

Supporting Information

Controlled Ni doping on g-C₃N₄/CuWO₄ Photocatalyst for Improved Hydrogen Evolution

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1. Experimental section:

1.1 Materials:

Urea (Himedia, 99.0%), CuCl₂.2H₂O (Sigma Aldrich, 99.0%), NiCl₂ (anhydrous, Alfa Aesar, 98.0%), polyethylene glycol 4000 (SRL), methanol (Himedia, 99.8%) chemicals were used for this research purpose. All the purchased chemicals are of analytical grade and were used directly without further treatment.

1.2 Catalyst preparation:

1.2.1 Synthesis of g-C₃N₄:

The bulk g-C₃N₄ can be easily synthesised by thermal polymerisation of urea. Urea is cost-effective and easily available and therefore, it can be utilised as the extremely useful precursor for the synthesis of g-C₃N₄. Typically, 20 g urea was taken in a silica crucible covered with a lid and calcined in a muffle furnace at 550°C for 2 h with heating rate 5°C min⁻¹ under air atmosphere. After cooling to room temperature yellow coloured bulk g-C₃N₄ was obtained as the desired product.

1.2.2 Synthesis of Ni-CuWO₄ (NCW):

Ni-CuWO₄ nanocompound can be synthesized by chemical precipitation method. In a typical synthesis, 1 mmol of CuCl₂.2H₂O was added to the solution of Na₂WO₄.2H₂O dissolved in 2% PEG-4000 with a molar ratio of 1:1. A blue precipitate was obtained. After sonicated for half an hour, 1 mmol of NiCl₂ was added to it and mixed well. The blue precipitate turned bluish green after the addition of NiCl₂. The pH of the solutions were maintained at nearly 7 before mixing. The mixture was then again sonicated in an ultrasonicator bath for 2 h and stirred for 6 h. The bluish green precipitate formed was filtered and washed with deionized water several times followed by ethanol. The precipitate was dried under vacuum at 60°C and finally calcined at 500°C in a muffle furnace for 4 h to get the desired product.

1.2.3 Synthesis of Ni-CuWO₄/g-C₃N₄ nanocomposite (NCWCN):

For the synthesis of Ni-CuWO₄/g-C₃N₄ nanocomposite, the highly porous bulk g-C₃N₄ (340 mg) was first dispersed in 50 mL of methanol. Then the suspension of g-C₃N₄ was ultrasonicated for almost 10 h for exfoliation. Afterwards, a certain amount of as prepared Ni-CuWO₄ (60 mg) was added to this solution and was sonicated for almost 5 h to make uniform dispersion. The solution was then kept stirring for about 24 h. The product obtained was filtered and washed with distilled water followed by ethanol several times. Finally, the product was dried under vacuum at 60°C. The products obtained were labelled as x NCWCN, where x was denoted as the value of mass ratio of Ni-CuWO₄ and g-C₃N₄. Thus the as synthesized nanocomposite would contain mass ratio of 0.2. Accordingly, different mass ratio containing Ni-CuWO₄/g-C₃N₄ such as 0.05, 0.1, 0.3 etc. nanocomposites were also synthesized. The percentage composition of main metal elements Cu, Ni, W in the catalysts with different mass ratio were included in Table S1.

Table S1. Percentage of main metal elements (Cu, Ni, W) of the as synthesized catalysts (determined from XPS data)

Catalyst	Cu (atomic wt%)	Ni (atomic wt%)	W (atomic wt%)
0.05 Ni-CuWO ₄ /g-C ₃ N ₄	0.7%	0.4%	1.1%
0.1 Ni-CuWO ₄ /g-C ₃ N ₄	1.4%	0.7%	1.6%
0.2 Ni-CuWO ₄ /g-C ₃ N ₄	1.9%	1.1%	1.7%
0.3 Ni-CuWO ₄ /g-C ₃ N ₄	2.3%	1.7%	2.1%

1.3 Photocatalytic H₂ production:

The photocatalytic hydrogen production of the as synthesised materials were carried out in a Pyrex glass double-walled photoreactor which is fitted with air tight rubber septum at the top portion. In a typical experiment, 20 mg of the catalyst was taken with 18 mL of deionized water and 2 mL of methanol as sacrificial electron donor. Prior to light irradiation, the reaction mixture was degassed with N₂ gas and the insertion of the inert atmosphere (N₂) have been carried out for a period of 30 min through this portion of the reactor. Then the reactor was kept under a 420 W Xe arc lamp ($\lambda \geq 420$ nm) light irradiation (Newport Co., Ltd., USA) with constant stirring. The evolved H₂ gas was analyzed at a regular interval of every hour) using gas chromatography (Perkin Elmer Clarus 590 GC containing molecular Sieve/5 °A column) with a thermal conductivity detector using N₂ as a carrier gas. The AQY is calculated to be 6.49%.

Apparent Quantum Yield (AQY) calculation

The light source was used 420 W Xe arc lamp (Newport Co., Ltd., USA) of intensity 0.16 W. cm⁻² and used cut-off filter ($\lambda \geq 420$ nm) for irradiation. We have used an optical power/energy meter (Newport, Model: 842-PE) for determination of the number of incident photons (N_{photons}). The values of N_{photons} and AQY (%) was calculated using the following equations:

$$N_{\text{photon}} = \frac{P\lambda t}{hc}$$

Here, P represents power of the light (0.16 J s⁻¹ cm⁻²) in an area of 11.17 cm², λ is the wavelength of the light (420 nm), t is the duration of irradiation (3 h), h is the Planck's constant (6.626 x 10⁻³⁴ J s) and c is the velocity of light (3 x 10⁸ m s⁻¹). The yield of H₂ evolution in 3 h is found to be 2195 μ mol over optimised photocatalyst 0.2 NCWCN.

$$N_{\text{photon}} = \frac{0.16 \text{ J s}^{-1} \text{ cm}^{-2} \times 11.17 \text{ cm}^2 \times 420 \times 10^{-9} \text{ m} \times 3 \times 3600 \text{ s}}{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}} = 4.07 \times 10^{22}$$

$$\text{AQY} = \frac{2 \times \text{numbers of evolved H}_2 \text{ molecule}}{\text{numbers of incident photons (N}_{\text{photon}})} \times 100$$

$$AQY = \frac{2 \times \text{yield of hydrogen production} \times 10^{-6} \times 6.023 \times 10^{23}}{4.07 \times 10^{22}} \times 100$$

$$= 6.49\%$$

1.4 Photo-Electrochemical Measurements

The PEC measurements at room temperature were recorded on the CH Instruments Inc., USA, CHI6005E, Electrochemical Workstation with Potentiostat using a three-electrode system comprising photoactive materials coated thin film ITO as the working electrode, Pt wire as counter electrode, saturated calomel electrode (SCE) as reference electrode. The artificial solar simulator of AM 1G illuminator being a photon source accounted during the measurements. The electrochemical cell was a conventional three-electrode cell with a 3 mm thick Pyrex glass eyelet. A 0.25 M Na₂SO₄ aqueous mixture with deoxygenating was employed as the electrolyte. To prepare the photoelectrode, 4 mg of each as-prepared photocatalyst was dispersed into a suspension that contained 0.4 mL ethanol and 30 μL Nafion by 30 min of ultrasonication. The working electrodes were fabricated by drop casts of the suspension (300 μL) onto an ITO plate (4 cm²) and dried at 60°C for 10 min to evaporate the solvent and then desiccated at RT. Electrochemical impedance spectroscopy (EIS) was detected over a frequency scale from 1 to 10⁵ Hz.

2. Catalyst characterisation:

The synthesized catalysts were characterised by PXRD (Powder X-ray Diffractometer), UV-Visible spectrophotometer, RAMAN spectrophotometer, SEM (Scanning Electron Microscope), TEM (Transmission Electron Microscope), N₂ adsorption-desorption isotherm etc. The PXRD measurement was carried out on a Rigaku, ultima IV X-ray diffractometer of 2θ range 2-80° using Cu K_α-source of wavelength, λ= 1.54 Å. Nitrogen adsorption measurements were performed on Autosorb-iQ (Quantachrome USA) adsorption analyser which measures adsorption isotherm, specific surface area, pore volume mechanically. The samples were degassed at 250°C for 4 h. The RAMAN spectra of the as synthesised materials were conducted on Thermo Scientific DXR2 RAMAN spectrometer. The UV-Visible spectroscopy of the synthesized catalysts was recorded on SHIMADZU UV-1800 spectrometer and the fluorescence spectroscopy was recorded on Horiba Scientific Fluorolog 3 spectrometer to generalise the optical properties. For analysing the surface, scanning electron microscopy

images (SEM) were obtained Carl Zeiss SIGMA scanning electron microscope. The compositional analysis of the sample was performed by Energy Dispersive X-ray spectroscopy on Oxford EDS attached with the same instrument. TEM images were recorded on JEOL, JEM-2100 Plus Electron Microscope. XPS analysis was performed on an X-ray Photoelectron Spectrometer (ESCALAB Xi+, Thermo Fischer Scientific Pvt. Ltd., UK) using monochromatised AlK_{α} radiation. The photocatalytic experiments were carried out under external light source using a 420 W Xenon arc lamp (Newport, USA). GC analysis was performed by gas chromatograph TCD detector (Perkin Elmer Clarus 590 GC containing molecular Sieve/5Å column) using nitrogen (N_2) as carrier gas.

3. Morphological study

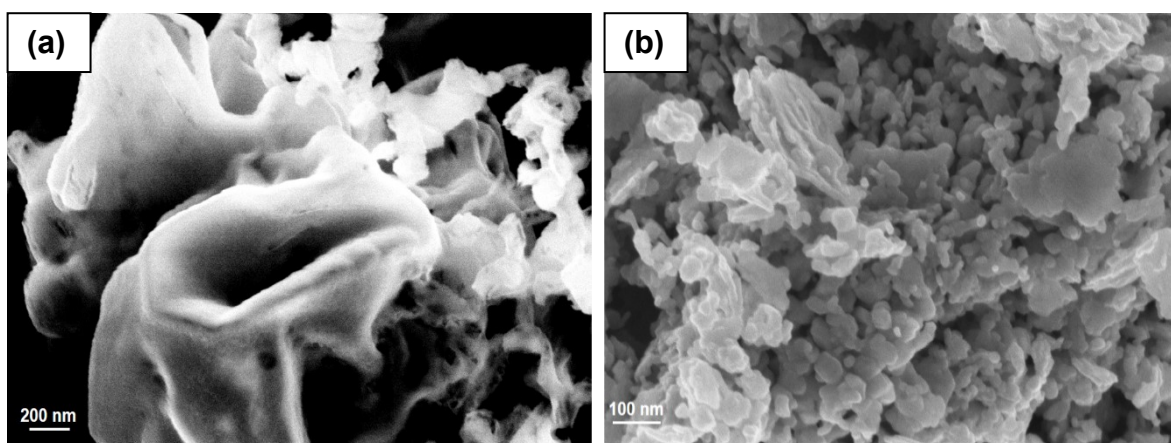


Figure S1. FESEM images of (a) pure $g-C_3N_4$ and (b) $Ni-CuWO_4$.

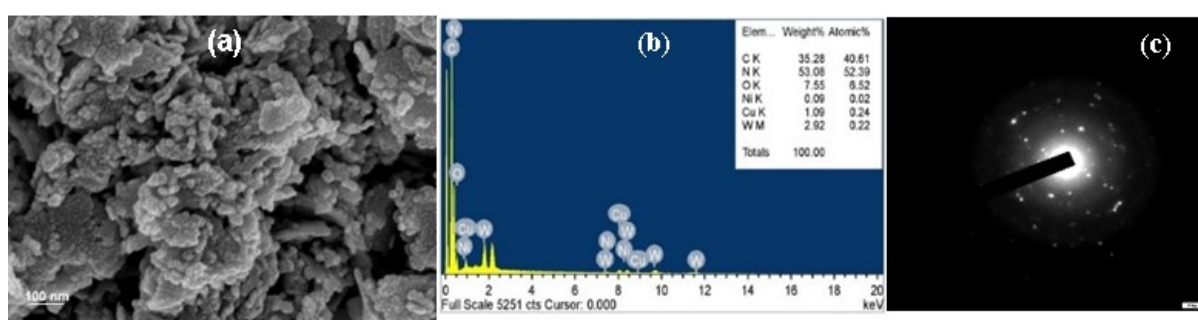


Figure S2. (a) FESEM image, (b) EDX image and (c) SAED pattern of composite 0.2 NCWCN.

4. Characterisation of recovered catalyst

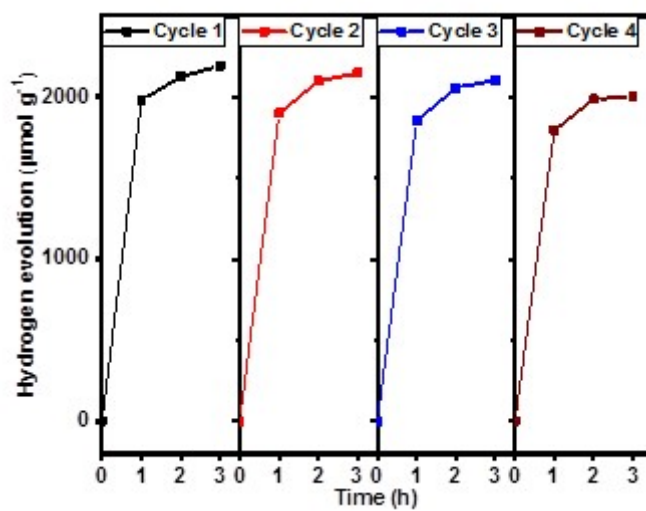


Figure S3. Recyclability of photocatalytic H₂ evolution over 0.2 NCWCN.

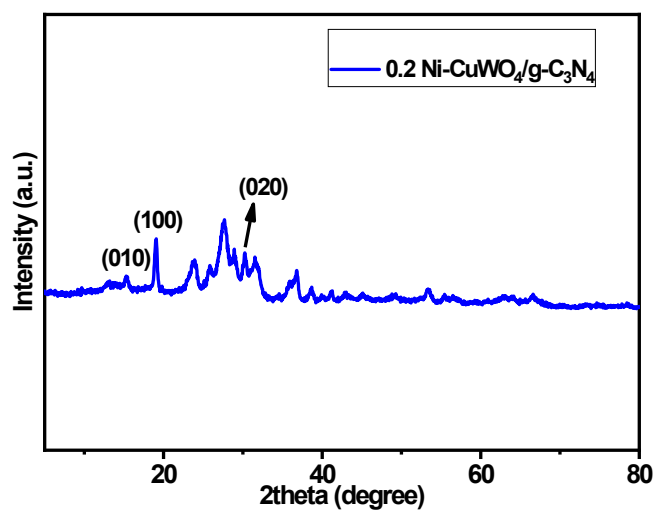


Figure S4. PXRD pattern of recovered catalyst 0.2 Ni-CuWO₄/g-C₃N₄ (0.2 NCWCN).

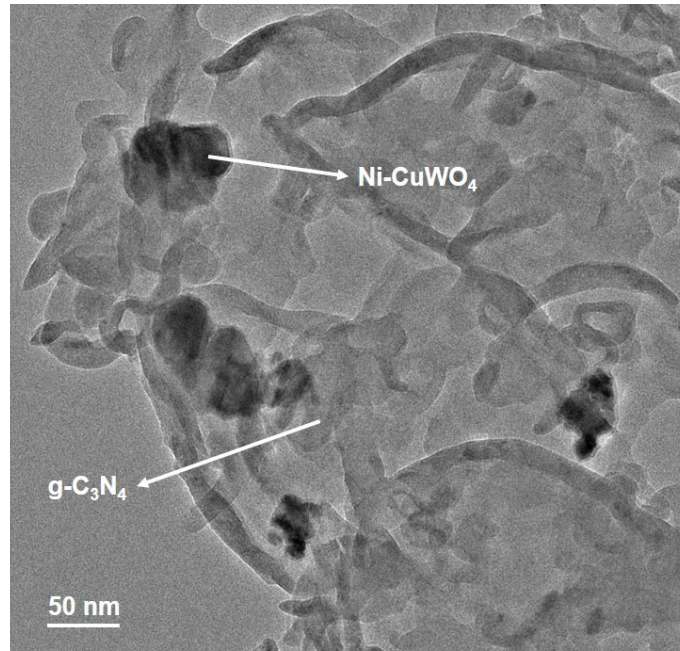


Figure S5. TEM image of recovered catalysts 0.2 Ni-CuWO₄/g-C₃N₄ (0.2 NCWCN).

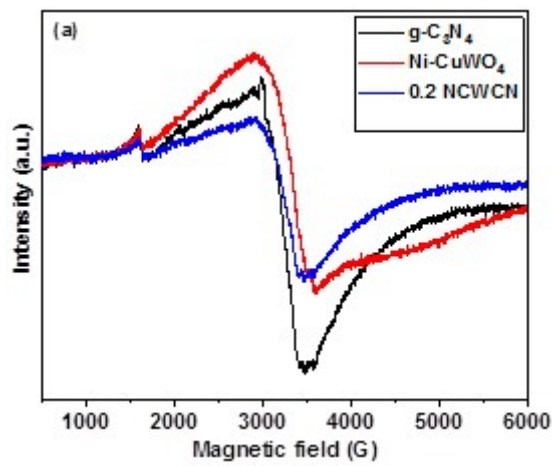


Figure S6. EPR spectra of g-C₃N₄, Ni-CuWO₄ and its composite 0.2 NCWCN.

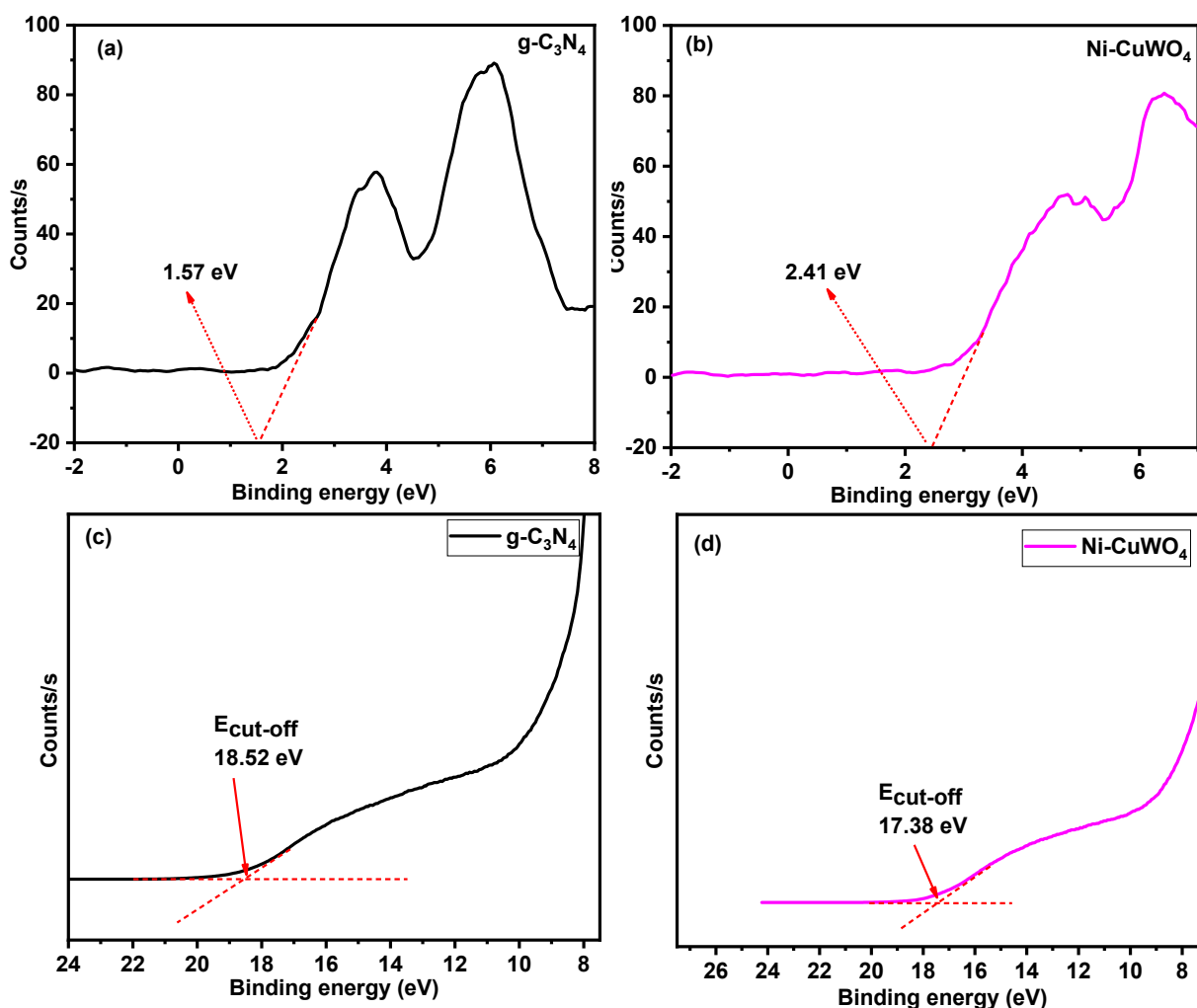


Figure S7. VB XPS of (a) g-C₃N₄, (b) Ni-CuWO₄ and UPS spectra of (c) g-C₃N₄, (d) Ni-CuWO₄.

5. Computational methodology

Here all the quantum chemical calculations have been performed within the context of density functional theory (DFT) methodology as implemented in SIESTA 4.1 computational package.¹ The exchange-correlation effects are treated with Perdew-Burke-Ernzerhof (PBE) within a generalized gradient approximation (GGA)² and 300 Ry kinetic energy cut-off is used to describe the linear combination of atomic orbital basis set. The core-valence interactions have been described using Troullier–Martins type norm-conserving pseudopotential^{3,4} along with double zeta polarized basis set. Structural relaxation has been achieved by optimizing both ions as well as a cell without imposing any symmetry constraint. The convergence threshold for energy and force are set to 10⁻⁴ eV and 0.01 eV Å⁻¹, respectively. Sampling of the Brillouin zone of the modeled surfaces has been done using 3 × 3 × 1 and 5 × 5 × 1 Monkhorst–Pack k-

point grid for geometry optimization and electronic structure calculations, respectively. To prevent superficial interactions between two successive periodic images a 15 Å vacuum spacing is kept along the non-periodic direction.

The absorption spectra can be estimated from the frequency-dependent complex dielectric function using the relation $\alpha(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}$, where, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ stands for the real and imaginary parts of the dielectric function.

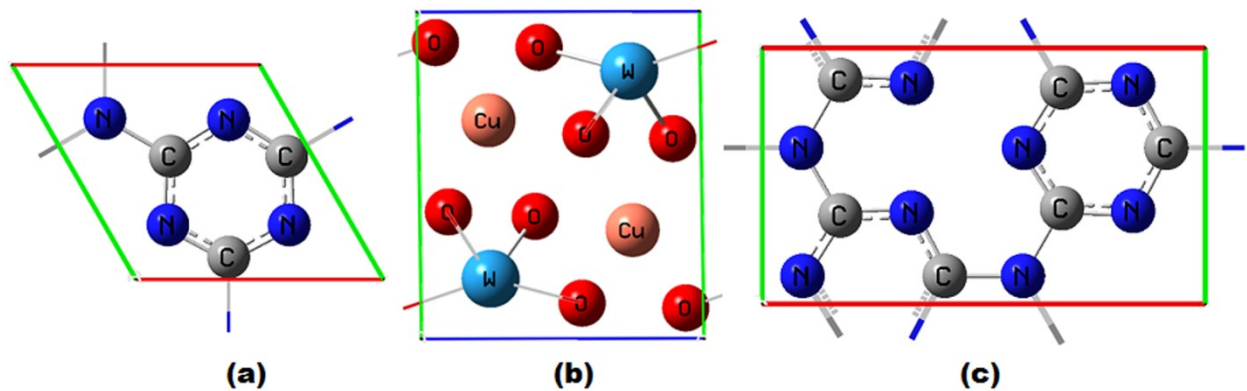


Figure S8. Optimized structure of (a) unit cell of g-C₃N₄, (b) unit cell of CuWO₄ and (c) rectangular supercell of g-C₃N₄ of size $\sqrt{3} \times 2$.

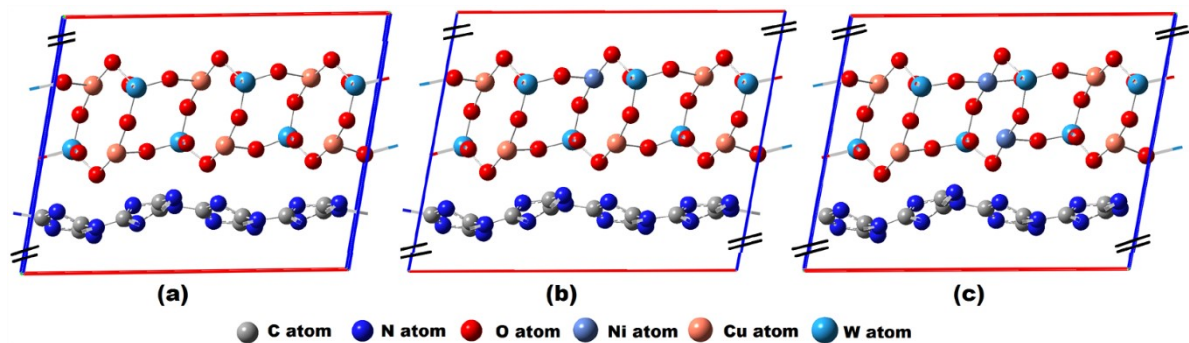


Figure S9. Optimized structure of (a) CuWO₄/g-C₃N₄ composite, (b) 1Ni-CuWO₄/g-C₃N₄ composite and (c) 2Ni-CuWO₄/g-C₃N₄ composite.

References:

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2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.
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