

Supplementary Information

Materials & Experimental Procedure

Chemicals:

Ce(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O, sodium carbonate, sodium hydroxide, ammonium chloride, sodium hypochlorite solution (4% w/v) tri-sodium citrate dehydrate, salicylic acid, sodium nitro ferricyanide dehydrate, hydrochloric acid, hydrazine monohydrate, ethanol, and sodium sulphate were purchased from Merck India. Sulphur powder was purchased from HIMEDIA and sodium hypophosphite and Nafion solution was purchased from sigma Aldrich. All the chemicals were of analytical grade (Merck) and used as received without further purification. Doubly distilled water was used throughout the experiments.

Sample Preparation

Ceria nanosheets were prepared by our previous papers. The binary hybrid Fe₂O₃-CeO₂NSs was prepared by insitu production of iron oxide from iron(III) solution in presence of CeO₂NSs. Briefly, at first, CeO₂NS were dispersed in the beaker containing 20mL of water. Then calculated amount of iron nitrate solids are further dissolved in the CeO₂ suspension. Then the pH of the solution was adjusted to 12 by addition of 0.5M NaOH solution and was stirred for 12h. Then the solution was poured into the autoclave was sealed and, kept in an autoclave for 28h at 180⁰C, was cooled down in room temperature and, was further aged for 24h. Then the precipitates were collected and washed with distilled water and kept in an oven at 80⁰C for further use. To obtain FeP-CeO₂ (CP), the resulting product and NaH₂PO₂ were grinded uniformly and put in a quartz boat at the middle of the furnace. The resultant solid was annealed in N₂ at 300⁰C for 3 h, at a ramping rate of 2 °C min⁻¹. Further, the obtained product was washed with distilled water and, ethanol and dried in vacuum oven at 60⁰C. For FeS₂-CeO₂ (CS), the Fe₂O₃-CeO₂ powder along with S powder was grounded uniformly and

was taken in quartz boat and annealed in the same above mentioned environment for 2h. The ternary $\text{FeS}_2\text{-FeP-CeO}_2$ (CPS1-3) were prepared by taking a calculated amount of $\text{Fe}_2\text{O}_3\text{-CeO}_2$ powder, S powder and sodium hypophosphite powder in a mortar pestle and was grounded uniformly. Then the mixed powder was taken in a quartz boat and was placed at the middle of the tubular furnace. Then N_2 gas was passed throughout the furnace for 15min, in order to make the environment inert completely. Then the solid was annealed at 300°C for 3 h, at a ramping rate of 2°C min^{-1} and throughout the reaction procedure, N_2 gas was purged continuously in the system. The P to S ratio was varied for the samples. Pristine FeP and FeS_2 were synthesized same as CP and CS respectively, only by changing the precursor to FeOOH .

Materials Characterization

The TEM and HRTEM images were taken from a Philips TECNAI G² electron microscope operated at an accelerating voltage of 200 kV.-The X-ray diffraction patterns were obtained by Rigaku Miniflex XRD instrument with a monochromator equipped with Cu ($K\alpha$) radiation ($\lambda=0.15418$ nm) having voltage 40kV and current of 40mA from 20° to 70° at a scan rate of $5^\circ/\text{min}$. Raman spectrum was obtained by using a Seki STR500 Raman spectrometer, at an excitation wavelength of 532 nm. XPS characterization was carried out in ESCA+, (omicron nanotechnology, Oxford Instrument Germany) equipped with Al $K\alpha$ X-ray monochromatizing source and binding energy of C1s core (284.6ev) was taken as reference. JASCO V-750 spectrophotometer was used to obtain the UV-visible diffuse reflectance spectrum in the range of 200 to 800 nm. By using JASCO FP-8300 spectrofluorimeter, the photoluminescence properties were evaluated with an excitation wavelength of 340nm. EPR measurement was carried out in JES-FA200, ESR spectrometer instrument.

The photocatalytic activities of the materials were evaluated by monitoring the reduction of N_2 under UV-visible light irradiation, using a 250W Hg lamp as the light source. For each

experiment 15 mg of catalyst was dispersed in 50 mL of double distilled water, in a quartz reactor. The reactor was equipped with circulating water outer jacket in order to maintain at a temperature of 25°C by Julabo chiller. N₂ gas was slowly bubbled to the dispersed catalyst suspension solution for 60 min to obtain a N₂-saturated aqueous suspension. Before the lamp was turned on, the dispersed solutions were stirred in the dark for 30 mins in order to achieve the sorption equilibrium. At regular intervals, 5 mL aliquots of the reaction solution were collected using a syringe, and then immediately centrifuged to remove the catalyst. The gas-phase effluent was passed into a second quartz vessel containing diluted H₂SO₄ to capture the NH₃ produced for later analysis. The NH₃ in both the reactant vessel and the captured vessel were measured for the final concentration of ammonia. The concentration of ammonia was determined by both indophenol method and N₂H₄ products were determined by colorimetric using para-dimethylamino benzaldehyde. UV-Vis absorption spectra of the colored complexes formed were recorded on a JASCO V-750 UV-Vis spectrometer. The concentrations of ammonia and hydrazine were determined by using standard calibration curves of absorbance versus concentration for each complex. Further NMR was carried out to confirm the generation of ammonia by FT-NMR, Bruker Advance 400MHz. The Blank test was also performed in the absence of photocatalysts. In the case of photocatalytic N₂ fixation with the sacrificial agent, the concentration of sacrificial agent i.e. methanol is kept at 10 vol%. Further, the pH of the solutions is adjusted by dil.HCl.

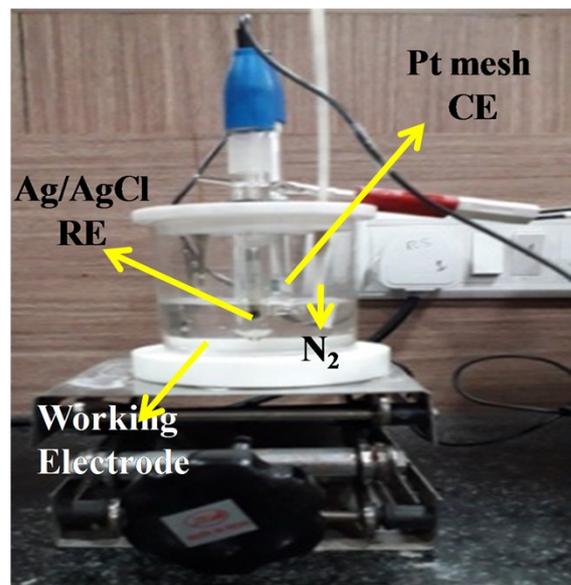
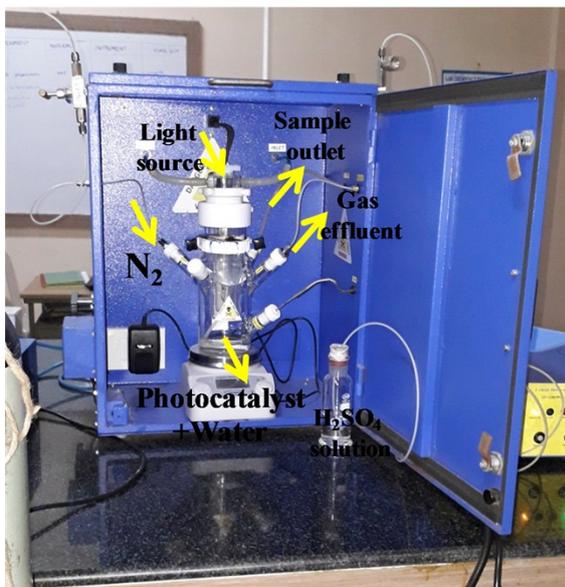
Photoelectrochemical studies were carried out on IVIUMn STAT electrochemical workstation equipped with a standard three electrode cell and a 300W Xe lamp. The working electrodes were prepared by a dip coating technique using slurry containing 5mg catalyst, 0.1mL ethanol and 300uL 1% Nafion solution and then coated it on the surface of FTO. The counter and reference electrodes were Pt electrode and Ag/AgCl. The Mott-Schottky

measurement was obtained at 500Hz in 0.1MNa₂SO₄ solution under dark condition. However, the Nyquist plot was done at 10⁵ Hz to 10² Hz at zero bias in the presence of light at open circuit potential. The chronoamperometry measurements were evaluated at -0.3V vs NHE in the solution containing 0.1M Na₂SO₄ solution at OCP under light irradiation. The kinetic study of photo electrochemical N₂ fixation was carried out in N₂ saturated 0.5M Na₂SO₄ (+H₂SO₄, pH=1.5) solution and the corresponding CA measurement (-0.6V vsNHE) was carried out in the same environment at OCP. Before the measurement N₂ was purged in the system for 30min. The electron transfer number in the photocatalytic N₂ fixation was determined as follows. According to Laviron, for an adsorption-controlled and irreversible electrode process, E_p is calculated by the following equation:

$$E_p = E^0 + (RT/anF)\ln (RTK^0/anF) (RT/anF)\ln v$$

where E⁰ be formal potential T is thermodynamic temperature, R is molar gas constant, a be the transfer coefficient, F is faraday constant, n is electron transfer number involved in the rate-determining step, K⁰ is standard rate constant of the reaction and v is scan rate (mV/S).

For an irreversible electrode process, a≈0.5.¹



Photocatalytic and photoelectrochemical nitrogen fixation experimental setup.

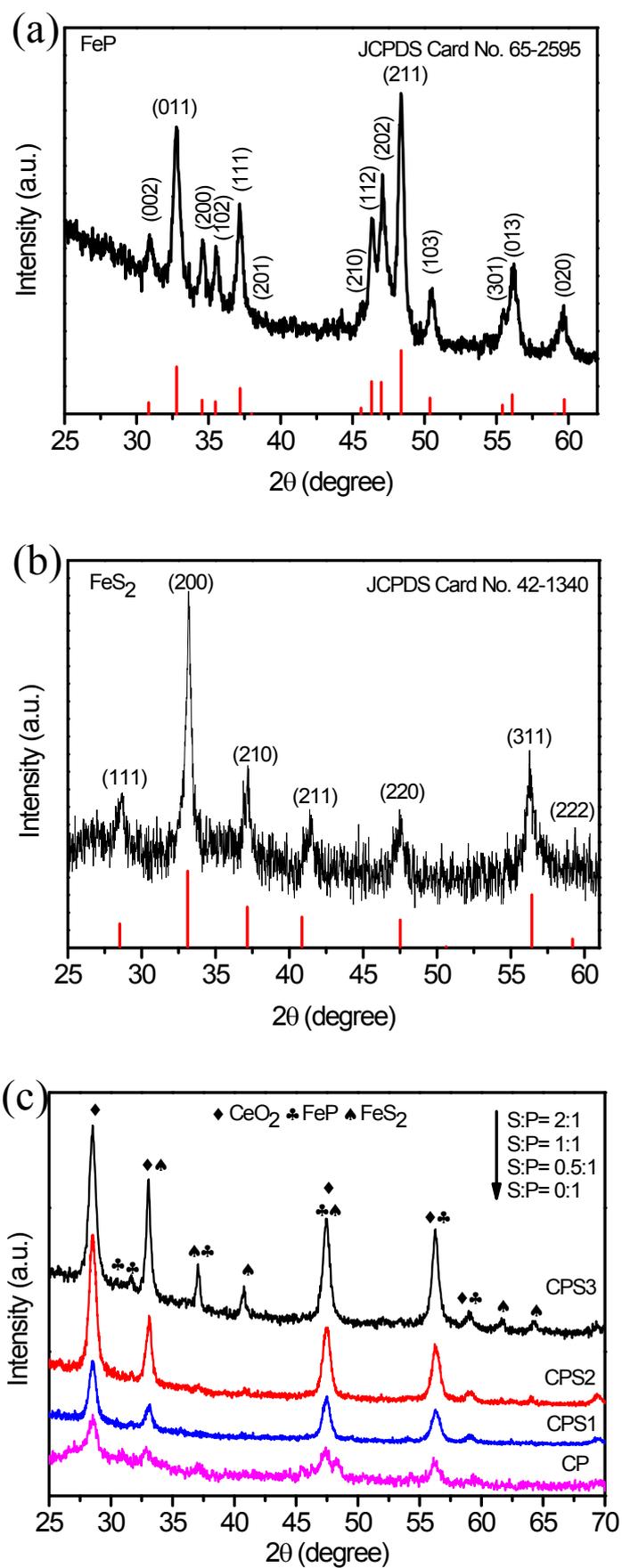


Fig. S1 XRD spectra of neat (a) FeP, (b) FeS₂ and (c) binary and ternary hybrids.

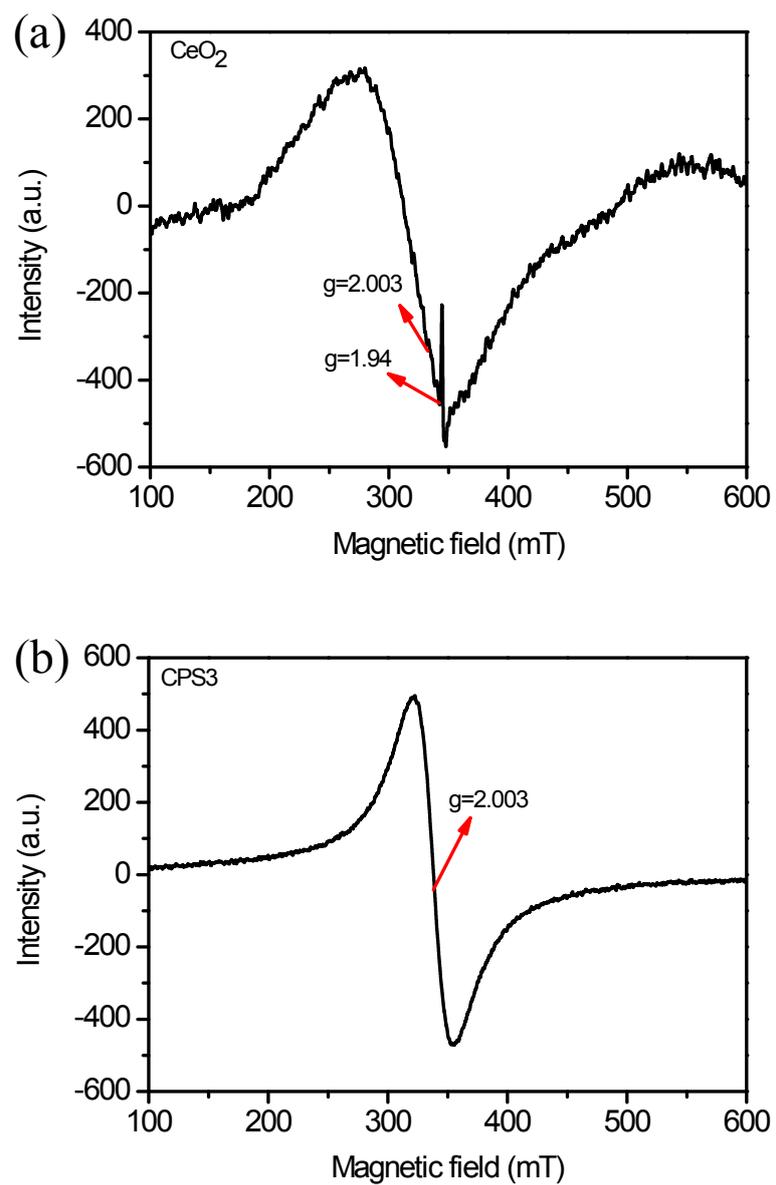


Fig. S2 EPR spectra of (a) neat CeO_2 and (b) CPS3 ternary hybrids.

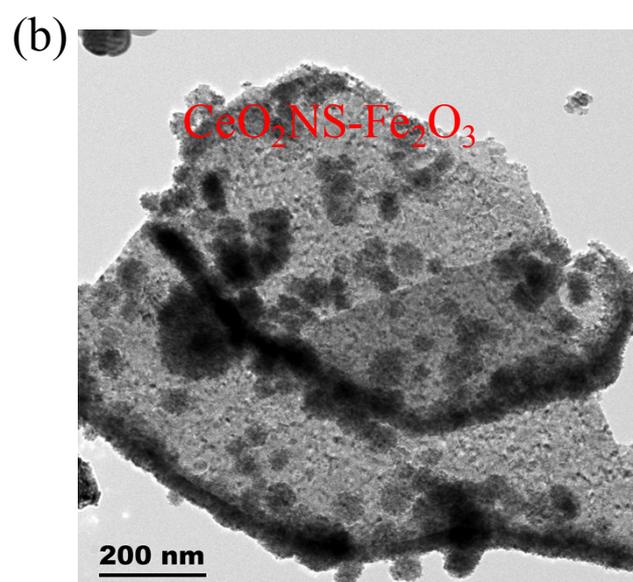
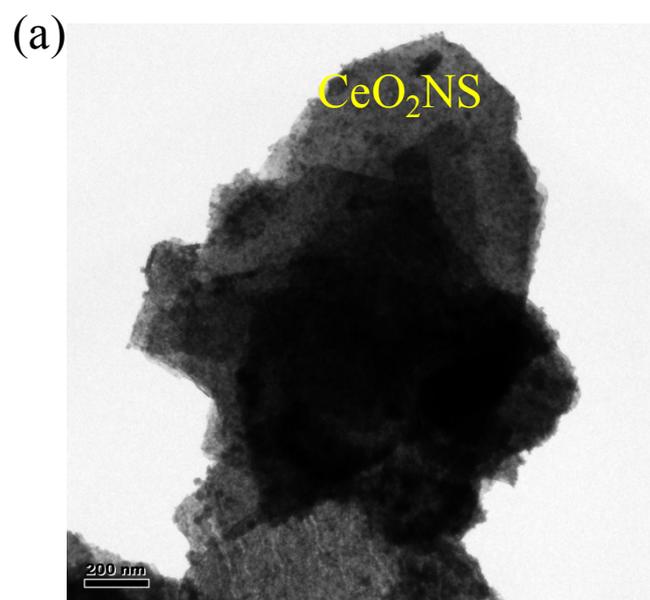
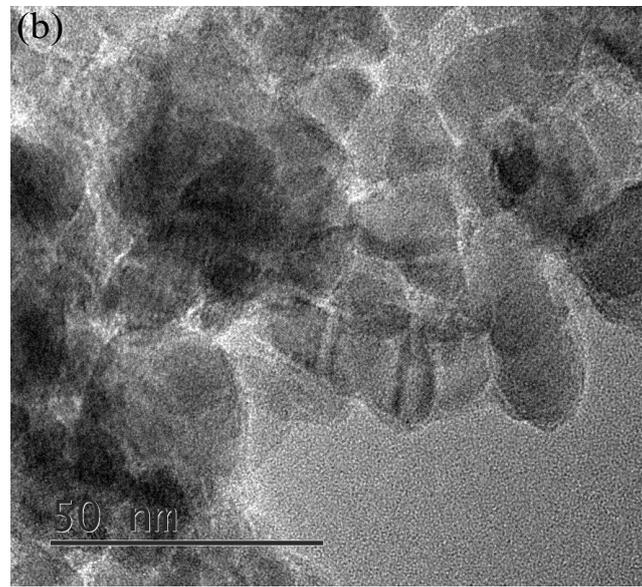
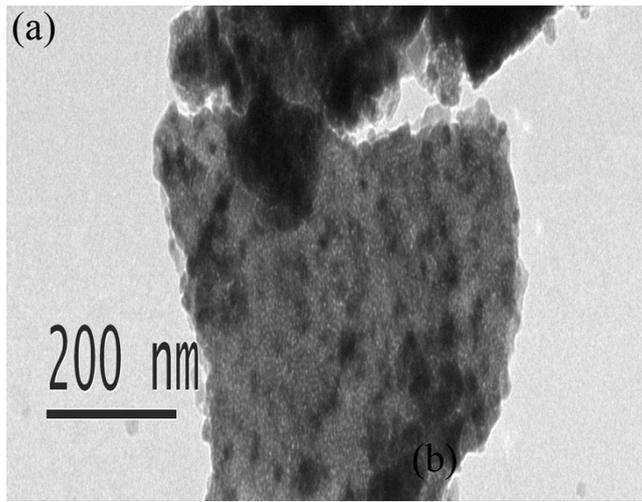
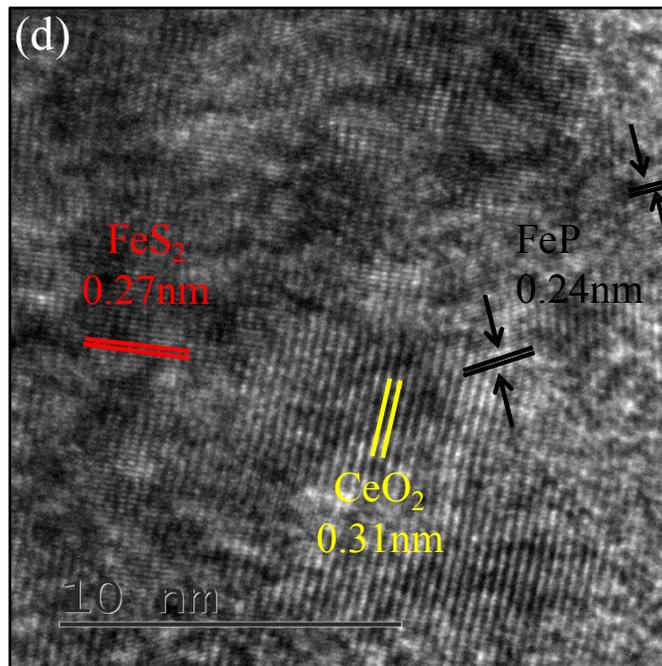
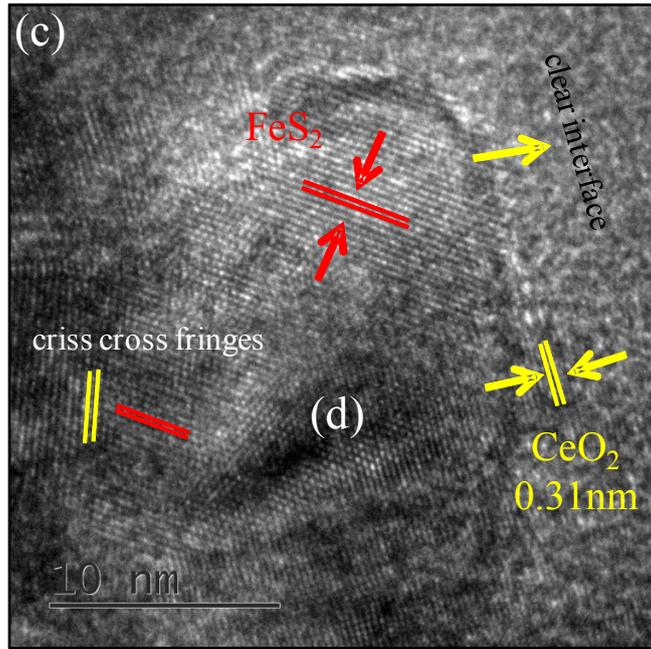


Fig. S3 TEM images of (a) CeO₂NS and (b) CeO₂NS-Fe₂O₃.





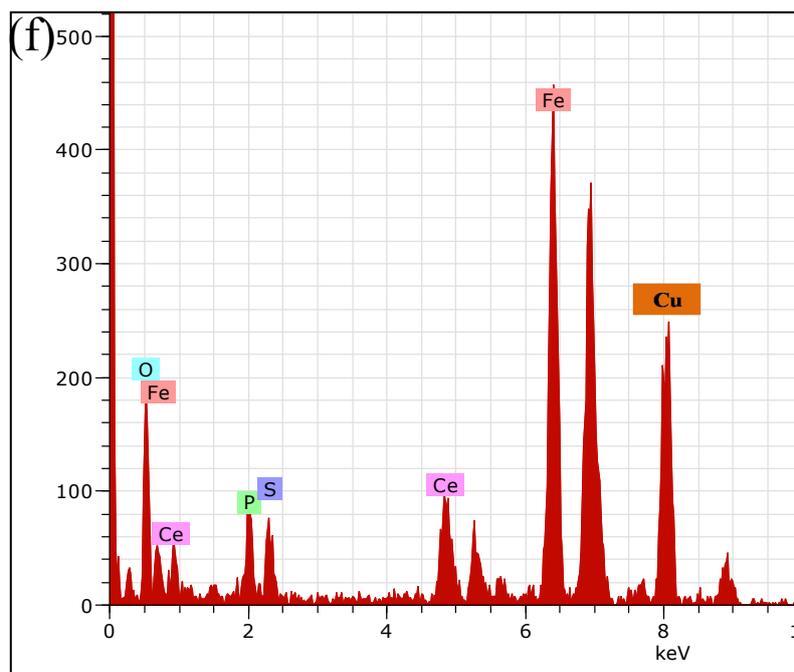
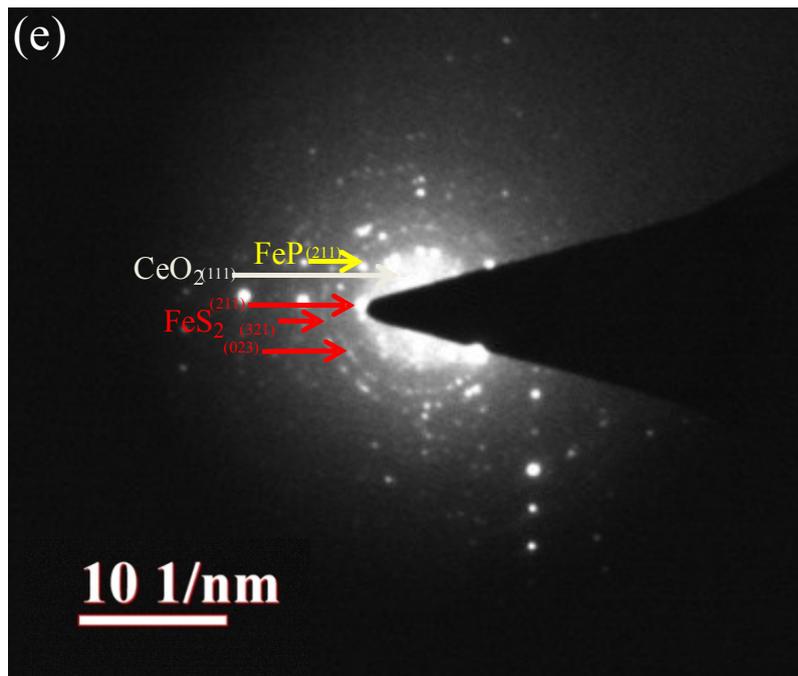
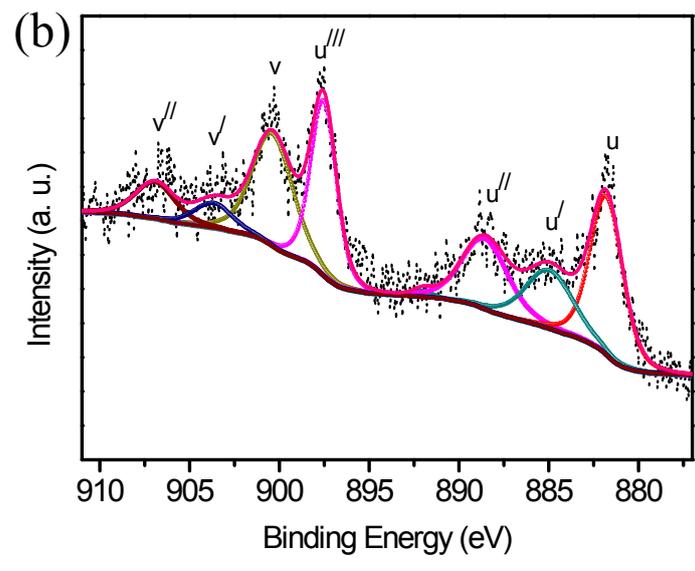
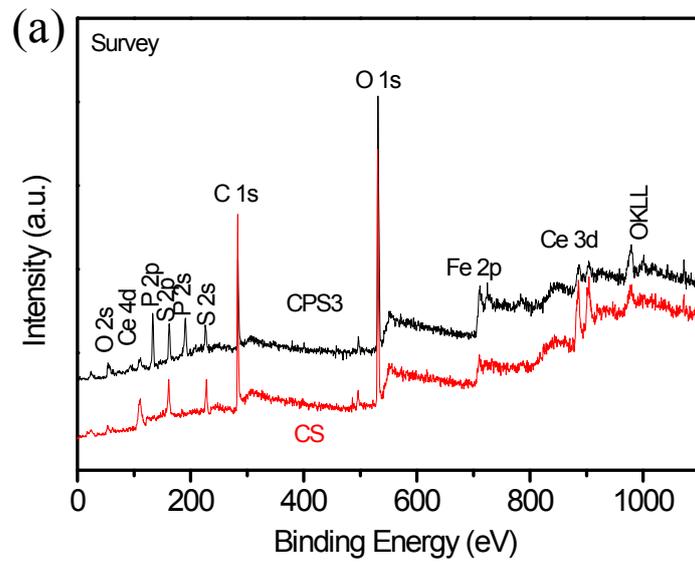


Fig. S4 TEM image of CPS3 (a), (b) and HRTEM images of (c), (d) showing lattice fringes of CeO_2 and FeS_2 and FeP respectively, (e) and (f) SAED and EDX pattern of CPS3.



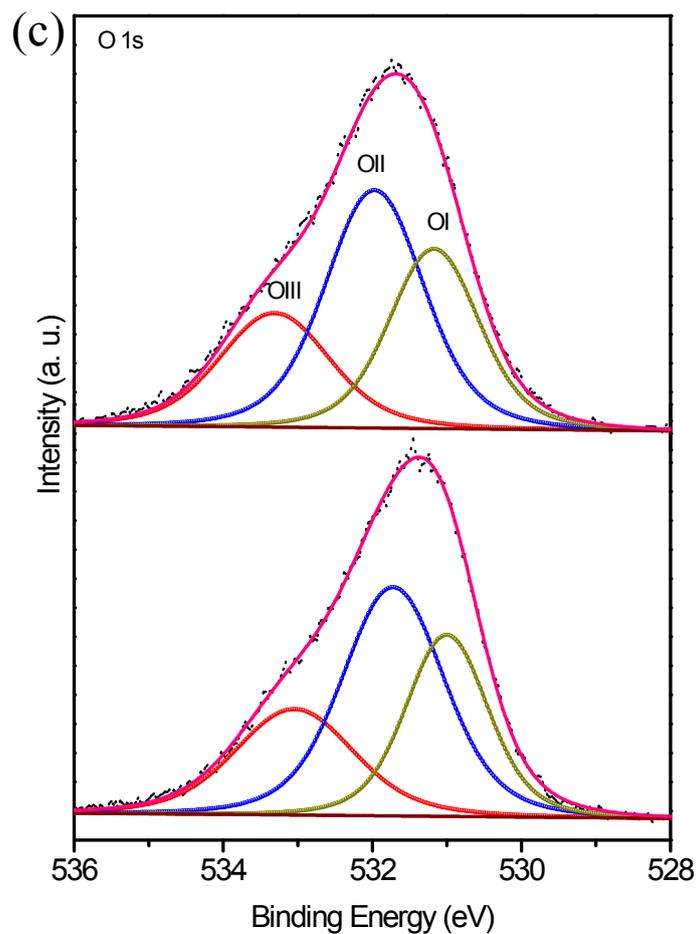
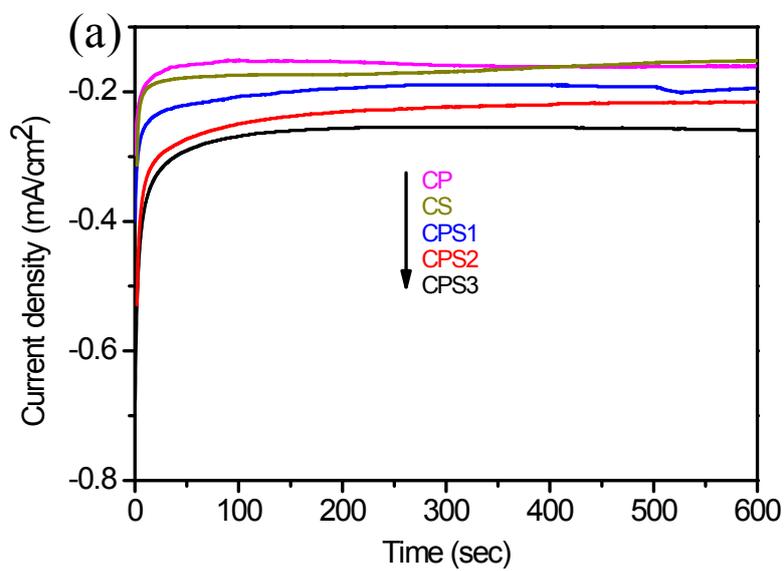


Fig. S5 XPS survey spectrum (a), Ce3d spectrum of neat CeO₂ (b) and high resolution O1s spectrum (c) of CS and CPS3.



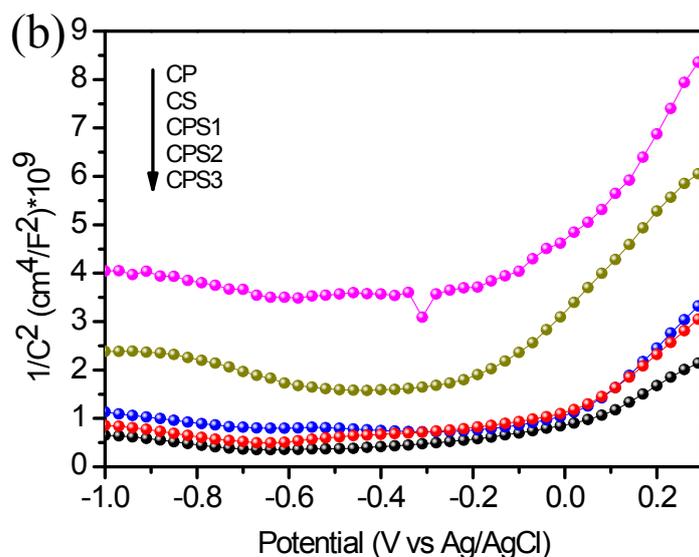
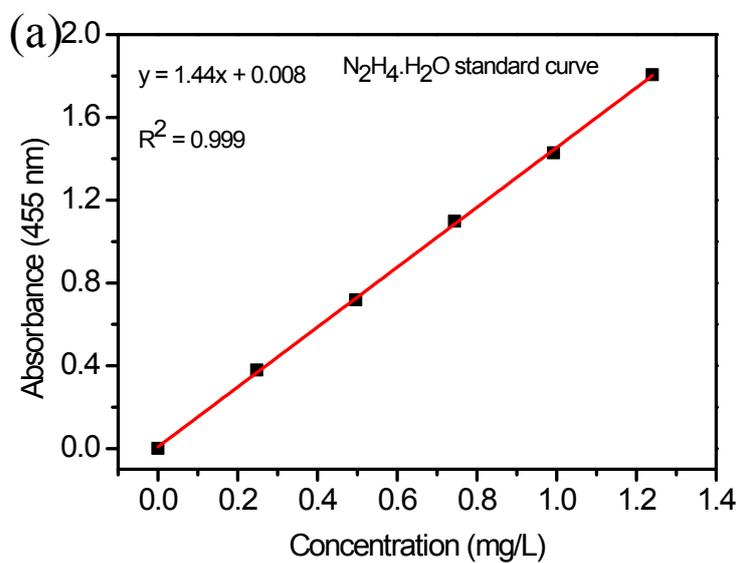
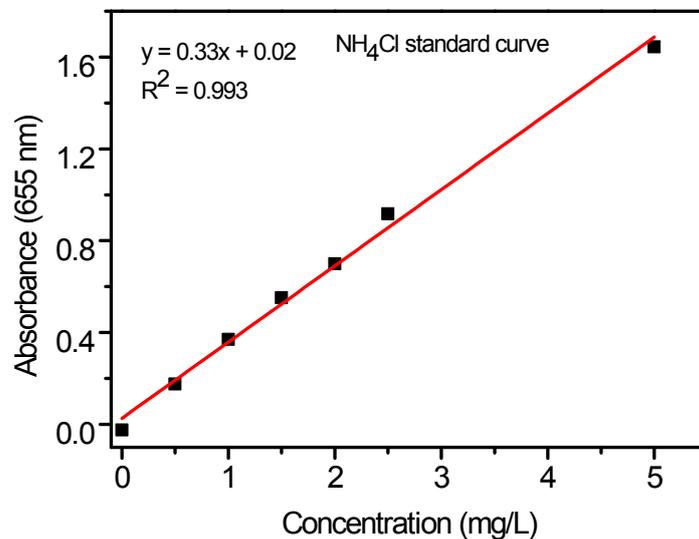


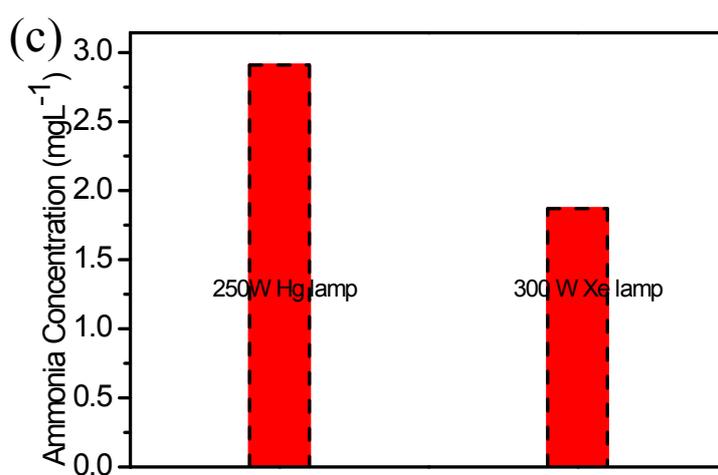
Fig. S6 (a) Chronoamperometry and (b) Mott-Schottky studies of CP, CS, CPS1, CPS2 and CPS3.



Watt and Chrisp (para-dimethylamino-benzaldehyde)³ method for estimating $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ concentration. The absorbance at 455 nm was measured by UV-vis Spectrophotometer, and the fitting curve shows the good linear relation of absorbance with N_2H_4 ion concentration ($y = 1.44x + 0.008$, $R^2 = 0.999$) in calibration curves.



Absolute calibration of the indophenol blue method using ammonium chloride solutions of known concentrations as standards.⁴ The absorbance at 655 nm was measured by UV-vis spectrophotometer, and the fitting curve shows the good linear relation of absorbance with NH_4^+ ion concentration ($y = 0.33x + 0.02$, $R^2=0.993$) in calibration curves.



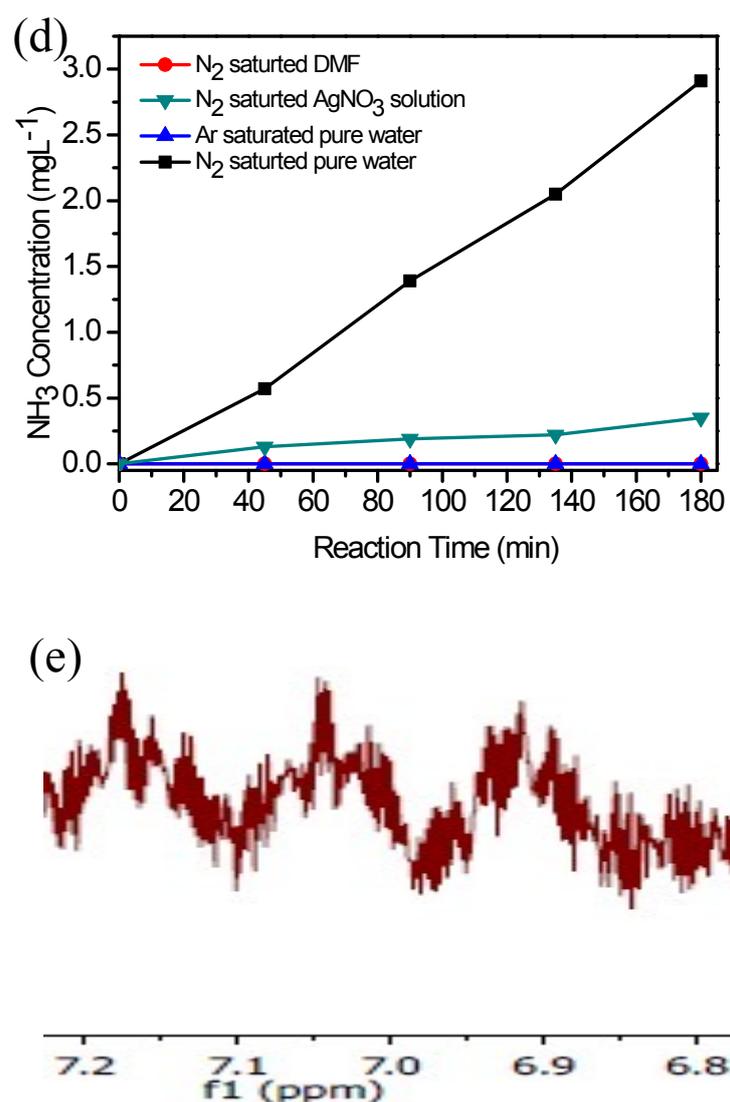


Fig. S7 calibration curve used for estimation of (a) N_2H_4 concentration and (b) NH_3 by NH_4^+ ion concentration, (c) ammonia concentration over CPS3 dispersed in distilled water in 250W Hg and 300W Xe lamp, (d) Photocatalytic N_2 fixation with CPS3 in aprotic solvent DMF and photocatalytic N_2 fixation with CPS3 using AgNO_3 as the electron scavenger, N_2 fixation with CPS3 in Ar saturated solution, N_2 saturated solution in pure water and (e) ^1H NMR spectrum of the obtained ammonia from photocatalytic NRR of CPS3 (12h).

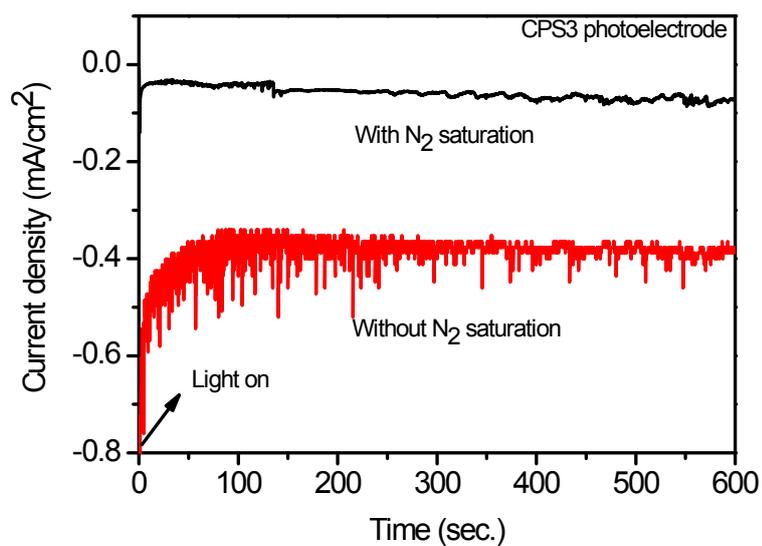


Fig. S8 Chronoamperometry response of CPS3 in N₂ saturated and without N₂ saturated 0.5M Na₂SO₄ solution under light irradiation at -0.6V vs NHE.

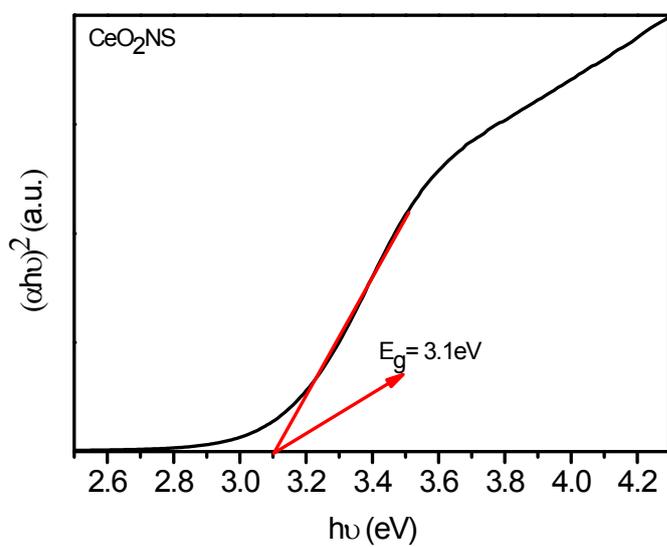


Fig. S9 Tauc plot of neat CeO₂NS.

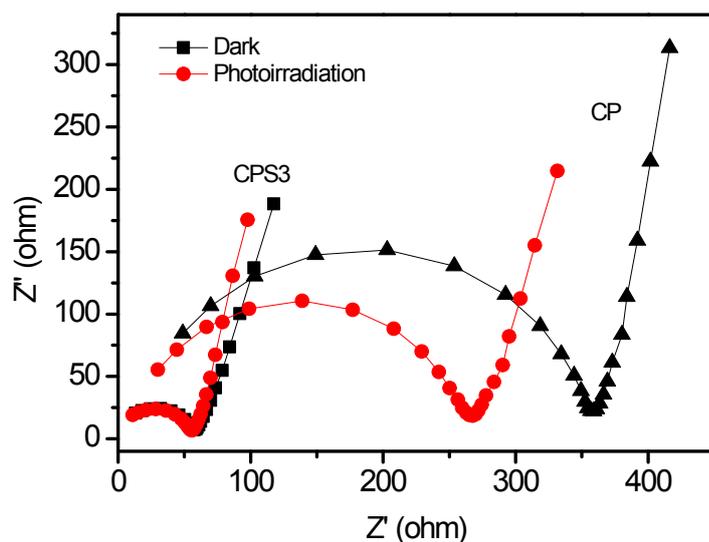


Fig. S10 Nyquist EIS plot for CP and CPS3 electrodes in both light and dark.

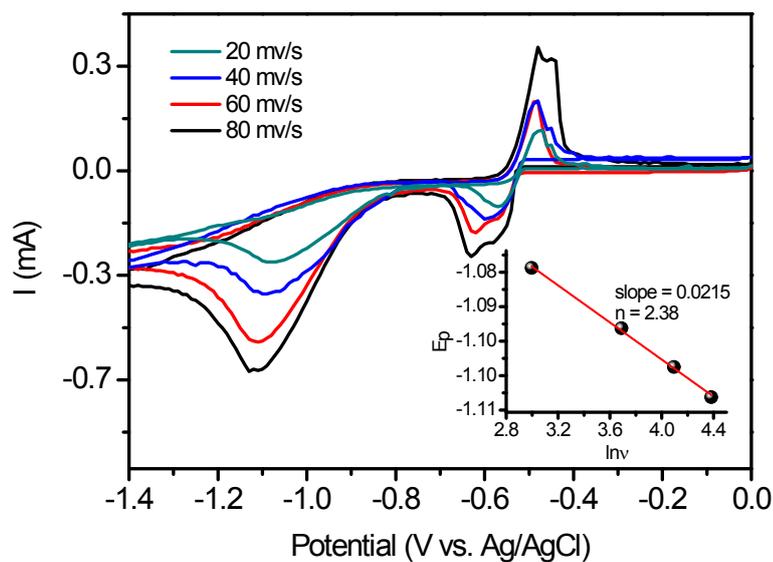


Fig. S11 Kinetic study of N_2 photofixation by photoelectrochemical measurements: Cyclic voltammograms of CPS3 nano hybrid at different scan rates in N_2 saturated 0.5 M Na_2SO_4 (pH = 1.5) under room temperature ($25^\circ C$) and UV-vis light irradiation; Inset: the plot for the reduction peak potential (E_p) vs. $\ln v$ (scan rate).

References

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2. S. Sultana, S. Mansingh and K. Parida, *J. Mater. Chem. A*, 2018, 6, 11377-11389.
3. D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nature Mater.*, 2013, 12, 836.
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