



Why Averaged X-ray Diffraction Descriptors Cannot Rank the Photocatalytic Hydrogen-Evolution Potential of NiFe₂O₄/g-C₃N₄ Composites: A Peak-Resolved Reassessment with Literature Benchmarking

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Abstract

Predicting the photocatalytic hydrogen-evolution ranking of ferrite/g-C₃N₄ composites from routine X-ray diffraction (XRD) and scanning electron microscopy (SEM) descriptors is attractive but rarely scrutinised. Here, XRD and FE-SEM data for pure g-C₃N₄, pure NiFe₂O₄ and NiFe₂O₄:g-C₃N₄ composites (25:75, 50:50 and 75:25 by mass, prepared by sonication-assisted physical mixing) were re-analysed at the level of individual reflections. The composition trends published for the mean spinel lattice constant (8.2534, 8.2769 and 8.3484 Å) and mean Scherrer size (10.99, 10.25 and 13.01 nm) could not be reproduced as stated. The averages combine sharp Bragg reflections (FWHM 0.12–1°) with features 3–9° wide; two averages treat the g-C₃N₄ (002) reflection inconsistently; and $\beta \cos\theta$ varies 23- to 39-fold within a single pattern, which is incompatible with size-only broadening (Williamson–Hall $R^2 \leq 0.10$). Per-peak lattice constants of two samples drift systematically with diffraction angle, a signature of specimen displacement. Nelson–Riley extrapolation gives $a_0 = 8.371 \pm 0.013$, 8.344 ± 0.021 and 8.325

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$\pm 0.013 \text{ \AA}$ for the pure ferrite and the 25:75 and 50:50 composites, values that bracket the bulk value of $8.341 \text{ \AA}$ and show no resolvable composition trend. The $g\text{-C}_3\text{N}_4$ (002) spacing recomputed for the 25:75 composite is $3.175 \text{ \AA}$, a contraction rather than the reported expansion. A benchmark of four verified studies places the optimum NiFe_2O_4 fraction between 12 and 49 wt% and shows four non-comparable hydrogen metrics. Averaged XRD descriptors from these data therefore cannot rank hydrogen-evolution activity. A minimal characterisation and reporting protocol is proposed. No hydrogen-evolution measurements were made in this work.

Highlights

- Published XRD composition trends for $\text{NiFe}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites are not reproducible from the underlying peak lists.
- Peak widths within each pattern span a factor of 23–39 in $\beta \cos\theta$, so mean Scherrer sizes are not physically meaningful.
- Nelson–Riley extrapolation shows no resolvable lattice-constant trend across the composition series.
- Verified literature places the optimum NiFe_2O_4 loading anywhere from 12 to 49 wt%, with non-comparable H_2 metrics.
- A minimal characterisation and reporting protocol is proposed for structure–activity claims.

Keywords: graphitic carbon nitride; nickel ferrite; heterojunction; X-ray diffraction; Williamson–Hall analysis; Nelson–Riley extrapolation; photocatalytic hydrogen evolution

1. Introduction

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) was shown to evolve hydrogen from water under visible light in the presence of a sacrificial donor [1], and it has since become a standard partner for narrow-gap semiconductors in heterojunction photocatalysts. Spinel ferrites such as NiFe_2O_4 are attractive partners because they absorb visible light and are magnetically recoverable. Computed and measured band gaps of NiFe_2O_4 are in the region of 1.5 eV; one theoretical study reproduced the experimental absorption spectrum with a minimum indirect gap of 1.53 eV [6].

Hydrogen-evolution studies of NiFe_2O_4 -containing composites report widely different optimum compositions and metrics. In the $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ system, a calcination-derived binary composite with 49.4% NiFe_2O_4 was the best binary sample in a plasmonic $\text{Au}/g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ study [2]; a phosphorus-doped $g\text{-C}_3\text{N}_4$ core–shell variant peaked at 20 wt% ferrite [3]; NiFe_2O_4 on mesoporous $g\text{-C}_3\text{N}_4$ gave the highest hydrogen yield among four ferrites in a dye-sensitised system [4]; and in the related $\text{NiFe}_2\text{O}_4/\text{TiO}_2$ system the best loading was 12 wt% [5]. Because direct hydrogen-evolution measurements are laboratory- and protocol-specific, there is a recurring temptation to infer the best composition from structural descriptors such as lattice constant, crystallite size and morphology.

This paper examines whether that inference is justified for one such series. XRD and FE-SEM data were collected for $g\text{-C}_3\text{N}_4$, NiFe_2O_4 and three $\text{NiFe}_2\text{O}_4:g\text{-C}_3\text{N}_4$ composites, and a structural ranking had been proposed on the basis of average lattice constants and average Scherrer sizes. Here the underlying peak lists



are re-analysed reflection by reflection, with explicit treatment of peak width, systematic angle-dependent errors and uncertainty, and the results are placed against four verified literature studies. Our aims are (i) to test whether the published structural trends are reproducible; (ii) to establish what the data can and cannot support; and (iii) to define a minimal protocol so that future composition series can support a structure–activity argument. No hydrogen-evolution rates were measured, and none are reported or inferred.

2. Materials and Experimental Data

2.1 Samples

Five samples were studied: pure g-C₃N₄ (A), pure NiFe₂O₄ (B), and NiFe₂O₄:g-C₃N₄ composites with mass ratios 25:75 (C), 50:50 (D) and 75:25 (E). All reagents (nickel nitrate hexahydrate, iron nitrate nonahydrate, citric acid, ammonium hydroxide, melamine, ethanol) were of analytical grade and used as received.

g-C₃N₄ was obtained by thermal polymerisation of melamine in a covered alumina crucible, heated to 550 °C at 5 °C min^{−1}, held for 4 h in air and cooled naturally. NiFe₂O₄ was prepared by citrate sol–gel auto-combustion: nickel and iron nitrates (Ni:Fe = 1:2) were combined with citric acid (metal nitrate: citric acid = 1:3), the pH was adjusted to about 7 with ammonium hydroxide, and the solution was heated at 80–90 °C through sol, gel and auto-combustion stages; the powder was calcined at 600 °C for 4 h. The composites were prepared by dispersing the two powders in ethanol in the stated mass ratios, sonicating for 1 h, drying at 80 °C and grinding lightly. No thermal treatment was applied after mixing (Table 1).

Table 1. Samples and preparation routes.

Sample	Composition (NiFe ₂ O ₄ :g-C ₃ N ₄ , mass)	Preparation	Data available
A	0:100 (pure g-C ₃ N ₄)	Melamine, 550 °C, 4 h	XRD (002 reflection), SEM
B	100:0 (pure NiFe ₂ O ₄)	Citrate auto-combustion; 600 °C, 4 h	XRD (10 reflections), SEM
C	25:75	Ethanol dispersion, 1 h sonication, 80 °C	XRD (11 spinel + (002)), SEM
D	50:50	As C	XRD (10 spinel + (002)), SEM
E	75:25	As C	SEM only; no XRD peak list available

2.2 Characterisation data

XRD patterns were recorded at room temperature with Cu K α radiation ($\lambda = 1.5406$ Å). For each pattern the fitted peak position (2θ) and full width at half maximum (FWHM) were available as tabulated values; the instrument model, step size, slit configuration and any internal standard were not recorded in the source material. Consequently no instrumental-broadening correction could be applied, and all crystallite sizes below are apparent sizes that include instrumental contributions. Surface morphology was recorded by

field-emission SEM (JEOL) at 20 kV in secondary-electron mode at $\times 6000$, with a 2 μm scale bar. The 75:25 sample has no XRD peak list and its micrograph is featureless (Section 4.1).

No photocatalytic hydrogen-evolution experiment was carried out for this series.

3. Analysis Methods

All calculations use the tabulated peak positions and widths listed in Appendix A and are reproducible with the accompanying script (xrd_reanalysis.py). The apparent crystallite size of each reflection was obtained from the Scherrer relation [7,10]:

$$D = K\lambda / (\beta \cos \theta) \quad (1)$$

with shape factor $K = 0.9$, β the FWHM in radians and θ half the diffraction angle. Size and strain contributions can be separated by a Williamson–Hall plot [8]:

$$\beta \cos \theta = K\lambda/D + 4\epsilon \sin \theta \quad (2)$$

A single straight line in this plot is expected only if size and strain broadening are isotropic and all reflections belong to one well-defined profile family. The cubic lattice constant follows from each indexed reflection as

$$a = (\lambda / 2 \sin \theta) (h^2 + k^2 + l^2)^{1/2} \quad (3)$$

Specimen displacement and absorption shift peak positions by amounts that depend on angle, so per-peak lattice constants drift with θ . The Nelson–Riley procedure [9] regresses a against

$$f(\theta) = \frac{1}{2} [\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta] \quad (4)$$

and takes the intercept a_0 at $f = 0$ ($\theta = 90^\circ$) as the corrected lattice constant.

Reflections were indexed to the cubic inverse spinel (space group Fd-3m) by assigning each observed position to the nearest calculated position for the reference constant $a = 8.341 \text{ \AA}$, the value refined by neutron diffraction for undoped NiFe_2O_4 [11]. Reflections more than 0.6° from the nearest calculated position were flagged and excluded from the extrapolation (sample C: 38.22° and 76.73° ; sample D: 77.10°), leaving $n = 10, 8$ and 9 reflections for samples B, C and D. Regression standard errors are reported as uncertainties. Two cautions apply: the highest-angle reflection available is at $2\theta = 77.1^\circ$, whereas extrapolation is considered reliable only when at least one reflection lies near $\theta = 90^\circ$ [9,10], so the intercepts are uncertain by more than their regression errors suggest; and the extrapolation assumes that the angle-dependent error follows the Nelson–Riley form. A secondary analysis restricted to sharp reflections (FWHM $< 1^\circ$) is reported where it has at least three points, and is treated as indicative only.

4. Results and Discussion

4.1 Morphology

Figure 1 shows the micrographs. Pristine $\text{g-C}_3\text{N}_4$ (A) appears as compact, wrinkled and folded flakes with little visible porosity. The NiFe_2O_4 sample (B) is finely granular and densely packed, with horizontal scan-line noise visible in the image. The 25:75 composite (C) shows rounded grains distributed over a porous,

interconnected scaffold, and the 50:50 composite (D) shows coarser, rounded clusters forming a continuous porous network with larger voids. The 75:25 sample (E) is almost featureless. The most plausible explanation, as proposed when the micrograph was recorded, is specimen charging of a poorly conducting, densely packed oxide imaged without a conductive coating; this is an interpretation rather than an observation of the surface and should be tested by re-imaging E with a conductive coating or at lower accelerating voltage.

Figure 1. FE-SEM micrographs of Samples A-E
(20 kV, secondary-electron imaging mode, $\times 6,000$; scale bars = 2 μm as marked)

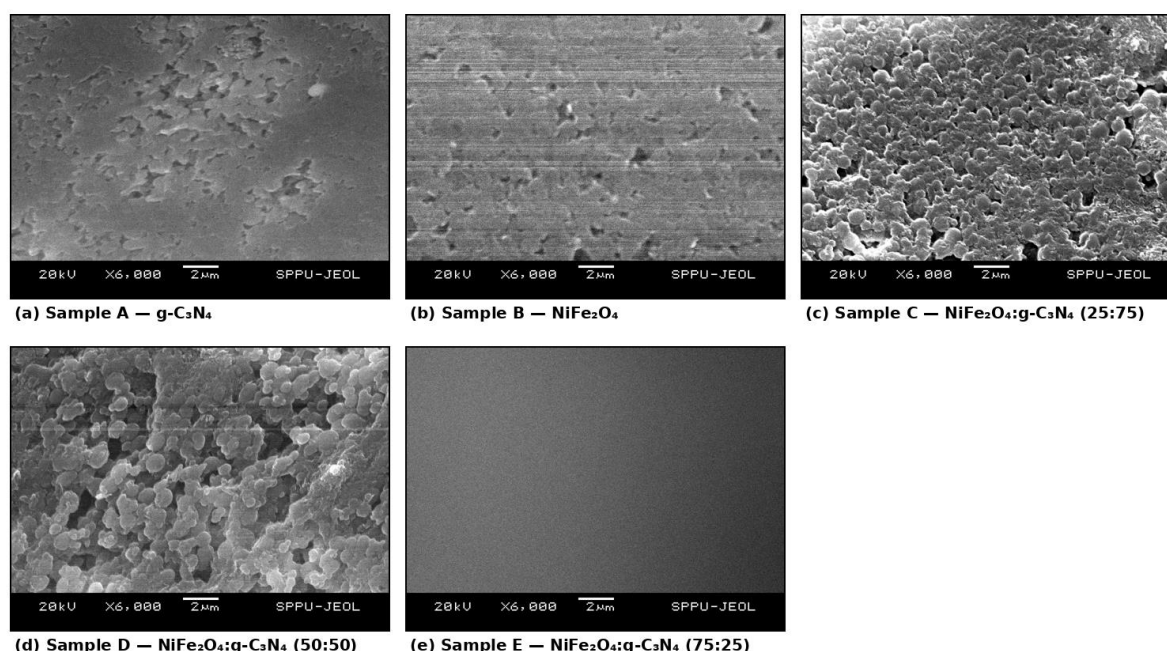


Figure 1. FE-SEM micrographs of (a) $\text{g-C}_3\text{N}_4$, (b) NiFe_2O_4 , (c) 25:75, (d) 50:50 and (e) 75:25 $\text{NiFe}_2\text{O}_4:\text{g-C}_3\text{N}_4$ (20 kV, secondary-electron mode, $\times 6000$, scale bar 2 μm).

Two points limit what the micrographs can support. First, at $\times 6000$ the visible features are of sub-micrometre to micrometre size judged against the 2 μm bar, while the crystallites discussed below are of order 10–30 nm; roughness and porosity at the micrometre scale therefore reflect aggregation and cannot be linked to crystallite size. Second, no surface-area measurement is available, so statements that rougher images imply larger active surface area remain qualitative.

4.2 Reproducing the published XRD descriptors

The published mean lattice constants (8.2534, 8.2769, 8.3484 Å) are exactly the arithmetic means of the per-peak values in the original tables, so the averages are internally consistent with those tables. The per-peak tables, however, were computed from positions rounded to 0.1° and use peak lists that differ from the Scherrer tables: the pure-ferrite lattice table has eleven positions including 79.8°, whereas the



corresponding Scherrer table contains ten reflections, the last at 75.24° , and the (533) and (622) entries were assigned at 75.8° and 79.8° . Recomputing a from the unrounded positions gives 8.2939, 8.2587 and 8.3285 Å for the all-peak means of B, C and D (Table 2). The change is largest for B (+0.040 Å), which is the sample from which the "deviation from the parent phase" is measured.

The crystallite-size averages are only partly reproducible. The pure-ferrite value (10.99 nm) is reproduced exactly. For the 25:75 composite the spinel reflections average 10.78 nm (10.13 nm if the $g\text{-C}_3\text{N}_4$ (002) reflection is included), not the reported 10.25 nm. For the 50:50 composite the spinel reflections average 14.07 nm; the reported 13.01 nm is obtained only if the $g\text{-C}_3\text{N}_4$ (002) reflection (2.39 nm) is added to the average, although the table note describes it as a spinel-phase average. The published increase in spinel crystallite size from the 25:75 to the 50:50 composite (10.25 $\rightarrow$ 13.01 nm) is therefore a +2.76 nm change that arises partly from this inconsistency; the like-for-like spinel-only values are 10.78 and 14.07 nm.

Table 2. Published structural descriptors compared with values recomputed here from the same peak lists.

Quantity	As reported	Recomputed here	Comment
Mean a , B (Å)	8.2534	8.2939	Reported value uses rounded 2θ and an 11-position list
Mean a , C (Å)	8.2769	8.2587 (8.2777, $n = 8$)	Parenthesis: reflections within 0.6° of an assigned position
Mean a , D (Å)	8.3484	8.3285 (8.3429, $n = 9$)	As above
Mean D , B (nm)	10.99	10.99	Reproduced ($n = 10$)
Mean D , C (nm)	10.25	10.78	Spinel only, $n = 11$; 10.13 with (002) included
Mean D , D (nm)	13.01	14.07	Spinel only, $n = 10$; 13.01 only if (002) is included
$d(002)$, A (Å)	3.2158	3.2169	Small difference (0.03%)
$d(002)$, C (Å)	3.279	3.1753	Tabulated $2\theta = 28.079^\circ$ gives a contraction, not an expansion
$d(002)$, D (Å)	"close to pristine"	3.2120	-0.15% relative to A
$D(002)$, A (nm)	8.14	8.20	$K = 0.9$; 0.7% difference

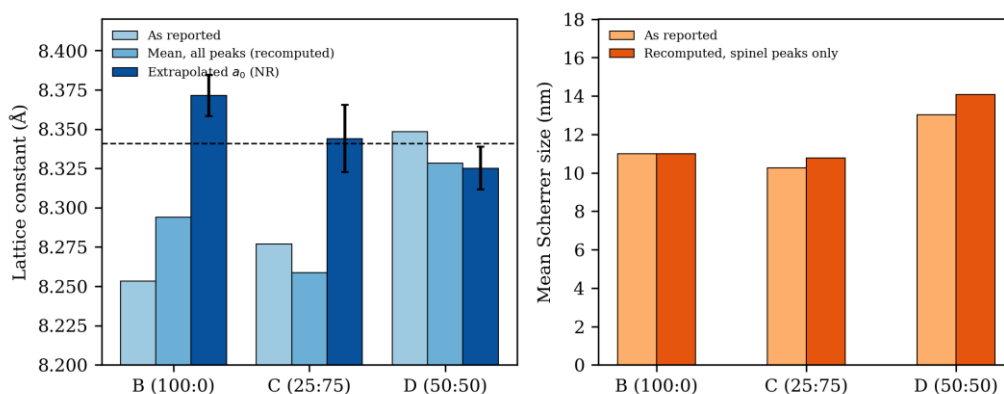


Figure 2. Left: spinel lattice constants as reported, as the all-peak mean recomputed from the unrounded peak positions, and as the Nelson–Riley intercept a_0 (error bars: one regression standard error); the dashed line is the bulk value 8.341 Å [11]. Right: mean Scherrer size as reported and recomputed from spinel reflections only. The vertical axis of the left panel is truncated.

4.3 Peak widths and the Williamson–Hall test

Within each pattern the fitted widths span more than an order of magnitude: FWHM ranges are 0.26–9.04° (B), 0.20–4.56° (C) and 0.12–5.01° (D). For isotropic size broadening $\beta \cos\theta$ is constant; here it varies by factors of 30 (B), 23 (C) and 39 (D). A crystallite size of 10 nm would produce a width of about 0.8° at $2\theta \approx 36^\circ$ for Cu K α , so widths of 3–9° would correspond to sizes of 1–3 nm, which is implausible for a ferrite calcined at 600 °C and inconsistent with the sharp reflections (FWHM < 1°) that coexist in the same pattern.

The all-peak Williamson–Hall regressions confirm that no single size–strain model describes the data (Figure 3): $R^2 = 0.10$ (B), 0.0001 (C) and 0.04 (D). Restricting to the sharp reflections gives sizes of 10.5–32.1 nm (B, four reflections), 15.4–50.1 nm (C, three) and 9.1–76.9 nm (D, three), while the broad features give 1.1–2.8, 2.2–5.6 and 2.0–3.6 nm. The bimodal widths are the likely reason why the arithmetic mean (10–14 nm) lies between two populations that correspond to neither. Possible causes include automatic fitting of overlapping, low-intensity or background features as peaks, strongly anisotropic broadening, or the presence of two populations of crystallites; the available data cannot distinguish these. What they do show is that an average Scherrer size from this peak list is not a defensible descriptor of the ferrite crystallites, and that differences of 1–3 nm between samples are far smaller than the spread within each sample.

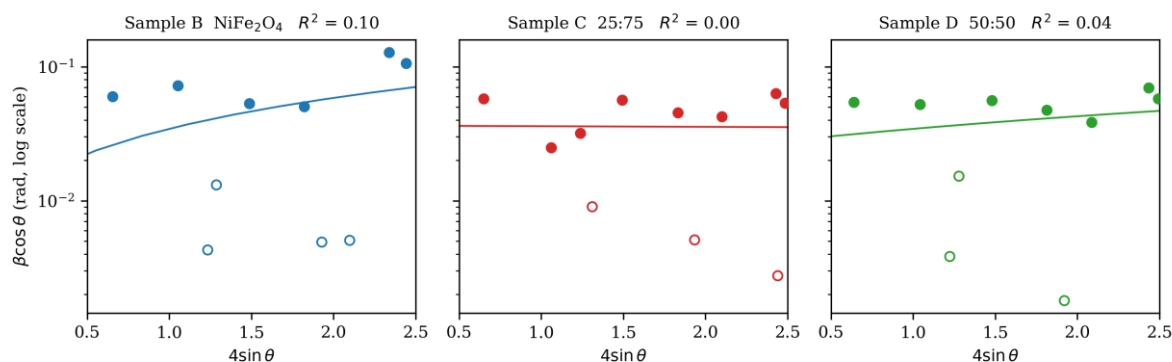


Figure 3. Williamson–Hall plots ($\beta \cos\theta$ on a logarithmic scale against $4 \sin\theta$) for samples B, C and D. Open markers are reflections with $\text{FWHM} < 1^\circ$; the line is the all-peak linear fit and R^2 is its coefficient of determination.

4.4 Lattice constants and angle-dependent error

Plotting the per-peak lattice constant against the Nelson–Riley function (Figure 4) shows a clear systematic trend for samples B and C: a falls from about 8.37 Å at high angle to about 8.17–8.21 Å at the lowest angle, with regression slopes of -0.032 ($R^2 = 0.85$) and -0.027 ($R^2 = 0.69$). Sample D shows almost no trend (slope +0.007, $R^2 = 0.24$). A drift of this kind is the classical signature of specimen displacement or zero-angle error, which shifts low-angle reflections more in a than high-angle ones. Averaging all reflections therefore biases the lattice constant of a displaced pattern towards low values, and the bias is larger the more weight low-angle reflections carry. This accounts for the low reported mean for pure NiFe_2O_4 (8.2534 Å), which lies 0.09 Å below the neutron-diffraction value of 8.341(5) Å [11].

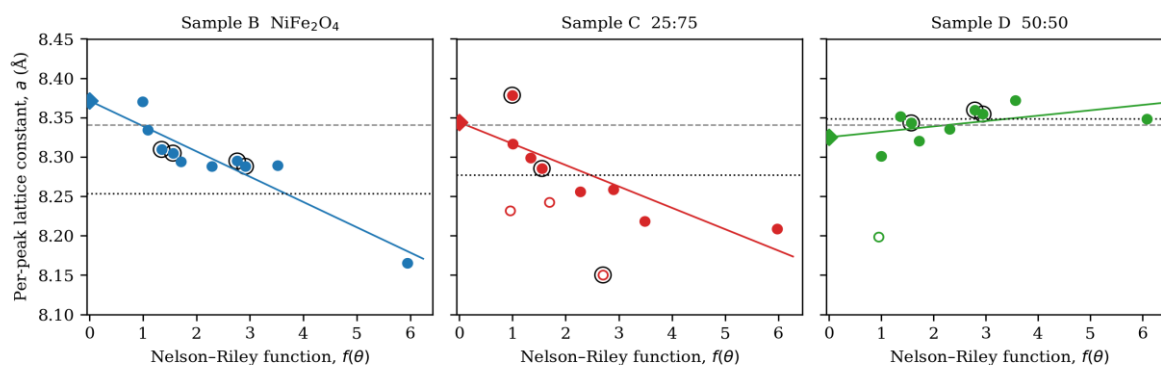


Figure 4. Per-peak lattice constant against the Nelson–Riley function $f(\theta)$ for samples B, C and D. Solid line: ordinary least-squares fit to the filled markers; diamond: extrapolated a_0 ; dashed line: bulk value 8.341 Å [11]; dotted line: mean value reported for the sample; open markers: reflections more than 0.6° from their assigned position (excluded); black rings: reflections with $\text{FWHM} < 1^\circ$.

Extrapolating to $\theta = 90^\circ$ gives $a_0 = 8.371 \pm 0.013$ Å (B, $n = 10$), 8.344 ± 0.021 Å (C, $n = 8$) and 8.325 ± 0.013 Å (D, $n = 9$) (Table 3). All three lie within about 0.03 Å of the bulk value, and the differences among

them are of the order of two combined standard errors. If anything, the sign of the difference between B and D is opposite to the published $8.2534 \rightarrow 8.3484 \text{ \AA}$ sequence. Restricting the fit to sharp reflections gives $8.325 \pm 0.004 \text{ \AA}$ for B ($n = 4$) and $8.328 \pm 0.011 \text{ \AA}$ for D ($n = 3$). For C the three sharp reflections give an unstable slope and an intercept of $8.50 \text{ \AA}$, which is not physically meaningful and is not used. We conclude that these data do not resolve a lattice-constant change across the series at the $0.03\text{--}0.05 \text{ \AA}$ level. A 1% change would also be unexpected from the preparation route: the composites were mixed in ethanol and dried at 80°C , with no step that could incorporate cations or change their distribution within the spinel.

Table 3. Nelson–Riley analysis of the spinel reflections.

Sample	n	Slope ($\text{\AA}$)	R^2	a_0 ($\text{\AA}$)	Mean a ($\text{\AA}$)	Sharp-only a_0 ($\text{\AA}$)
B	10	-0.0321	0.85	8.3714 ± 0.0132	8.2939	8.3245 ± 0.0045 ($n = 4$)
C	8	-0.0272	0.69	8.3440 ± 0.0214	8.2777	not meaningful ($n = 3$)
D	9	0.0068	0.24	8.3252 ± 0.0135	8.3429	8.3276 ± 0.0111 ($n = 3$)

4.5 The g-C₃N₄ (002) reflection

The (002) interlayer reflection of pristine g-C₃N₄ lies at $2\theta = 27.709^\circ$, corresponding to $d = 3.217 \text{ \AA}$, with FWHM 1.00° . In the 25:75 composite the tabulated position is 28.079° ($d = 3.175 \text{ \AA}$, FWHM 2.68°) and in the 50:50 composite 27.751° ($d = 3.212 \text{ \AA}$, FWHM 3.43°). A shift to higher angle means a smaller spacing: relative to pristine g-C₃N₄ the interlayer distance is $-0.042 \text{ \AA}$ (-1.3%) in C and $-0.005 \text{ \AA}$ (-0.15%) in D. The published value of $3.279 \text{ \AA}$ for the 25:75 composite, described as an increase, cannot correspond to the tabulated position of 28.08° ($3.279 \text{ \AA}$ would appear at about 27.2°). The widths of the (002) reflection in the composites are 2.7 and 3.4 times that of the pristine sample, so the positional uncertainty is correspondingly larger, and the shift in C is of a size that could arise from peak overlap with the broad ferrite features nearby or from displacement. The data therefore neither establish an interlayer expansion nor demonstrate a contraction, and they do not provide evidence of interfacial bonding.

4.6 Benchmark against verified literature

Table 4 collects the four studies identified above whose abstracts could be checked for the composition and the hydrogen metric. They differ in the partner phase, the synthesis route, the sacrificial agent or sensitizer, the light source and the metric reported: a rate per gram and hour [2], a rate per hour without a mass normalisation [3], a cumulative yield per gram [4] and a cumulative yield after a fixed time [5]. These quantities have different dimensions and cannot be compared without the full experimental conditions. The optimum NiFe₂O₄ content spans 12 wt% to 49.4%, so there is no universal optimum to which a structural argument could be anchored.



Table 4. Verified literature on NiFe_2O_4 -containing hydrogen-evolution photocatalysts: composition optima and the metric reported.

Study	System	Optimum NiFe_2O_4	Hydrogen result as stated	Conditions noted
Zeng et al. (2016) [2]	Au/g- $\text{C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$; binary g- $\text{C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ by calcination	49.4% (best binary)	Binary $0.351 \text{ mmol g}^{-1} \text{ h}^{-1}$; ternary with 1.0 wt% Au $1.607 \text{ mmol g}^{-1} \text{ h}^{-1}$ ($30.9 \times \text{NiFe}_2\text{O}_4$, $28.7 \times \text{g-C}_3\text{N}_4$)	Visible light
Mishra et al. (2019) [3]	NiFe_2O_4 @P-doped g- C_3N_4	20 wt%	$904 \mu\text{mol h}^{-1}$	Visible light
Aksoy et al. (2020) [4]	MFe_2O_4 /mesoporous g- C_3N_4 (M = Mn, Fe, Co, Ni)	Single loading; NiFe_2O_4 best of the four ferrites	$14.56 \text{ mmol g}^{-1}$ ($6.75 \times$ pristine support)	Eosin-Y sensitiser, triethanolamine donor
Firtina-Ertis & Kerkez-Kuyumcu (2022) [5]	$\text{NiFe}_2\text{O}_4/\text{TiO}_2\text{-Ag}^+$	12 wt% (before Ag^+ addition)	$137 \mu\text{mol g}_{\text{cat}}^{-1} \text{ after 5 h}$ (12NFT-0.50Ag^+)	Solar light, methanol/water

The only binary g- $\text{C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ composition optimum in this set (49.4% NiFe_2O_4 [2]) is closest to the 50:50 sample (D) of the present series, not to the 25:75 sample (C) that had been favoured on structural grounds. This is not evidence that D would perform better, because the synthesis route (calcination in [2], ethanol mixing here), the support and the test conditions differ; but it shows that a 25:75 prediction cannot be defended by appeal to the literature either.

4.7 Status of the structure–activity argument

Table 5 summarises which statements derived from the structural data survive the re-analysis.

Table 5. Status of structural claims after peak-resolved reassessment.

Claim	Status	What would be needed
Spinel lattice constant increases systematically with ferrite loading	Not supported; extrapolated values overlap	Internal-standard XRD; whole-pattern (Rietveld/Le Bail) refinement with uncertainties
Spinel crystallite size is smallest for 25:75	Not supported; spread within each pattern exceeds the differences	Instrument-corrected size from well-resolved reflections; TEM size distributions



Claim	Status	What would be needed
g-C ₃ N ₄ (002) spacing expands in the 25:75 composite	Not supported; tabulated position implies contraction, within peak-width uncertainty	Peak-fit with uncertainty; (002) separated from the ferrite background
Composite forms a heterojunction rather than a physical mixture	Not demonstrated by XRD	Interface-sensitive evidence (TEM lattice imaging, XPS shifts, photoluminescence, photocurrent)
25:75 gives the highest H ₂ rate	Untested; prediction not supported by structural data or by the benchmark	Measured H ₂ rates for the series under a defined protocol, with replicates

5. A Minimal Characterisation and Reporting Protocol

The analysis suggests the following minimum set of practices for composition series of ferrite/carbon-nitride photocatalysts that are to support a structure–activity argument.

1. **XRD.** Record patterns with an internal standard (for example silicon or LaB₆ powder) and measure the instrumental resolution function; use identical specimen preparation and height for all samples; report step size, counting time and optics.
2. **Pattern analysis.** Use whole-pattern fitting (Le Bail or Rietveld) with phase fractions, lattice constants and size/strain parameters reported with uncertainties; do not average widths of reflections that do not belong to one profile family; report the (002) position of g-C₃N₄ with its uncertainty.
3. **Morphology.** Coat or otherwise charge-compensate oxide-rich samples, record several fields at two magnifications, and add elemental mapping so that ferrite and carbon nitride can be located.
4. **Texture and optics.** Measure specific surface area and pore volume, UV–visible diffuse reflectance with a stated band-gap method, and photoluminescence or photocurrent response, so that surface area, light harvesting and charge separation are each documented.
5. **Controls.** Include physical-mixture controls and the pristine components prepared under the same conditions, and replicate syntheses for the compositions of interest.
6. **Hydrogen evolution.** State catalyst mass, reactor volume, light source, spectral range and intensity at the sample, sacrificial agent and concentration, gas-chromatography calibration, blank and dark controls, test duration and repeatability; report the rate per gram per hour together with the absolute amount, and an apparent quantum yield under monochromatic light where possible.
7. **Composition grid.** Use a finer grid (for example every 10–15% around the expected optimum) because reported optima range from 12 to 49 wt% in related systems.



6. Conclusions

A reflection-by-reflection analysis of XRD data for $\text{NiFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites shows that the average lattice constants and average Scherrer sizes used to rank the samples are not robust. Fitted widths within one pattern vary by factors of 23–39 in $\beta \cos\theta$, the two averages for the composites mix spinel and carbon-nitride reflections inconsistently, and per-peak lattice constants of two samples drift with angle in the manner of specimen displacement. After Nelson–Riley extrapolation the lattice constants of the pure ferrite and the 25:75 and 50:50 composites (8.371, 8.344 and 8.325 Å) bracket the bulk value of 8.341 Å without a resolvable trend. The recomputed (002) spacing of $\text{g-C}_3\text{N}_4$ in the 25:75 composite is a contraction of 1.3% (within the uncertainty set by the peak width), not the reported expansion. SEM shows clear changes in aggregate morphology between pristine and composite samples, but these are at a scale far above that of the crystallites and cannot be converted into a hydrogen-evolution ranking. The verified literature places the optimum NiFe_2O_4 content anywhere between 12 and 49 wt% and reports hydrogen in four non-comparable metrics. The central conclusion is therefore negative but useful: averaged XRD descriptors from these data cannot rank hydrogen-evolution activity, and the proposed composition ordering is untested. Direct hydrogen-evolution measurements across the series, supported by the characterisation protocol in Section 5, are required before any composition can be recommended.

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Appendix A. Peak lists and recomputed quantities

The columns give the tabulated 2θ and FWHM, the assigned (hkl), the distance to the calculated position for $a = 8.341 \text{ \AA}$, the lattice constant recomputed from the unrounded 2θ , the Scherrer size ($K = 0.9$) and the product $\beta \cos\theta$. Entries marked † were excluded from the Nelson–Riley regression.

Table A1. Sample B (NiFe_2O_4): spinel reflections.

2θ (°)	FWHM (°)	(hkl)	Offset (°)	a (Å)	D (nm)	$\beta \cos\theta$ (10^{-3} rad)
18.808	3.479	111	0.40	8.1653	2.31	59.90
30.478	4.272	220	0.19	8.2891	1.93	71.94
35.907	0.260	311	0.24	8.2881	32.12	4.32
37.530	0.797	222	0.22	8.2949	10.53	13.17
43.648	3.265	400	0.29	8.2882	2.62	52.90
54.129	3.238	422	0.33	8.2939	2.76	50.33
57.626	0.323	511	0.27	8.3049	28.07	4.94
63.254	0.343	440	0.27	8.3096	27.20	5.10
71.541	9.035	620	0.07	8.3344	1.08	127.94
75.244	7.653	622	0.31	8.3702	1.31	105.79



Table A2. Sample C (25:75): spinel reflections.

2 θ (°)	FWHM (°)	(hkl)	Offset (°)	a (Å)	D (nm)	$\beta \cos\theta$ (10^{-3} rad)
18.708	3.335	111	0.30	8.2087	2.41	57.43
30.746	1.483	220	0.46	8.2186	5.56	24.96
36.039	1.920	311	0.37	8.2589	4.35	31.87
38.222	0.548	222 †	0.91	8.1502	15.35	9.03
43.826	3.485	400	0.47	8.2561	2.46	56.44
54.496	2.915	422 †	0.70	8.2423	3.07	45.23
57.775	0.334	511	0.42	8.2854	27.19	5.10
63.345	2.859	440	0.36	8.2989	3.27	42.46
74.799	4.560	533	0.26	8.3165	2.19	63.22
75.157	0.200	622	0.40	8.3785	50.12	2.77
76.735	3.919	622 †	1.18	8.2320	2.59	53.62

Table A3. Sample D (50:50): spinel reflections.

2 θ (°)	FWHM (°)	(hkl)	Offset (°)	a (Å)	D (nm)	$\beta \cos\theta$ (10^{-3} rad)
18.393	3.159	111	0.02	8.3482	2.55	54.42
30.170	3.113	220	0.11	8.3717	2.64	52.46
35.612	0.231	311	0.06	8.3545	36.08	3.84
37.229	0.925	222	0.09	8.3596	9.07	15.29
43.389	3.448	400	0.03	8.3353	2.48	55.92
53.941	3.043	422	0.14	8.3206	2.93	47.34
57.337	0.118	511	0.02	8.3433	76.94	1.80
62.900	2.586	440	0.09	8.3516	3.60	38.50
74.962	5.010	533	0.42	8.3011	2.00	69.39
77.103	4.213	622 †	1.55	8.1987	2.41	57.51



Table A4. g-C₃N₄ (002) reflection.

Sample	2 θ (°)	FWHM (°)	d (Å)	D (nm)
A	27.709	0.998	3.2169	8.20
C	28.079	2.684	3.1753	3.05
D	27.751	3.425	3.2120	2.39