A direct Z-scheme g-C3N4/FeWO4 nanocomposite for Enhanced and Selective Photocatalytic CO2 Reduction under Visible Light

Reshma Bhosale, Srashti Jain, Chathakudath Prabhakaran Vinod, Santosh Kumar, and Satishchandra Ogale

*ACS Appl. Mater. Interfaces, Just Accepted Manuscript* • DOI: 10.1021/acsami.8b22434 • Publication Date (Web): 25 Jan 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
A Direct Z-scheme g-C₃N₄/FeWO₄ Nanocomposite for Enhanced and Selective Photocatalytic CO₂ Reduction Under Visible Light

Reshma Bhosale, a Srashti Jain, a Chathakudath Prabhakaran Vinod, b Santosh Kumar, c* and Satishchandra Ogale a*

aDepartment of Physics and Centre for Energy Science, Indian Institute of Science Education and Research (IISER), Pune 411008, India.
bCatalysis Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India.
cDepartment of Chemical Engineering, University of Bath, Claverton, Bath, BA2 7AY, United Kingdom.

*Corresponding Author

Email: satishogale@gmail.com, S.Kumar@bath.ac.uk
ABSTRACT

Photocatalytic reduction of CO$_2$ to renewable solar fuels is considered to be the promising strategy to simultaneously solve both the global warming and energy crises. However, development of superior photocatalytic system with high product selectivity for CO$_2$ reduction under solar light is the prime requisite. Herein, a series of nature-inspired Z-scheme g C$_3$N$_4$/FeWO$_4$ composites are prepared for higher performance and selective CO$_2$ reduction to CO as solar fuel under solar light. The novel direct Z-scheme coupling of the visible light active FeWO$_4$ nanoparticles with C$_3$N$_4$ nanosheets is seen to exhibit excellent performance for CO production with a rate of 6 µmol/g/hr at ambient temperature, almost 6 times higher compared to pristine C$_3$N$_4$ and 15 times higher than pristine FeWO$_4$. More importantly, selectivity for CO is 100% over other carbon products from CO$_2$ reduction and more than 90% over H$_2$ product from water splitting. Our results clearly demonstrate that the staggered band structure between FeWO$_4$ and C$_3$N$_4$
reflecting nature-inspired Z-scheme system not only favors superior spatial separation of electron-hole pair in g-C$_3$N$_4$/FeWO$_4$, but also shows good reusability. The present work provides unprecedented insights for constructing the direct Z-scheme by mimicking nature for high performance and selective photocatalytic CO$_2$ reduction into solar fuels under solar light.

**KEYWORDS:** Photocatalysis, CO$_2$ reduction, solar fuels, C$_3$N$_4$, FeWO$_4$, Z scheme

**1. INTRODUCTION:**

Green-house effect and global warming are the most menacing concerns for the 21$^{st}$ century modern civilization, posing major challenges to the whole scientific community. With increase in the energy demand the consumption of fossil fuels has increased dramatically, contributing huge amounts of anthropogenic CO$_2$ emissions to the atmosphere and leading to environmental crisis.$^{1,2,3}$ Amongst the different potential solutions being considered, the use of abundantly available solar energy for CO$_2$ reduction to value added chemicals and/or fuels is considered to be the most attractive method to simultaneously solve both the energy and environmental problems.$^{3,4,5}$ However, the high thermodynamic stability and inertness of CO$_2$ with C=O bond dissociation energy of ~ 750 kJ/mol, which is higher than the other chemical bonds such as C-H (~430 kJ/mol) and C-C (~ 336 kJ/mol), necessitates high energy inputs for
the CO₂ conversions. Although a number of solar active catalysts have been developed and examined for CO₂ photoreduction, most of them continue to suffer from one or more of the negativities such as low energy conversion efficiency, selectivity, instability, and incapability to suppress the competing HER reaction. Therefore, the design and development of highly active photocatalyst with product selectivity is still a grand challenge.

In recent years, organic polymeric photocatalyst, graphitic carbon nitride (g-C₃N₄) has emerged as a sustainable, cost effective, and environmental friendly visible light active semiconductor with suitable band gap of 2.6-2.8 eV. More importantly, g-C₃N₄ has relatively more negative conduction band potential w.r.t. to the CO₂ reduction potential, which demonstrates its high suitability for photocatalytic CO₂ reduction into wide range of value added chemicals and fuels such as CO, CH₄, and CH₃OH. Despite its appropriate band-structure however, the photocatalytic efficiency still remains low due to the rapid recombination of photogenerated electrons and holes before they could participate in the surface reactions. In order to slow down the recombination, several interesting strategies have been devised to improve the overall performance of g-C₃N₄. Among them, coupling of C₃N₄ with other semiconductors with suitable band structure has proved to be an effective pathway to increase the life time of photogenerated charge carriers through the spatial separation of electrons and holes within the interfacial area. For example, Peng et al, reported novel coupling of ZnO with
C$_3$N$_4$ for selective photoreduction of CO$_2$ to CH$_3$OH. Similarly, Xu et al.\textsuperscript{19} illustrated the improved charge separation in C$_3$N$_4$ by coupling of SnS$_2$ for enhanced photocatalytic CO$_2$ reduction to CH$_4$ and CH$_3$OH. Although, there are many such reports on coupling C$_3$N$_4$ with both large band gap, (ZnO\textsuperscript{18,20} and TiO$_2$\textsuperscript{21,22}) and low band gap (In$_2$O$_3$, NaNbO$_3$, Ag$_3$PO$_4$ and SnS$_2$)\textsuperscript{23,24,25,19} semiconductors for photocatalytic CO$_2$ reduction, achieving high efficiency and product selectivity still remains elusive. In coupling methodology, the nature-inspired Z-scheme mechanism has also been a more effective strategy as the photogenerated electrons with high reduction ability is restored in one photocatalyst whereas holes with high oxidizing ability are restored in other photocatalyst of photosystem, which are subsequently utilized for respective surface reactions.\textsuperscript{26,27} Thus, superior charge separation and in turn high photocatalytic yield along with selectivity of products is achieved. Unfortunately, thus far, these systems are mostly examined for their application to photocatalytic water splitting or pollutant degradation.\textsuperscript{28,29,30,31,32,33,34} Moreover, most of the existing Z-schemes have employed an additional sacrificial mediator, so-called indirect Z-scheme mechanism.\textsuperscript{25,35,36} Therefore, for a scalable photocatalytic system with C$_3$N$_4$, developing a direct Z-scheme heterostructured material with suitable band-structure match is highly sought so as to achieve efficient spatial separation of charge carriers and thereby high performance as well as product selectivity.
With the current interesting and challenging scenario as a prerequisite, herein we introduce a new direct Z-scheme photocatalyst comprising FeWO\(_4\) (band gap of 1.8-2.5 eV)\(^{37,38}\) and C\(_3\)N\(_4\) (band gap of 2.5-2.8 eV)\(^{8,9}\) with highly suitable staggered band-structure for efficient and selective CO\(_2\) photoreduction to CO under visible light. FeWO\(_4\) was chosen particularly due to its visible light responsive nature, and most importantly its relatively negative conduction band potential (0.4 V – 0.7 V vs NHE)\(^{39,40}\)w.r.t. to the C\(_3\)N\(_4\) valence band potential. In principle, Ferrous Tungstate FeWO\(_4\) belongs to fascinating family of wolframite type which has attracted tremendous attention due to its various technological applications in scintillators,\(^{41}\) optical fibres,\(^{28}\) sensors,\(^{43}\) and catalysis\(^{44,45,46,47}\). So far, FeWO\(_4\) is not investigated much in the field of photocatalysis. Few reports on photocatalytic dye degradation such as methyl orange,\(^{38}\) methylene blue,\(^{37,40}\) Rhodamine B \(^{48}\) and 4-nitrophenol \(^{40}\) have appeared. In the present work, FeWO\(_4\) was successfully coupled with C\(_3\)N\(_4\) by simple wet chemical method as an efficient photocatalyst for the direct Z scheme without utilization of any mediator for photoreduction of CO\(_2\) to CO. The obtained Z-scheme nanocomposite g-C\(_3\)N\(_4\)/FeWO\(_4\) exhibited 6-fold and 15-fold enhancement in selective photocatalytic CO\(_2\) reduction to CO over C\(_3\)N\(_4\) and FeWO\(_4\), respectively. Moreover, CO selectivity shown by this Z scheme photocatalyst is 100% over C\(_1\) and other higher hydrocarbons and almost ~ 91% over the undesired H\(_2\) evolution from water splitting. Our results clearly show that the direct Z scheme mechanism with staggered band structure of FeWO\(_4\) band potential with C\(_3\)N\(_4\) band edges favors superior charge separation of electron-hole pair in C\(_3\)N\(_4\) and restores its reduction.
ability leading to enhanced photocatalytic activity. Moreover, to best of our knowledge, FeWO$_4$ based materials have not been reported as CO$_2$ reduction photocatalyst till date.

2. EXPERIMENTAL SECTION:

2.1. Material Synthesis

a) Synthesis of C$_3$N$_4$: C$_3$N$_4$ was synthesized by following the protocol given in previously reported literature.$^{49}$ Briefly, Melamine (C$_3$N$_3$ (NH$_2$)$_3$ (S D Fine Chem Limited) and NH$_4$Cl (Loba chemie) were mixed in 1:3 ratio by weight and ground properly in motor pestle. This mixture was heated in inert atmosphere at 550 °C for 4 h with 5°C/min in alumina boat. The sample was cooled down to room temperature and the obtained pale yellow coloured C$_3$N$_4$ powder was collected for further use.

b) Synthesis of FeWO$_4$: Simple hydrothermal route was used to synthesize FeWO$_4$ nanoparticles. 2mmol of Sodium Tungstate [Na$_2$WO$_4$.2H$_2$O, Loba chemie] and 2 mmol of Ferrous Ammonium Sulfate [(NH$_4$)$_2$ Fe (SO$_4$)$_2$.6H$_2$O,] (FAS, Rankem) was separately dissolved in 25 ml of distilled water. FAS solution was added dropwise to the sodium tungstate solution with continuous stirring. The pH of the obtained solution was adjusted to 8 by adding a few drops of aq. NaOH solution. The overall mixture was transferred to 100 ml Teflon lined autoclave and kept for 12 h at 180°C. The final product thus obtained was washed thrice with distilled water and kept overnight for drying at 60°C.
c) Synthesis of C$_3$N$_4$/FeWO$_4$ composites: For preparing the 80% composite, 80 mg of 
C$_3$N$_4$ and 20 mg of FeWO$_4$ were dispersed in 10 ml of distilled water separately and 
sonicated for an hour to get well dispersed homogenous suspensions. Then, the two 
solutions were mixed and sonicated for the next 2 hrs. The mixed solution was dried 
onight at 80°C. The obtained powder was collected and heated in Ar at 400°C for 2 h 
with 5°C/min in alumina boat. Finally, the composite sample was cooled down to room 
temperature and collected. Similar method was used for 50% and 30% composites with 
respective C$_3$N$_4$ and FeWO$_4$ weight ratios.

2.2. Characterization:

Material Characterization: The structural phases of samples C$_3$N$_4$, FeWO$_4$ and 
C$_3$N$_4$/FeWO$_4$ were confirmed by X-ray diffraction (Bruker D8 Advance X-ray 
diffractometer equipped with Cu K$_{\alpha}$ lamp source for irradiation 1.54 Å). For the 
morphology study Field Emission Scanning Electron Microscopy (FESEM, FEI NOVA 
NANO SEM) and High-Resolution Transmission Electron Microscopy (HRTEM) (JEOL 
JEM-2200FS, from JEOL, Japan at an acceleration voltage of 200 keV) techniques were 
used. For surface area and porosity estimation, measurements were performed on 
Quantochrome Autosorb automated gas sorption analyser at 77 K. Fourier Transform 
Infrared Spectroscopy (FTIR) was performed on Thermo scientific NICOLET 6700 FTIR 
spectrophotometer in the range of 250-4000 cm$^{-1}$ with BaSO$_4$ pellet as reference. 
Photoluminescence (PL) spectra of the samples were recorded at room temperature on
steady state spectrofluorometer FLS 980 (Edinburgh Instruments) equipped with 450 W Xenon lamp. The Ultraviolet-Visible diffuse reflectance spectrum (UV-VIS DRS) was obtained by using SHIMADZU UV-3600 plus UV-VIS-NIR spectrophotometer with integrating sphere attachment. The X-ray Photoelectron Spectroscopy (XPS) measurement was carried out using Thermo Kalpha+ spectrometer using micro focused and monochromated Al K\(_{\alpha}\) radiation with energy 1486.6 eV.

2.3 Photoelectrochemical Measurements: The on-off transient measurements were carried out in a three electrode system using AUTOLAB PGSTAT 30 potentiostat under the illumination of solar simulator (Newport) with UV (\(\lambda > 420\) nm) cut off filter and 100mW/cm\(^2\) power density. Ag/AgCl was used as the reference electrode, and platinium as the counter electrode. The sample coated on Fluorine doped Tin oxide (FTO) served as the working electrode. The electrolyte used was 0.5 M Na\(_2\)SO\(_3\). The photoelectrodes were fabricated by preparing the slurry in mortar pestal by adding 40 mg sample, 200 \(\mu\)l Nafion (5\%) and 1ml iso-propanol (IPA). The obtained paste was coated on FTO with 1cm\(^2\) area and heated at 250°C for 1hr to get homogenous film. Mott Schottky plots were recorded at a scan rate of 10mV/s in Na\(_2\)SO\(_3\) neutral solution in dark at a frequency of 10 KHz.

2.4 Photocatalytic measurements: Photocatalytic CO\(_2\) reduction experiments were carried out in stainless-steel photoreactor with quartz window set-up under the illumination of solar simulator (100 mW/cm\(^2\)) with Xenon lamp of 300 W. About 50mg sample was
dispersed in 20 ml 0.5 M Na$_2$SO$_3$. Prior to irradiation the reaction set up was purged with He (20 ml/min for 1 hr) to remove the air and then purged with high purity CO$_2$ (1bar, 5 ml/min) for 1 hr. During irradiation, 1 ml of gaseous product from the set-up was sampled and subsequent analysis was done by Gas Chromatography (Shimadzu Tracera GC-2010 Plus) with Barrier Ionization Detector (BID) and He carrier gas. Blank experiments were carried out in absence of CO$_2$ and light to confirm that these two factors are indispensable for photocatalytic CO$_2$ reduction reaction. For stability test, the selected photocatalyst was collected after each run, refreshed by washing with water and its performance was re-evaluated by the aforementioned procedure.

The selectivity of formed CO was deduced according to the following equation $^{50}$

$$\text{% of CO selectivity} = \frac{2N_{CO}}{2N_{CO} + 2N_{H_2}} \times 100$$

Here, $N_{CO}$ and $N_{H_2}$ stand for the yield of reactively formed CO and H$_2$, respectively.

Apparent quantum yield (AQY) of the photocatalyst was calculated using the following equation$^{50}$:

$$\text{AQY %} = \frac{\text{The number of evolved CO molecules}}{\text{The number of incident photons}} \times 2 \times 100$$

3. RESULTS AND DISCUSSION:
In the present study, the composite C$_3$N$_4$/FeWO$_4$ was synthesized by simple ultrasonic assisted (sonochemical) method followed by post-thermal treatment which is illustrated schematically in **Scheme 1**. Individually, C$_3$N$_4$ nanosheets and FeWO$_4$ nanoparticles were ultrasonicated to get exfoliated C$_3$N$_4$ nanosheets and uniformly dispersed FeWO$_4$ nanoparticles. In the next step, the two solutions were mixed together and ultrasonicated again which allows the coupling between C$_3$N$_4$ and FeWO$_4$ through electrostatic interactions. The positively and negatively charged surfaces of C$_3$N$_4$ and FeWO$_4$, respectively, help them assemble into heterojunction configurations driven by the forces of electrostatic attraction as confirmed by Zeta potential data$^{19,34,50,51}$ presented in the supporting information Figure S1. Further, the attachment is enhanced by thermal treatment given to composite at 400°C for 2hrs. With the above-mentioned protocol 80 wt.%, 50 wt.% and 30 wt.% C$_3$N$_4$/FeWO$_4$ composites were prepared and evaluated for photocatalytic reduction of CO$_2$.

The crystal structures of C$_3$N$_4$, FeWO$_4$ and their composites were confirmed by XRD as given in **Figure 1**. The pristine C$_3$N$_4$ showed two characteristic peaks at 13.0° and 27.4° indexed respectively to (100) diffraction plane corresponding to in-plane packing motif of tri-s-triazine and (002) plane corresponding to interlayer stacking of aromatic rings.$^{18,50}$ For FeWO$_4$ all the peaks are well matched with (JCPDF-0712390) confirming Wolframite family with monoclinic crystal structure. Besides, no other phases were observed indicating the phase purity of samples. In all the cases of composites, characteristic peaks of C$_3$N$_4$ and FeWO$_4$ were observed indicating the co-existence of both the phases.
Neither any shift in the peaks nor any other impurity peaks were observed. Although, the characteristic peak of C$_3$N$_4$ in 30% composite is not clearly seen (though it can be clearly seen on the log scale as shown in the supporting information S2), but as the percentage of C$_3$N$_4$ is increased in the composite the peak of (002) plane can be seen distinctly especially in the case of 80% C$_3$N$_4$/FeWO$_4$.

FESEM and TEM were employed to investigate the morphology and the microstructure of the as-prepared samples. Figure 2a shows stacked curly 2D nanosheet like structure of C$_3$N$_4$, whereas Figure 2b displays cuboid like nanoparticles of FeWO$_4$ with particle size of ~ 40-50 nm. In the composite case (Figure 2c), stacked and compact nanosheet of C$_3$N$_4$ loaded with nano particles of FeWO$_4$ is seen. It can be seen from the image that particles are not only decorated on the sheet but are also present in between the stacked nanosheets of C$_3$N$_4$. In either case, it is clear that the FeWO$_4$ nanoparticles are firmly anchored onto the C$_3$N$_4$ nanosheets. Elemental Dispersive X-ray Spectroscopy (EDS) spectra (supporting information S3) and Elemental mapping (supporting information S4) of composite (80 wt. % C$_3$N$_4$/FeWO$_4$) clearly indicates that sample is composed of elements C, N, Fe, W and O and there is uniform distribution of FeWO$_4$ nanoparticles on the surface of C$_3$N$_4$ nanosheets.

The TEM image in Figure 2d also confirms the 2D nanosheet like morphology of C$_3$N$_4$. On the other hand, FeWO$_4$ shows cuboid like nanoparticles of size ~ 40 nm as presented in Figure 2e. In the composite, aggregates of FeWO$_4$ nanoparticles with increased size
of ~ 50-60 nm were seen to be embedded on ultrathin nanosheet of $C_3N_4$. The HRTEM images given in Figure 2 g and 3h denote the d-spacing of 0.325 nm and 0.377 nm corresponding to (002) plane of $C_3N_4$ and (110) plane of FeWO$_4$, respectively. Similarly, in the composite case, both the planes are seen indicating close proximity of the two components in the composite. No particles are seen to be separated or unanchored from nanosheet implying strong interaction between $C_3N_4$ and FeWO$_4$ which can form heterojunction structure instead of a simple physical mixture. Formation of such heterojunction between the two components can promotes favorable charge transfer of photogenerated charges at the interface junction.

Nitrogen absorption–desorption isotherms (Supporting information Figure S5) of $C_3N_4$, FeWO$_4$ and 80% $C_3N_4$/FeWO$_4$ samples show type IV adsorption-desorption isotherms characteristic with H3 hysteresis loop indicating slit like mesopores (2-50 nm) generated by aggregation of sheets like material or particles respectively, whereas in case of composite much more narrower slit like pores are generated. The results presented in Table S1 indicate lower surface area, pore volume and pore diameter of composite as compared to pristine $C_3N_4$ and FeWO$_4$. The decline in the different parameters of composite implies that nano particles of FeWO$_4$ are filling the original slit pores of $C_3N_4$ matrix making it much narrower, ultimately leading to the high degree of interfacial contact between $C_3N_4$ and FeWO$_4$.

The FTIR spectra of $C_3N_4$, FeWO$_4$ and (30 wt. %, 50 wt. % and 80 wt. %) $C_3N_4$/FeWO$_4$ are given in Figure 3. In pure $C_3N_4$, the peak at 1628 cm$^{-1}$ corresponds to C-N stretching
vibration modes while the peaks at 1410, 1323 and 1235 cm\(^{-1}\) belong to aromatic C-N stretching. The characteristic peak at 809 cm\(^{-1}\) is ascribed to the breathing modes of tris-triazine units.\(^{18,50}\) In the IR spectrum of FeWO\(_4\), the peaks at 500 cm\(^{-1}\) and 550 cm\(^{-1}\) are assigned to asymmetric vibrational mode of Fe-O whereas the peaks at 633 cm\(^{-1}\) and 700 cm\(^{-1}\) correspond to the stretching modes of W-O. The broad band at 844 cm\(^{-1}\) is the characteristic peak of asymmetric vibration of the bridge oxygen atom of Fe-O-W.\(^{37,52}\) In the FTIR spectrum of composites, all the peaks of C\(_3\)N\(_4\) and FeWO\(_4\) are seen but major shift is seen in Fe-O and W-O vibrational modes. Similarly, in Fe-O-W mode red shift is seen with the increased introduction of C\(_3\)N\(_4\) in the composite as given in enlarged inset figure of FTIR. Inversely, the characteristic vibrational modes of tris-s-triazine units in C\(_3\)N\(_4\) also showed gradual red shift with increased introduction of FeWO\(_4\) in the composite. Such kind of simultaneous shift in the characteristic peaks of C\(_3\)N\(_4\) and FeWO\(_4\) in composite photocatalyst implies strong interaction at the C\(_3\)N\(_4\)/FeWO\(_4\) heterostructure interface.

To discover the surface chemical bonds of the photocatalyst, XPS data was recorded and are presented in Figure 4. In figure 4a, C1s spectra of pure C\(_3\)N\(_4\) and 80 wt.% C\(_3\)N\(_4\)/FeWO\(_4\) are compared. The peak centered at 284.6 eV corresponds to C-C bond, whereas peak at 288 eV corresponds to tertiary carbon C-N\(_3\).\(^{33,34,19}\) Both the peaks are present in pure C\(_3\)N\(_4\) as well as in the composite without any shift. In the N1s spectrum (Figure 4b), three binding energies 398.9 eV (C=N-C), 400.3 eV (C\(_3\)-N) and 401.5 eV (N-H) are attributed to pure C\(_3\)N\(_4\) which are shifted to lower binding energy in C\(_3\)N\(_4\)/FeWO\(_4\)
composite, indicating the change in the chemical environment of C$_3$N$_4$ after introduction of FeWO$_4$.\textsuperscript{33,34,19} Similar fact was also observed in the O1s spectrum given in Figure 4c. Five deconvoluted peaks in the case of O1s spectrum of FeWO$_4$ are seen corresponding to the lattice oxygen of Fe-O (529.8 eV), -OH bond (530.7 eV), metallic oxide of Fe-O (531.4 eV), W-O-W (532.4 eV) and water molecule (533.4 eV) adsorbed on the surface, respectively.\textsuperscript{40} The same five peaks are also present in the composite but with downward shift in binding energy. The shifts in the O1s and N1s contributions establish that C$_3$N$_4$ and FeWO$_4$ have formed a heterostructure and the composite is not a simple physical mixture. This is of immense significance for the transfer of photogenerated charges across the interface as discussed later. In the Fe 2p spectra of FeWO$_4$ and C$_3$N$_4$/FeWO$_4$ composite, two main peaks of 2p$_{3/2}$ and 2p$_{1/2}$ are seen without presence of any satellite peak which indicates that Fe exists in pure + 2 state. Similarly, in W 4f spectrum two symmetric peaks of 4f$_{5/2}$ and 4f$_{7/2}$ are seen indicating W + 6 oxidation state.\textsuperscript{40}

To investigate and understand the opto-electronic properties of the prepared photocatalyst under study, UV-visible diffuse reflectance spectroscopy (UV-Vis DRS), photoluminescence (PL) and Mott-Schottky measurements were performed. From the DRS spectra given in Figure 5, it is clear that C$_3$N$_4$ has an absorption band edge at around 440 nm corresponding to band gap of 2.8 eV calculated from Tauc plot given in supporting information Figure S6 a, which is in agreement with previously reported values.\textsuperscript{8,9,19} In contrast, FeWO$_4$ exhibits wide absorption range till 530 nm corresponding to a band gap
of 2.3 eV (Figure S6 b). Markedly, different from the absorption features of pristine C$_3$N$_4$ and FeWO$_4$, the composite 80 wt.% C$_3$N$_4$/FeWO$_4$ shows two distinct optical absorption edges ascribed to the intrinsic absorption edges of individual components. This implies combined optical absorption property of C$_3$N$_4$ and FeWO$_4$.

The photoluminescence (PL) analysis was performed to study the interfacial charge transfer and separation efficiency of photogenerated electrons and holes in C$_3$N$_4$/FeWO$_4$. The PL spectra given in Figure 6a display a broad PL emission peak centered at 455 nm for pristine C$_3$N$_4$ which is in line with the previous reports. The peak is attributed to the band to band PL due to recombination of photo carriers in C$_3$N$_4$. In addition, strong PL quenching is possibly observed in case of C$_3$N$_4$/FeWO$_4$ composite suggesting the suppressed carrier recombination and improved charge separation, owing to the formation of C$_3$N$_4$/FeWO$_4$ heterostructure with strong interaction. Furthermore, charge transfer and separation efficiency were evaluated by transient photocurrent response given in Figure 6b. The strong photocurrent in the case of C$_3$N$_4$/FeWO$_4$ compared to pristine C$_3$N$_4$ reveals the higher separation rate of photocharges in the composite. Similarly, low charge transfer resistance in composite C$_3$N$_4$/FeWO$_4$ compared to pristine samples is observed by Electrochemical Impedance Spectra (EIS) given in supporting information S7. The reason lies in well-built interface of C$_3$N$_4$/FeWO$_4$ composite which is in good agreement with PL data as well as with the interpretation based on various aforementioned characterization techniques.
Further, Mott-Schottky (MS) analysis was done to investigate the fermi levels of the photocatalyst. The positive slopes of Mott-Schottky plots (Figure 6c and d) indicate n-type semiconducting feature of C₃N₄ and FeWO₄. Moreover, from the extrapolation of straight line to the x-intercept, calculated flat band potential (equivalent to conduction band) values for C₃N₄ and FeWO₄ are -1.35 V vs NHE and 0.42 V vs (NHE), respectively. The values indicate that CB of C₃N₄ is much more favorable for reduction reaction as compared to FeWO₄. The valence band values for C₃N₄ and FeWO₄ are 1.5 V and 2.8V vs NHE, respectively which were derived from UV-vis DRS spectra.

3.1 Photocatalytic Activity of C₃N₄/FeWO₄:

The photocatalytic CO₂ reduction performance of the pristine and composite photocatalysts was evaluated under solar light using Na₂SO₃ as a hole scavenger. The products were analyzed in regular interval of 1 hr as shown in Figure 7. CO (CO₂ + 2H⁺ + 2e⁻ → CO + H₂O) was found to be the main and direct product of photocatalytic CO₂ reduction. However, H₂ (2H⁺ + 2e⁻ → H₂) was also detected due to water splitting reaction, whereas holes are consumed by Na₂SO₃ (NaSO₃ + 2OH⁻ + 2h⁺ → Na₂SO₄ + H₂O). The control experiments (supporting information figure S8) in the absence of photocatalyst or light or CO₂ were also performed, confirming that the obtained CO is solely originating from CO₂ photoreduction and also illustrates that light, CO₂ and photocatalyst are essential for the photocatalytic CO₂ reduction.
Very interestingly, C$_3$N$_4$/FeWO$_4$ composites showed excellent performances for photocatalytic CO$_2$ reduction under solar light irradiation as shown in Figure 7a. After 5 hrs of irradiation, optimum photocatalytic activity over 80 wt. % C$_3$N$_4$/FeWO$_4$ was 30.6 µmol/g, which is almost 6-folds and 15-folds higher as compared to pristine C$_3$N$_4$ (6.02 µmol/g) and FeWO$_4$ (1.94 µmol/g) samples, respectively. The optimum CO production rate of 80 wt. % C$_3$N$_4$/FeWO$_4$ is also relatively higher than the other composites: 30% C$_3$N$_4$/FeWO$_4$ (18.9 µmol/g) and 50% C$_3$N$_4$/FeWO$_4$ (22.9 µmol/g). The low performance of C$_3$N$_4$ and FeWO$_4$ can be attributed to the electron-hole recombination prevailing in the system. Additionally, FeWO$_4$ possesses unfavorable energy levels for CO$_2$ reduction as seen from the MS plot (Figure 6d). Although, during photocatalytic CO$_2$ reduction, the undesired H$_2$ evolution from water splitting is also observed (Figure 7b), but the CO selectivity is greater than 90% over H$_2$ evolution. Notably, the selectivity of CO for 80 wt. % C$_3$N$_4$/FeWO$_4$ is almost 100% over hydrocarbons as no CH$_4$ or any other higher hydrocarbons were seen to evolve. Furthermore, the measured apparent quantum efficiency (AQE) for the 80 wt.% C$_3$N$_4$/FeWO$_4$ composite using 420 nm band pass filter is significant (~ 0.3%), and higher than the prior reported literature.$^{53,54,55}$

It is well-known that the catalyst reusability is always a critical issue for long run performance of CO$_2$ reduction in practical applications. In order to investigate the stability of the C$_3$N$_4$/FeWO$_4$ composite, three successive cyclic experimental runs were performed under the same experimental conditions. Each run was conducted after evacuation and purging of fresh CO$_2$ in the set up. As shown in Figure 8, the photocatalytic CO evolution
of composite is nearly constant even after 3 successive experimental runs of total 18 hrs of illumination. A slight decrease after 3rd cycle, retaining almost 97% original activity, is observed which may be due to inevitable loss of the catalyst during cyclic run. The reusability results are a direct evidence of firm attachment of FeWO$_4$ to C$_3$N$_4$ nanosheets, also indicating a strongly built-in heterojunction between them to produce a constant outcome throughout the long run.

3.2 Photocatalytic mechanism:

In order to understand the mechanism for enhanced photocatalytic activity for CO$_2$ reduction of the C$_3$N$_4$/FeWO$_4$ composites, band line-ups were obtained w.r.t. to CO$_2$ reduction potential, with the values derived from UV-Vis DRS and Mott Schottky plots. The derived energy level diagram given in Figure 9 clearly indicates that the conduction band (CB) edge of C$_3$N$_4$ is just above the reduction potential of CO$_2$ (-0.51V vs NHE)\textsuperscript{8,9} whereas that of FeWO$_4$ is below it. Thus, C$_3$N$_4$ has much more favorable energy levels compared to FeWO$_4$ individually but interestingly as a composite they exhibit enhanced photocatalytic activity.

Considering the band structures of C$_3$N$_4$ and FeWO$_4$ two possible charge transfers are possible: Type II heterojunction and direct Z-scheme. According to conventional type II heterojunction which is band to band charge transfer, the photogenerted electrons from the CB of C$_3$N$_4$ must be transferred to CB of FeWO$_4$ where CO$_2$ reduction is expected to occur, on other hand, holes are transferred from VB of C$_3$N$_4$ to VB of FeWO$_4$. However,
our catalytic activity and band-structure results clearly show this to be unlikely in the present heterostructure system due to unfavorable energy levels of FeWO₄ for CO₂ reduction to CO. Therefore, due to band-structure matching, Z-scheme is the feasible mechanism in the present system. In the Z-scheme C₃N₄/FeWO₄ composite system, the C₃N₄ and FeWO₄ photocatalysts are in contact with band matching in such a way that electrons from the CB of FeWO₄ will combine with the holes from the VB of C₃N₄ after photo excitation, leaving electron in C₃N₄, where CO₂ reduction to CO take place due to appropriate band potential for CO formation, and hole in FeWO₄, i.e electrons and hole are in spatially separated in different locations. This kind of spatially separated photocatalytic systems has great advantage as efficient charge separation can be achieved and thereby high performance is realized for photocatalytic reactions.

As seen from a Figure 9 FeWO₄ has relatively negative conduction potential (0.42 V vs NHE) w.r.t. to C₃N₄ valence band potential (1.5 V vs NHE) which effectively favors the Z-scheme mechanism. As a result, electrons in CB of C₃N₄ with high reducibility are greatly preserved (which would otherwise combine with its own holes from VB) whereas holes in the VB of FeWO₄ with their high oxidizibility are preserved. Consequently, more photogenerated electrons are available to perform photocatalytic reduction of CO₂. Ultimately, CO yield and selectivity both are enhanced in the C₃N₄/FeWO₄ composite as compared to its pure counterparts. Notably, despite the unfavorable energy levels of FeWO₄ for the CO₂ reduction, only 20% addition of FeWO₄ in the composite (80 wt. % C₃N₄/FeWO₄) has shown an immense enhancement in photocatalytic CO₂ reduction as
compared to 100% C\textsubscript{3}N\textsubscript{4}, which justifies the possible direct scheme mechanism. To confirm the role of FeWO\textsubscript{4} and Z-scheme mechanism in the present system, we studied the hydroxyl radical formation using terephthalic acid as a probe molecule in PL analysis. It is well-known that the terephthalic acid readily combines with OH radical and forms 2-hydroxyterephthalic acid which shows PL emission peak around 425 nm. Comparison of PL intensity for all the samples against irradiation time was monitored and given in Figure 10 b. For FeWO\textsubscript{4} (Supporting information figure S 9) and composite C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4} sample (Figure 10 a) gradual increase in PL intensity was observed as compared to C\textsubscript{3}N\textsubscript{4}, indicating the formation of OH radical on their surfaces upon illumination except for C\textsubscript{3}N\textsubscript{4}. Considering the relative band edge positions of C\textsubscript{3}N\textsubscript{4} and FeWO\textsubscript{4} along with standard redox potentials of OH/\textsuperscript{−} OH (2.5V vs NHE) and O\textsubscript{2}/O\textsubscript{2}\textsuperscript{−} (-0.3V vs NHE) \textsuperscript{33,56} given in Figure 9, only photogenerated holes in the VB of pristine FeWO\textsubscript{4} and FeWO\textsubscript{4} present in the composite C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4} can produce OH radical whereas photogenerated electrons in C\textsubscript{3}N\textsubscript{4} are able to produce only superoxide radical anion O\textsubscript{2}\textsuperscript{−}. If the obtained composite C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4} would have followed conventional heterojunction mechanism then neither OH radical nor superoxide radical anion O\textsubscript{2}\textsuperscript{−} would be produced, thus resulting in subsequent absence of the PL signal. However, strong PL signal in the composite was seen to increase linearly with time and has intensity greater than that for pristine FeWO\textsubscript{4} as shown in Figure 10 b. Thus, OH radicals were indeed produced in the case of the composite which confirms the direct Z-scheme mechanism in C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4} instead of conventional heterojunction type. Consequently, the prevailing recombination
in C₃N₄ is highly suppressed (evident from PL and on-off transient) as the holes from VB of C₃N₄ are very well quenched by electrons from CB of FeWO₄ under Z scheme mechanism, preserving the photogenerated electrons in C₃N₄ for photocatalytic CO₂ reduction. Thus, coupling of FeWO₄ with C₃N₄ under Z scheme mechanism has not only induced efficient charge separation in C₃N₄ but also restored its reducing capability resulting in almost 6-fold enhancement in photocatalytic performance along with high CO selectivity.

4. CONCLUSIONS:

In summary, a direct Z-scheme C₃N₄/FeWO₄ photocatalytic system was constructed by simple sonochemical method followed by post annealing treatment which assembled the two components in the composite through electrostatic attraction and through thermal attachment. The resultant composite exhibited excellent photocatalytic performance and selectivity for CO₂ reduction. The optimum C₃N₄/FeWO₄ showed highest CO production rate of 6 µmol/g/hr which is almost 6 times and 15 times higher than pure-C₃N₄ and FeWO₄ phases, respectively. Moreover, it showed almost ~ 91% CO selectivity with no CH₄ or any other higher hydrocarbon evolution. The overall performance of new photocatalytic system is ascribed to the direct Z scheme mechanism with appropriate band matching of FeWO₄ with respect to C₃N₄ band edges. The novel coupling under Z-scheme mechanism of hybrid photocatalyst not only favors superior charge separation of electron-hole pair in C₃N₄ but also restores the reducibility of C₃N₄ for CO₂
photoreduction. Importantly, the Z scheme photocatalyst was photostable even after successive experimental runs, without any obvious change in the activity. The present work provides significant insights for constructing a stable functional composite via Z-scheme for selective photocatalytic reduction of CO₂.

ASSOCIATED CONTENT

Supporting Information

Zeta Potential measurement, EDS, Elemental mapping, BET measurements, Tauc plot, EIS spectra, Photocatalytic control experiment, Time dependent PL of FeWO₄ in terephthalic acid.

AUTHOR INFORMATION

Corresponding Author

Email: satishogale@gmail.com, S.Kumar@bath.ac.uk

ACKNOWLEDGEMENTS
We thank DST Nanomission (Thematic Unit SR/NM/TP-13/2016), Govt. of India for research grant. SK also thanks the Engineering and Physical Sciences Research Council (EPSRC) (EP/R026041/1) for financial support.

5. REFERENCES


(7) Xie, S; Zhang, Q; Liu, G; Wang, Y. Photocatalytic and Photoelectrocatalytic reduction of CO$_2$ using heterogeneous catalysts with controlled nanostructures Chem. Commun. 2016, 52, 35–59.


Dhakshinamoorthy, A.; Navalon, S.; Garcia, H. Photocatalytic CO₂ Reduction by TiO₂ and


(34) Xu, Q.; Zhu, B.; Jiang, C.; Cheng, B.; Yu, J. Constructing 2D/2D Fe$_2$O$_3$/g-$\text{C}_3\text{N}_4$ Direct Z-


(43) Qu, W.; Wlodarski, W. Comparative Study on Micromorphology and Humidity Sensitive Properties of Thin-Film and Thick-Film Humidity Sensors Based on Semiconducting MnWO₄. *Sensors and Actuators* 2000, 64 (64), 76–82.


(55) Article, E.; Zhang, G.; Lan, Z.; Lin, L.; Lin, S.; Wang, X. Overall Water Splitting by Pt/g-

6. FIGURE CAPTIONS

**Scheme 1.** Schematic illustration of synthesis process of hybrid photocatalyst C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}

**Figure 1.** XRD pattern of C\textsubscript{3}N\textsubscript{4}, FeWO\textsubscript{4} and different composites of C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}

**Figure 2.** (a), (b) and (c) FESEM images, (d), (e) and (f) TEM images and (g), (h) and (i) HRTEM images of C\textsubscript{3}N\textsubscript{4}, FeWO\textsubscript{4} and C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}, respectively.

**Figure 3.** FTIR spectra of C\textsubscript{3}N\textsubscript{4}, FeWO\textsubscript{4} and different composites of C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}. Inset enlarge FTIR shows the characteristics peaks of C\textsubscript{3}N\textsubscript{4} and FeWO\textsubscript{4} and C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}, respectively, in the 750 cm\textsuperscript{-1} to 890 cm\textsuperscript{-1} region.

**Figure 4.** XPS spectrum of a) C 1s, b) N 1s, c) O 1s, d) Fe 2p and e) W 4f of C\textsubscript{3}N\textsubscript{4}, FeWO\textsubscript{4} and C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}.

**Figure 5.** DRS spectra of C\textsubscript{3}N\textsubscript{4}, FeWO\textsubscript{4} and C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}.

**Figure 6.** a) Photoluminous spectra b) On-off transient of C\textsubscript{3}N\textsubscript{4} and C\textsubscript{3}N\textsubscript{4}/FeWO\textsubscript{4}. Mott-Schottky plots of c) C\textsubscript{3}N\textsubscript{4} and d) FeWO\textsubscript{4}. 


Figure 7. Time dependent a) CO and b) H₂ over the synthesized sample (Conditions: 50 mg photocatalyst and 300 W Xenon lamp with UV cut-off filter.

Figure 8. Stability profile of C₃N₄/FeWO₄.

Figure 9. Schematic illustration of photocatalytic mechanism in C₃N₄/FeWO₄.

Figure 10. a) PL spectral changes observed during illumination of the 80% C₃N₄/FeWO₄ sample in the presence of 5 * 10⁻⁴ M terephthalic acid in 2 * 10⁻³ M NaOH solution. b) Comparison of PL peak intensity around 425 nm for the C₃N₄, FeWO₄ and 80% C₃N₄/FeWO₄.

7. FIGURES
Scheme 1

Stacked C$_3$N$_4$ nanosheets + FeWO$_4$ nanoparticles

1. Ultra-sonication
2. Grinding
3. $\Delta$, 400 $^\circ$C

C$_3$N$_4$/FeWO$_4$
Figure 1

The figure shows a series of X-ray diffraction patterns for different compositions of C₃N₄/FeWO₄. The patterns indicate the crystallographic structures of C₃N₄ and FeWO₄.

- 80% C₃N₄/FeWO₄
- 50% C₃N₄/FeWO₄
- 30% C₃N₄/FeWO₄

The peaks correspond to different crystal planes, as indicated by their Miller indices. The JCPDF identification code 07-12390 is also shown for FeWO₄.
Figure 2

(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

FeWO₄

C₃N₄

0.325 nm

0.377 nm

0.36 nm

(002)

(011)
Figure 3

![Graph showing vibrational spectra with labels for Fe-O, Fe-W-O, Trizine ring mode, C-N stretching, and C-NH-C stretching. The graph includes data for different compositions of FeWO₄ and C₃N₄.]
Figure 4
Figure 5

![Graph showing intensity vs. wavelength for different materials: C$_2$N$_4$, FeWO$_4$, and Composite.](image-url)
Figure 6
Figure 7

(a) CO evolution amount (μmol/g) vs. Irradiation Time (hrs)

(b) H₂ evolution amount (μmol/g) vs. Irradiation Time (hrs)
Figure 8

[Graph showing evolution amount (µmol/g) over time (hr) for CO and H₂, with 1ˢᵗ, 2ⁿᵈ, and 3ʳᵈ runs indicated.]
Figure 9
Figure 10

(a) Intensity (a.u.) vs. Wavelength (nm)

(b) PL Intensity (a.u.) vs. Irradiation time (min)

- **C₃N₄**
- **FeWO₄**
- **C₃N₄/FeWO₄**
SYNOPSIS:
An efficient direct Z scheme photocatalyst FeWO$_4$/C$_3$N$_4$ for selective CO$_2$ photoreduction to CO
TOC Figure