Electronic Supporting Information

Enhanced visible-light photoactivities of porous LaFeO$_3$ by synchronously doping Ni^{+2} and coupling TS-1 for CO$_2$ reduction and 2,4,6-Trinitrophenol degradation

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1.1 Photoluminescence spectroscopy

In this work, the photoluminescence (PL) spectra of as prepared samples were recorded with the help of model PE LS 55 Spectro fluorophotometer (Waltham, MA, USA) along with excitation and emission wavelength operating at 325 and 460 nm. The spectrophotometer work at different operating mode, one is excitation and the other one is emission wavelength. The excitation and emission scanning mood were fixed at sample absorption point at which their absorption maximum vice versa.

1.2 Photoelectrochemical measurement

The as prepared samples were checked for PEC measurement. In the typical procedure we took 0.1 g of as prepared sample in a small vial, dispersed in 1.0 mL of isopropyl alcohol followed by continuous stirring for 0.5 h to get homogeneous solution. Afterward add 0.1 g PEG and 0.05 mL acetyl acetone, sonicated, and stirred for next 1 hr, and then kept for next 3 day on continuous stirring in order to receive homogenies paste. The as prepared colloidal pastes were homogeneously dropped on the surface of clean FTO glasses. Then FTO glass containing paste are chip into 2.0 cm × 4.0 cm size small strips and thermally heated in muffle furnace for 30 min at 450 °C, in addition electrochemical impedance spectra were along with single wavelength photocurrent action spectra were analyzed. PCA were basically performed in 3 electrode system, including photocatalyst considered as working electrode, KCl wet Ag/AgCl electrode counted as reference electrode while Pt plate as counter electrode. Sodium sulphate 0.5 molar solution was used as electrolyte during experiment. All experiments were performed quartz cell along

with 500 W xenon lamp with cut off filter of 420 nm as monochromatic single wavelength sources, and V13806 (IVIUM, China) electrochemical (EC) workstation.

1.3 Measurement of the amount of hydroxyl free radicals

The fluorescence spectroscopy (FS) was performed to measure number of OH radical produced during photochemical reactions. In the typical procedure 0.05 g of the subject photocatalyst were dispersed in 50 mL of aqueous coumarin solution having concentration of about 0.05 g·L^{-1} (molar solution). The as prepared solution reaction vessel was irradiated by 150 W xenon lamp along with cut off filter (λ > 420 nm) for 1 h with vigorous stirring. The reaction vessel was kept at the distance of 10 cm from Xenon lamp to keep the light intensity of each experiment is consistent. After post irradiation, a small aliquot was taken, filtered by high-speed centrifuge, and analyzed by spectrofluorometer at excitation wavelength of 350 which was the typical excitation wavenumber of the produced 7-hydroxycoumarin.

1.4 Free radicals trapping experiments

In order to confirm photocatalytic mechanism and degradation involving species in degradation process, scavenger experiments were performed. In the typical procedure 3 different scavenging species including the widely used EDTA-2Na, the isopropyl alcohol (IPA) and benzoquinone (BQ) are utilized to detect the already phot excited holes, hydroxyl radicals ($^{\bullet}$OH) and superoxide radicals ($O_2^{\bullet-}$) accordingly. In the typical experimental procedure, took few drops of 1 mM scavenger solutions and added to TNP solution and irradiated for next 1 hr. After 1 h irradiation, we take 5 mL of solution, filter and checked for TNP concentration at 285 nm.

1.5 CO$_2$ TPD measurements

Analysis of CO$_2$ TPD carried out by utilizing Micromeritics AutoChem II 2920 apparatus. In standard experiment, about 50 mg of the defined sample are pre-treated to 280 °C for 45min in the presence highly pure Helium surge to take out the already absorbed humidity and gas phase molecule. After naturally cooling, the highly pure CO$_2$ gas introduced into the distinct samples at 50 °C with a flow spurt rate 45 mL·min^{-1} for 1 h. Afterwards, the resulting sample are allowed for physio-chemical type reaction under highly pure helium gas at 45 °C for 1 h in order to root out physically adsorbed CO$_2$ gas. Consequently, the defined temperature is reached to 650 °C at with heating rate at 5 °C for 2 h in the presence of helium gas. Notably, the well absorbed CO$_2$ gas are analyzed with TCD detector.

1.6 Photocatalytic pollutants degradation

The photocatalytic activities for 2,4,6-Trinitrophenol (TNP) degradation are accomplished in the presence of visible-light flash. In the typical procedure, specific amount (0.2 g) of photocatalyst, were dispersed in 80 mL of TNP solution (10 mg·L^{-1}). The reaction mixture was put into 250 mL of Pyrex glass beaker or glass reactor. Before starting reaction, the solutions mixture was vigorously stirred for 30 min in dark to get equilibrium and then irradiated under xenon lamp of 150 W along with visible-light cut off (> 400 nm). After specific time interval (1 hr interval), 5 mL of the solution was taken trough syringe, filtered, and checked for pollutant degradation activities measurements at wavelength of 285 nm, by utilizing UV-visible light spectrophotometer (model Shimadzu UV 2700).

1.7 Inductively coupled plasma emission spectroscopy (ICP-AES) measurements

The elemental contents and nature of the as synthesized samples are investigated ICP-AES. The analysis was carried out on an Agilent 720ES. In typical experiment, 0.1g (accurate to 0.0001g) are dissolved in water in a 150mL conical flask, consequently 20mL of perchloric acid are added after this 10mL of HCl are added. After complete digestion of sample, the standard experimental method is used to complete the reaction.

1.8 Photocatalytic CO$_2$ reduction

The standard experimental procedure for CO_2 reduction activities measurement as given: 0.2 g of photocatalyst were dispersed in 5 mL deionized water and transferred into a cylindrical steel reactor with 100 mL volume and area 3.5 cm^2 and sonicated for 5 min to get homogenous solution. Accordingly, highly pure and concentrated CO_2 was passed through water bubbler for pressure maintenance and consequently allow to defined reaction assembly. After 30 mints when the equilibrium position was attained, the reaction system was allowed for photocatalytic reaction with constant flow of CO_2 gas and irradiation under 300 W Xenon lamp with cut off filter ($\lambda \geq 420$ nm). After certain time interval of irradiation (1 h) 0.3 mL of gaseous product were collected through syringe and the collected sample were injected into GC by the TCD and FID detector gas chromatograph (Tech, GC-7920 by N_2 gas carrier with a CO_2 converter).

Fig. S1 Comprehensive synthetic scheme of Ni^{+2} species doped, and TS-1 coupled porous LaFeO$_3$ nanocomposite by utilizing carbon nanosphere (CNS) as sequential template approach (STA)
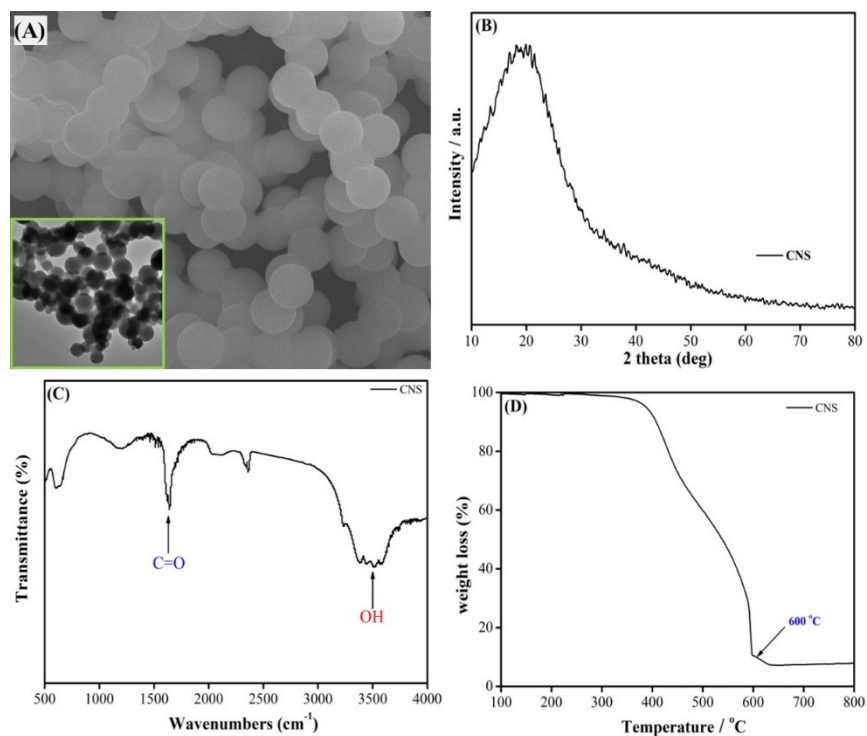
Fig. S2 SEM image with TEM image as the inset (A), XRD pattern (B), FTIR spectra (C), and TGA curve (D) of CNS template.
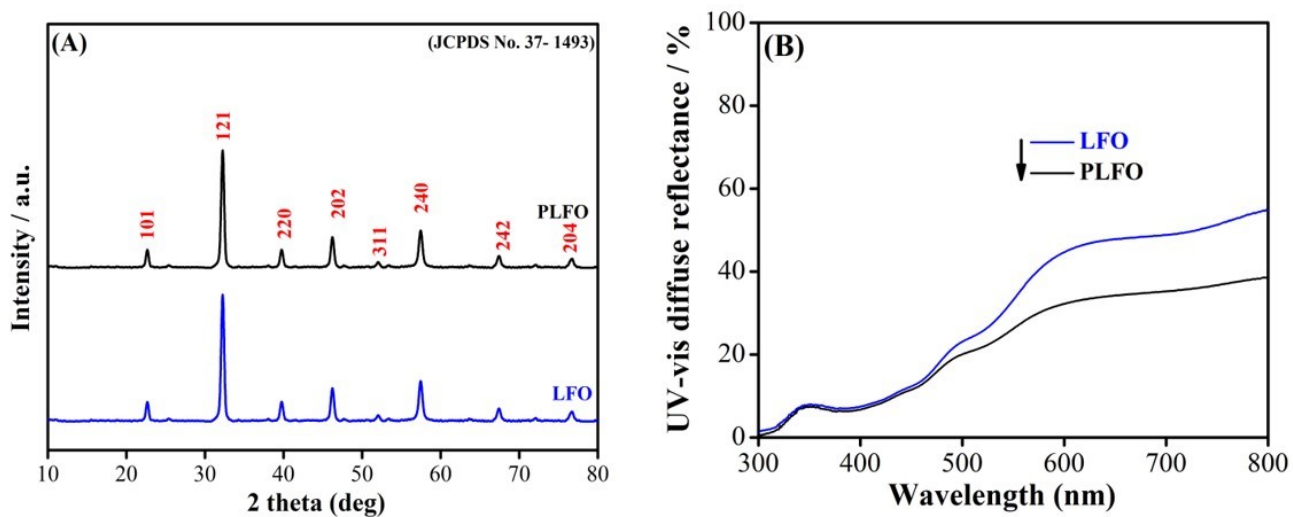
Fig. S3 XRD Patterns (A), and Uv-Vis DRS spectra (B) of LFO and PLFO samples.
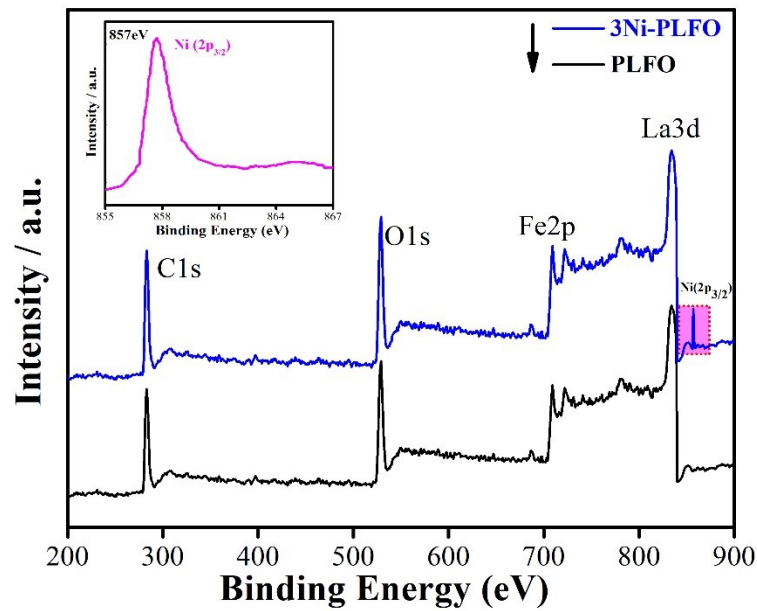
Fig. S4 High resolution XPS spectra with Ni spectra as the inset of PLFO and 3Ni-PLFO nanocomposite.
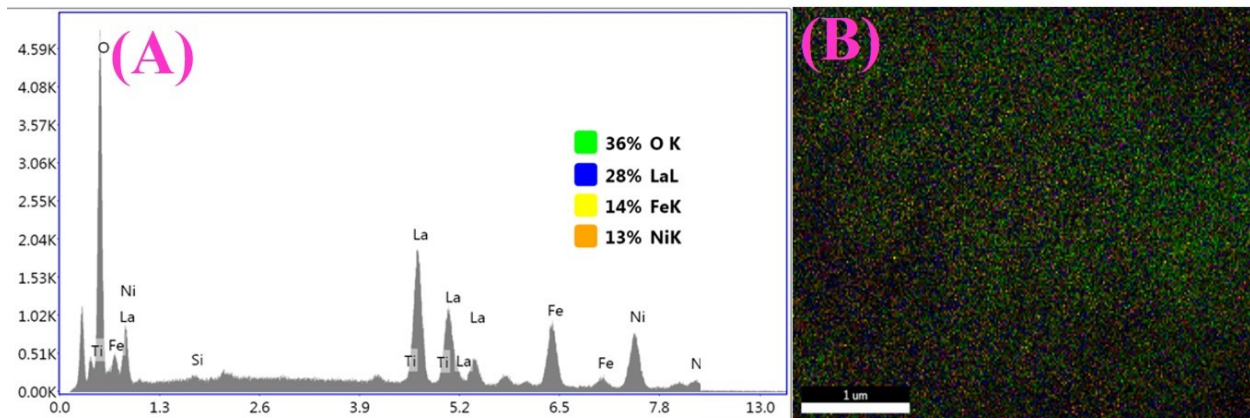
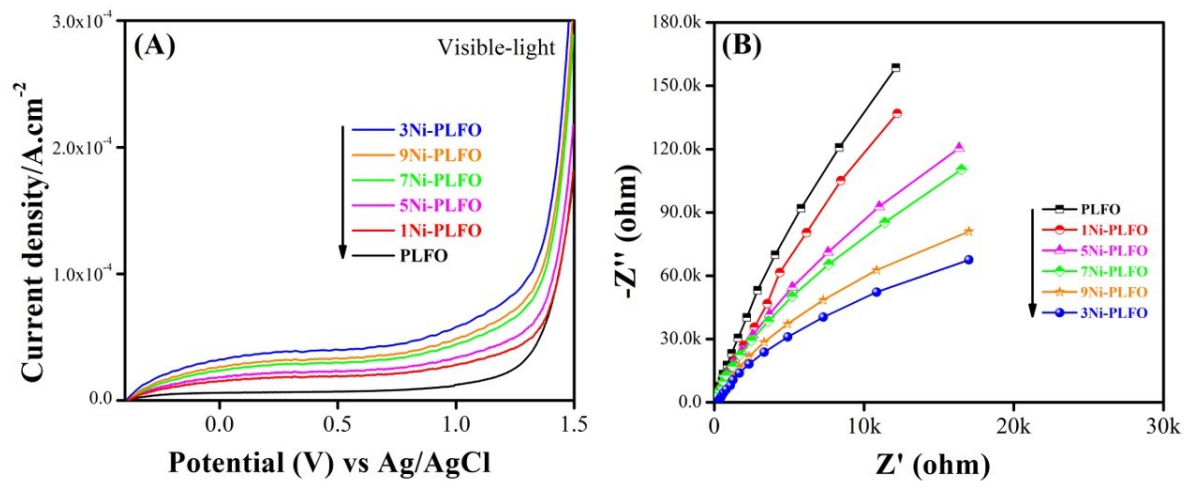**Fig. S5** TEM (EDX) and elemental mapping of PLFO and 3Ni-PLFO nanocomposite.

Fig. S6 PEC I-V curves (A), and electrochemical impedance spectra (B) of PLFO and XNi-PLFO nanocomposite.
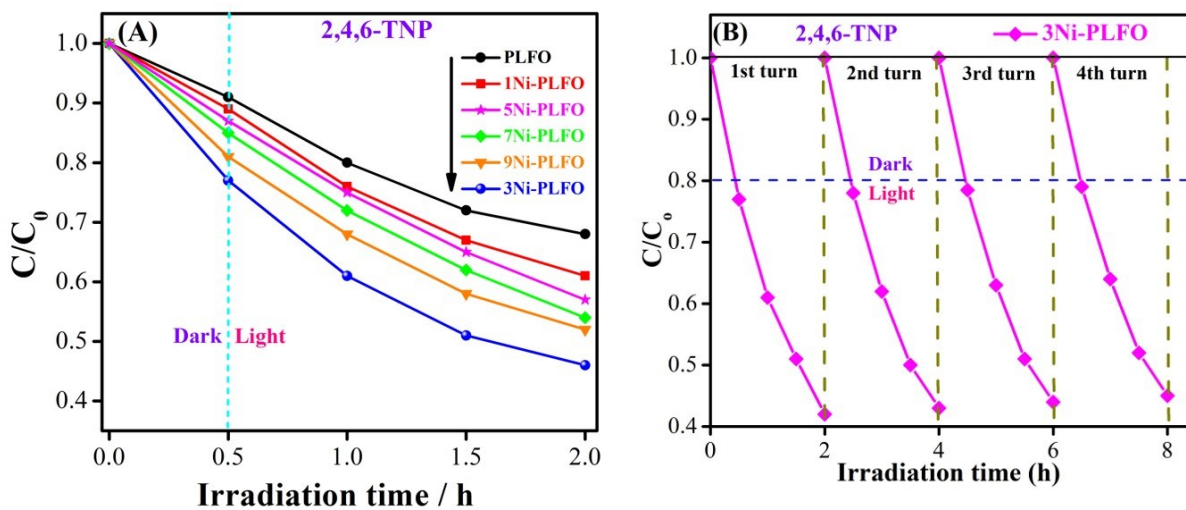
Fig. S7 Degradation rate of PLFO and XNi-PLFO (A), and stability test of 3Ni-PLFO (B) for 2,4,6 TNP degradation.
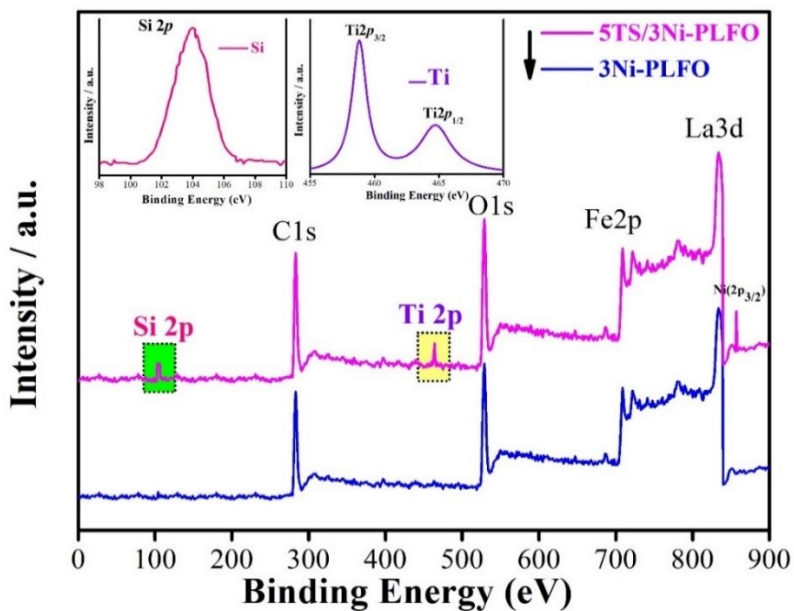
Fig. S8 High resolution XPS spectra with Si, Ti spectra as the inset of 3Ni-PLFO and 5TS/3Ni-PLFO nanocomposite.
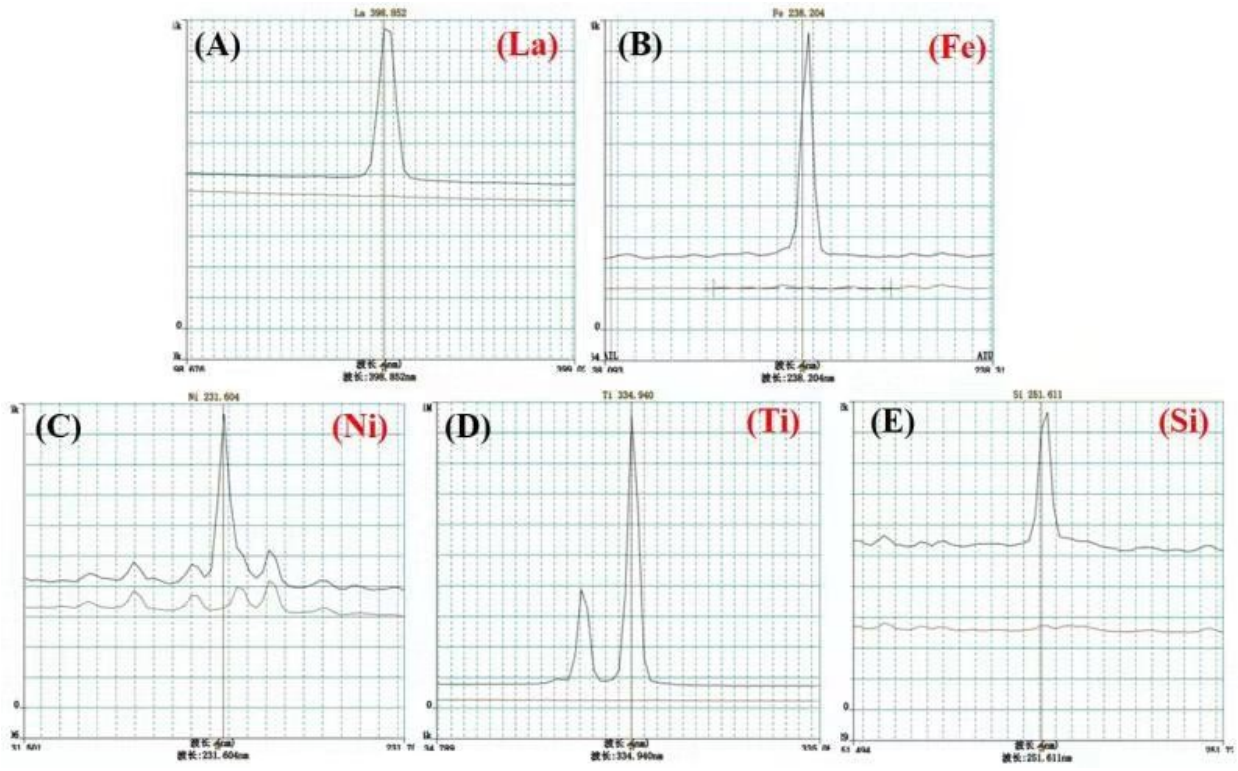
Fig. S9 Inductively coupled plasma emission spectroscopy (ICP-AES) for La (A), Fe (B), Ni (C), Ti (D), and Si (E) of resulting PLFO, 3Ni-PLFO, 5TS/3Ni-PLFO nanocomposite.
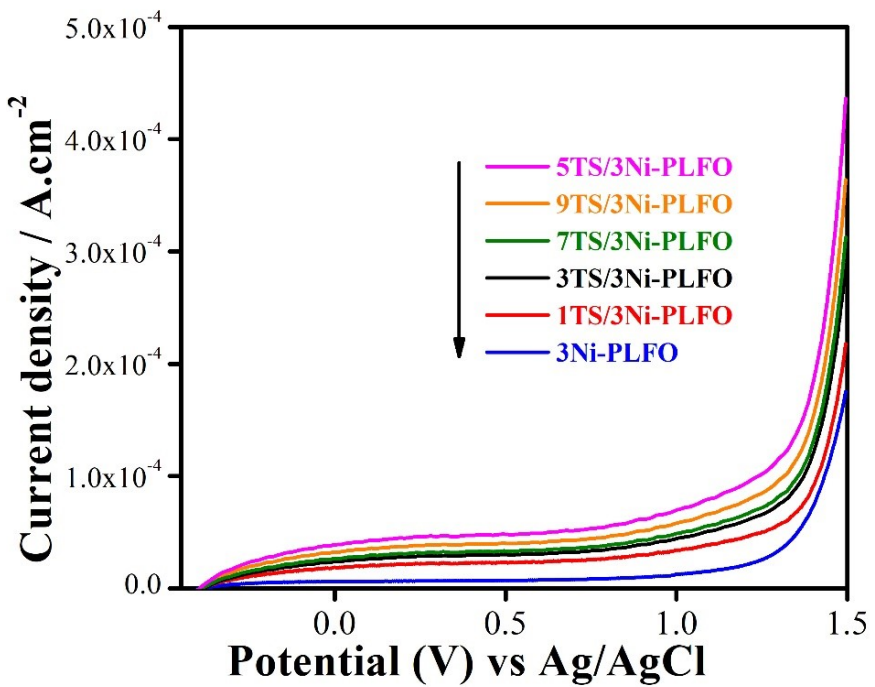
Fig. S10 PEC I-V curves of 3Ni-PLFO, and ZTS/3Ni-PLFO nanocomposite.
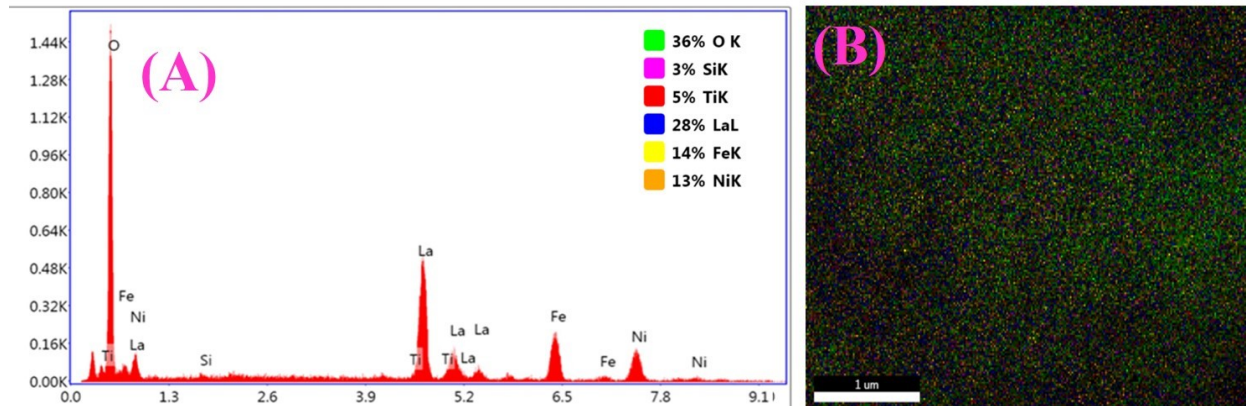
Fig. S11 TEM (EDX) and elemental mapping of PLFO, 3Ni-PLFO and 5TS/3Ni-PLFO nanocomposite.
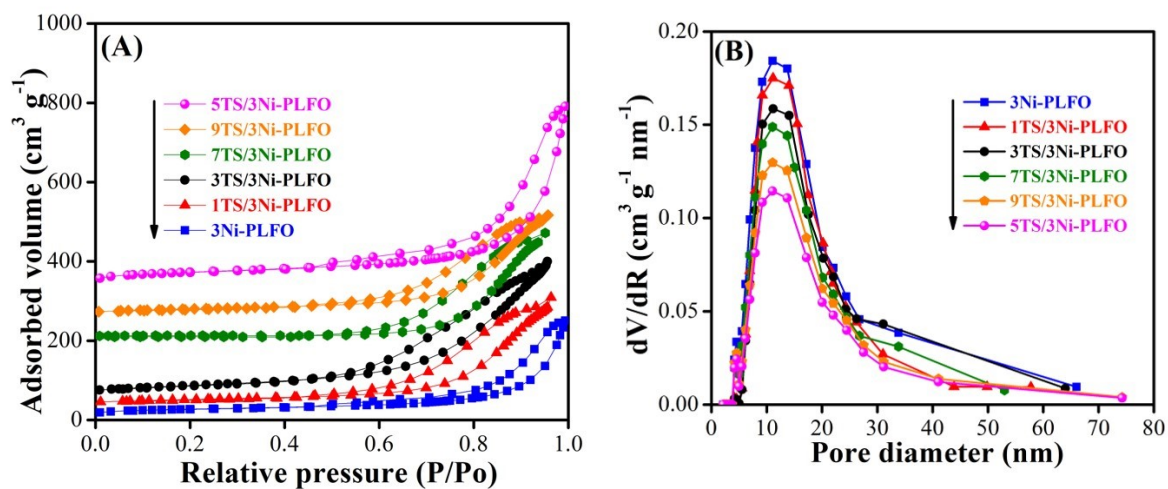
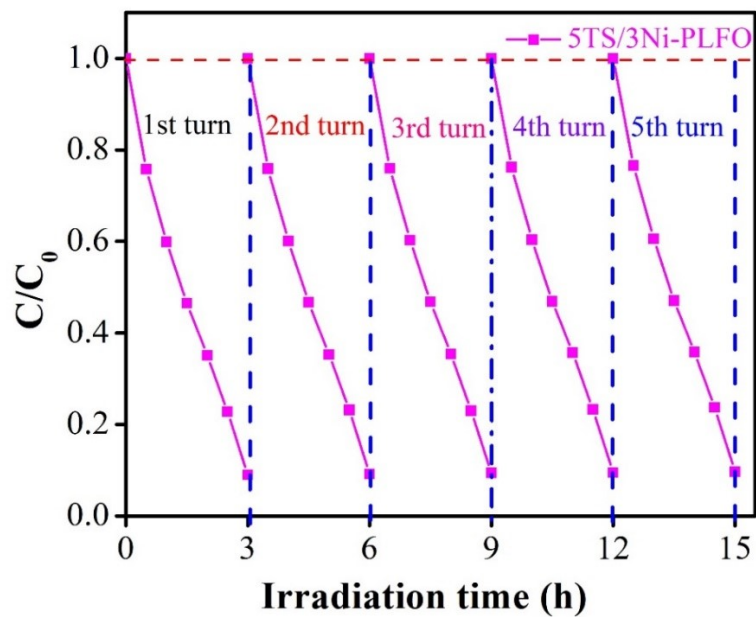**Fig. S12** Nitrogen adsorption-desorption isotherms (A) and pore diameter (B) of 3Ni-PLFO and ZTS/3Ni-PLFO nanocomposites.

Fig. S13 Stability test of 5TS/3Ni-PLFO nanocomposite for 2,4,6 TNP degradation.
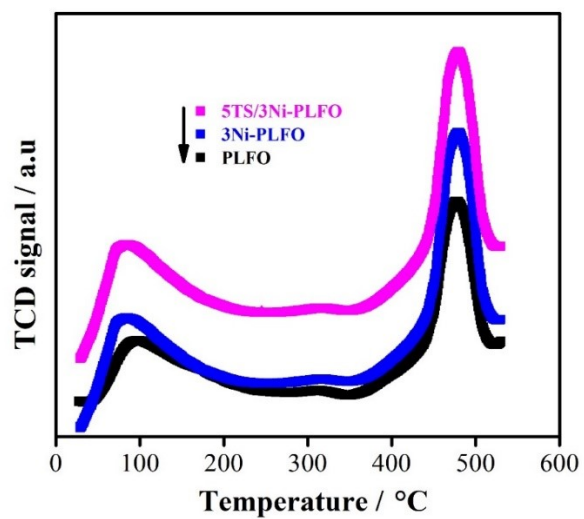
Fig. S14 CO_2-Temperature-programmed desorption curves of PLFO, 3Ni-PLFO and 5TS/3Ni-PLFO.
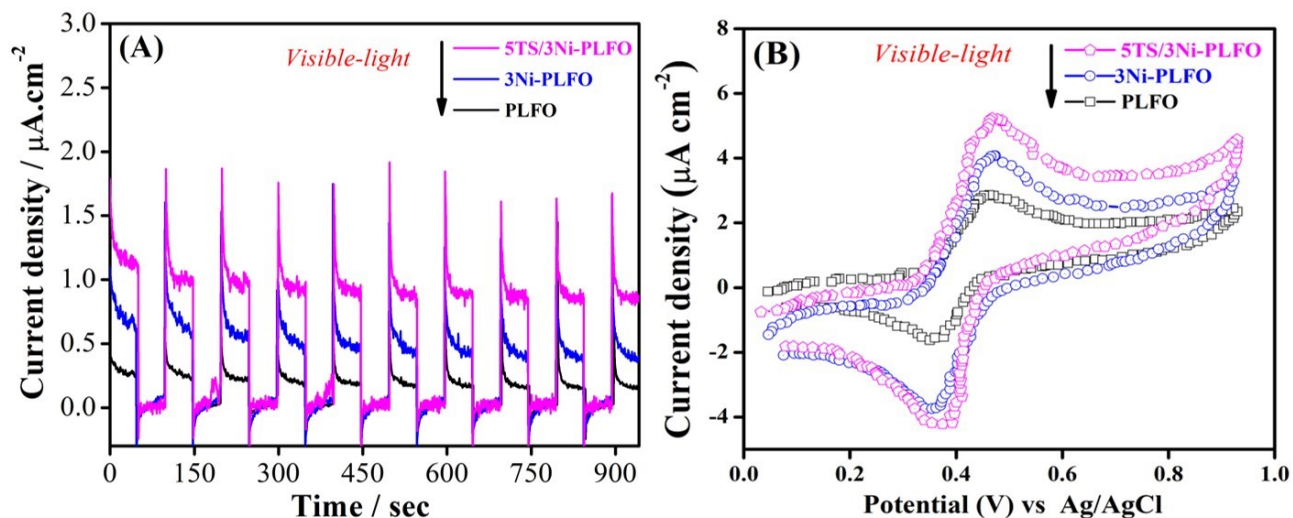
Fig. S15 PEC I-t curves (A) and CV curves (B) related to PLFO, 3Ni-PLFO and 5TS/3Ni-PLFO.
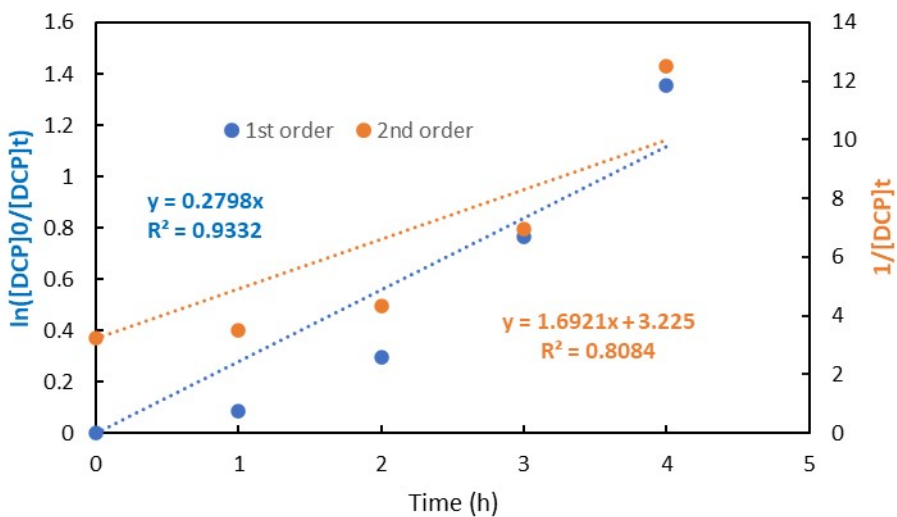

Fig. S16 1st order kinetics in terms of Langmuir-Hinshelwood mechanism for 2,4,6 TNP degradation over 5TS/3Ni-PLFO sample under visible-light irradiation.
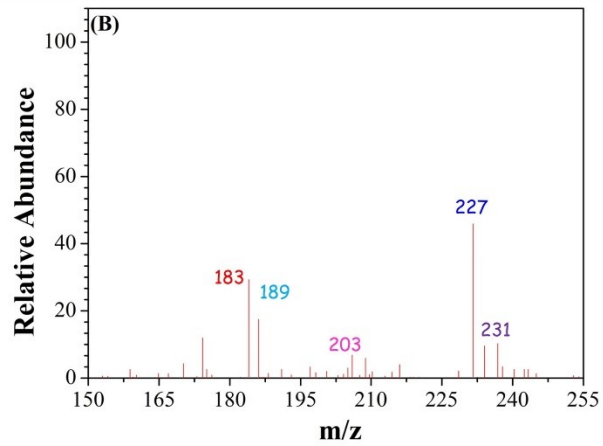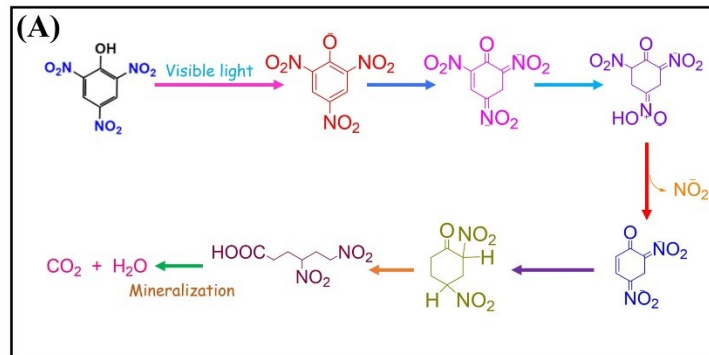
Fig. S17 Degradation pathway (A) and mass spectrum (B) for 2,4,6 TNP degradation over 5TS/3Ni-PLFO sample under visible-light irradiation.