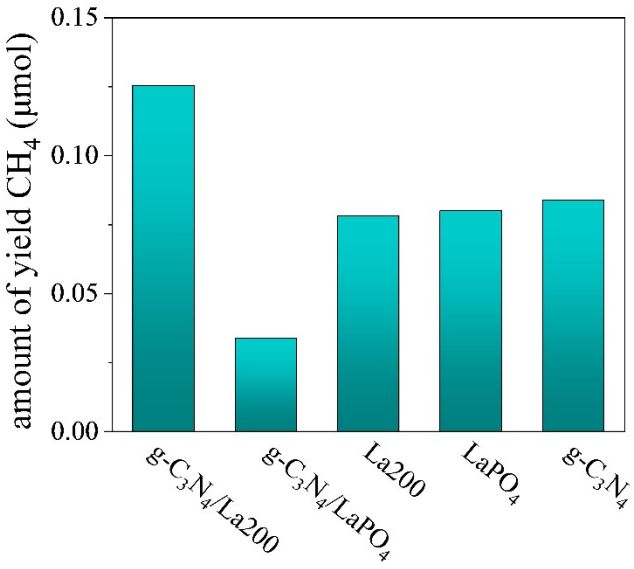

Figure S5. Photocatalytic results of photo-reduction of CO_2 into CH_4 for g-C_3N_4, $LaPO_4$, La200, g-C_3N_4/$LaPO_4$ and g-C_3N_4/La200.

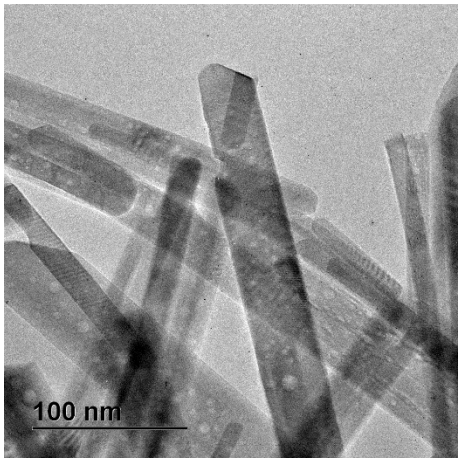

Figure S6. TEM image of g-C_3N_4/La200 samples after six runs of photocatalytic reaction.

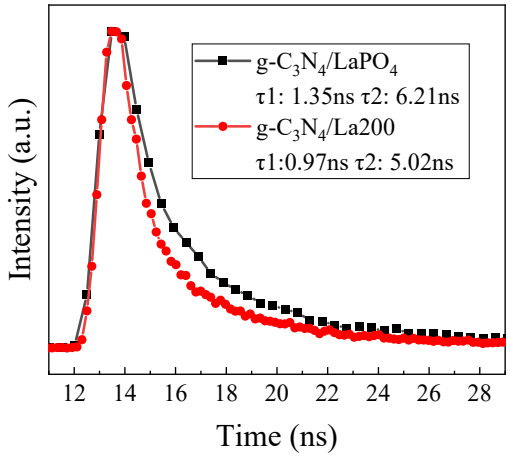

Figure S7. Time-resolved PL decay curves for g-C3N4/LaPO4 and g-C3N4/La200 (excited at 300 nm and monitored at 450 nm).