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Graphitic carbon nitride based nanocomposites: A review

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Abstract: Graphitic carbon nitride (g-C₃N₄), as an intriguing earth-abundant visible light photocatalyst, possesses a unique two-dimensional structure, excellent chemical stability and tunable electronic structure. Pure g-C₃N₄ suffers from rapid recombination of photo-generated electron-hole pairs resulting in low photocatalytic activity. Because of the unique electronic structure, the g-C₃N₄ could act as an eminent candidate for coupling with various functional materials to enhance the performance. According to the discrepancies in photocatalytic mechanism and process, six primary systems of g-C₃N₄-based nanocomposites can be classified and summarized. Namely, the g-C₃N₄ based metal-free heterojunction, g-C₃N₄/single metal oxide (metal sulfide) heterojunction, g-C₃N₄/composite oxide, g-C₃N₄/halide heterojunction, g-C₃N₄/noble metal heterostructures, and g-C₃N₄ based complex system. Apart from the depiction of fabrication methods, heterojunction structure and multifunctional application of the g-C₃N₄-based nanocomposites, we emphasize and elaborate on the underlying mechanisms in the photocatalytic activity enhancement of g-C₃N₄-based nanocomposites. The unique functions of p–n junction (semiconductor/semiconductor heterostructures), the Schottky junction (metal/semiconductor heterostructures), the surface plasmon resonance (SPR) effect, photosensitization, super conductivity, etc., are utilized in the photocatalytic processes. Furthermore, the enhanced performance of g-C₃N₄-based nanocomposites has been widely employed in environmental and energetic applications such as photocatalytic degradation of pollutants, photocatalytic hydrogen generation, carbon dioxide reduction, disinfection, and super capacitor. This critical review ends with a summary and some perspectives on the challenges and new directions in exploring g-C₃N₄-based advanced nanomaterials.

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1. Introduction

Over the past decades, the growing awareness of environmental protection and energy conservation has stimulated intensive research on solar energy utilization. In the domain of pollutants elimination and solar energy conversion, semiconductor photocatalysis has emerged as one of the most fascinating technologies. Nevertheless, the wide band gap and low solar-energy utilization efficiency remain the “bottleneck” of the photocatalysts to satisfy the requirement of applications in a practical way. For instance, the traditional TiO₂ is limited for its poor performances associated with visible light application. As a result, it is urgent to seek for efficient visible-light-driven (VLD) photocatalysts. For this objective, various modified TiO₂ and TiO₂-alternative photocatalysts have been fabricated.

Currently, it is still a challenge to design new photocatalysts that are abundant, stable and facile in fabrication besides high visible-light performance.

In the search for robust and stable VLD semiconductor photocatalysts, a polymeric semiconductor, graphitic carbon nitride (g-C₃N₄), has recently attracted tremendous attention. The heptazine ring structure and high condensation degree enable metal-free g-C₃N₄ to possess many advantages such as good physicochemical stability, as well as an appealing electronic structure combined with a medium-band gap (2.7 eV). These unique properties make g-C₃N₄ a promising candidate for visible light photocatalytic applications utilizing solar energy. In addition, g-C₃N₄ is abundant and easily-prepared via one-step polymerization of cheap feedstocks like cyanamide, thiourea, melamine and dicyandiamide. Nevertheless, pure g-C₃N₄ suffers from shortcomings such as rapid recombination of photo-generated electron-hole pairs, small specific surface area and low visible light utilization efficiency.

Consequently, the exploration of facile and dependable strategies to synthesize the modified g-C₃N₄-based photocatalysts with improved physicochemical properties and high photocatalytic activities is of increasing requirement. The g-C₃N₄ has a unique two-dimensional layered structure, which is favorable for hybridizing with other components. Very recently, several approaches have been employed to enhance the visible light photocatalytic performance of g-C₃N₄, such as formation of surface coupling hybridization utilizing TaON, Bi₂WO₆, graphene, construction of mesoporous structure, doping with metal or nonmetal species Fe, Ag, Au, Pd, S, B and P, and sensitizing by organic dyes. Among these approaches, formation of heterostructures demonstrates a great potential to promote the photocatalytic performance of g-C₃N₄ because the electron–hole pairs can be efficiently separated, and charge carriers could transfer across the interface of the heterostructure to restrain the recombination.

In a coupling process, g-C₃N₄ based heterostructures not only can be formed by combining with visible light excited photocatalytic semiconductor materials with a narrow band gap such as CdS, Bi₂WO₆, BiOI, but also can combine with UV excited photocatalysts with large band gap (such as TiO₂, ZnO, ZnWO₄), which can largely broaden the application of the g-C₃N₄ based nanocomposites. Nevertheless, not all materials can couple with g-C₃N₄ to form a heterostructures. The most important prerequisite condition to form an effective visible light excited g-C₃N₄ based heterostructure is that the candidates should have an appropriate band structure which is beneficial to create a coupling hybridization. Besides, the difference of chemical potential between the coupling semiconductor A and B generates band bending at the interface of junction. The band bending induces a built-in field, which impels the photogenerated electrons and holes to transfer in opposite directions, resulting in a spatially efficient separation of the electrons and holes pairs on different sides of heterojunction. In addition, the crystal structure in the junction domain of the heterostructure is also important in strengthening the quantum efficiency of the photocatalyst. A distinction in lattice spacing between two semiconductors could probably cause lattice mismatch. The lattice mismatch at the interface may cause defects, which will capture the photo-generated electronic carriers and thus inhibit the diffusion of electrons and holes. Thus, the formation of g-C₃N₄ based heterostructures is an effective approach to enhance charge separation efficiency for improved photocatalytic performance.

Recently, numerous researches have been made to couple g-C₃N₄ with various semiconductors to enhance the photocatalytic activities. For instance, Wang and co-workers firstly reported TiN/g-C₃N₄ multi-layers hybridization by using a dual-facing-target magnetron sputtering method at room temperature, and exhibited favorable properties in photocatalytic applications in 2008. This pioneering work has stimulated tremendous interests on the fabrication, modification, and application of g-C₃N₄-based semiconductor photocatalysts. Yan et al. successfully developed g-C₃N₄/TaON organic–inorganic composite photocatalyst with visible-light response by a milling-heat treatment method that demonstrated an enhanced photocatalytic performance for photodegradation of Rhodamine B (RhB) in aqueous solutions. Di et al. prepared the Au/g-C₃N₄ nanocomposites photocatalyst by depositing gold nanoparticles on the surface of a g-C₃N₄ semiconductor to generate metal–semiconductor junctions, which showed well-improved photocatalytic hydrogen evolution with visible light.

Now that significant advances have been made on the g-C₃N₄ based photocatalysts in recent years, we believe that a comprehensive review on this subject is necessary to accelerate further developments in this exciting research domain. This review article is focused on recent progress in the design, fabrication, mechanistic understanding, and the potential applications of these g-C₃N₄-based nanocomposites in various realms such as photodegradation of nitrogen oxides, organic contaminants photodegradation, photocatalytic hydrogen evolution, conversion carbon dioxide to methane fuel, oxygen reduction reaction (ORR), and photoelectrochemical...
determination of Cu^{2+}. Eventually, some concluding remarks and
invigorating perspectives on the current situation and further
prospects on the g-C_{3}N_{4}-related researches are presented, which
may promote the understanding and large scale application of the
g-C_{3}N_{4}-based nanocomposites.

2. g-C_{3}N_{4}-based nanocomposites
2.1 Preparation of g-C_{3}N_{4}
Generally, carbon nitride materials fabricated by directly
condensation of nitrogen-containing organic precursors (for
example urea, thiourea, melamine, dicyandiamide, cyanamide,
guanidine hydrochloride ) are bulk materials with a small surface
area, normally below 10 m^{2}/g. For practical applications of the
materials in domains such as a single catalyst or a support
substrate of co-catalysts (such as heterojunction), the introduction
of well-controlled porosity at the nanoscale in the bulk carbon
nitride is mandatory to strengthen its utilizations to a large scale.
And it is worth noting that formation of mesoporous and augment
of specific surface area are crucial to fine-tune the physicochemical
properties and improve the photocatalytic performance.52 As previously reported, the mesoporous g-C_{3}N_{4}
(mp-g-C_{3}N_{4}) was firstly obtained by nanocasting/replication of
mesoporous silica matrices, which were famous for the generation of the corresponding carbon nanostructures.53,54,55

Inspired by this hard template method, tremendous attempts were
stimulated to explore new strategies for g-C_{3}N_{4} modification,
such as soft template method,56-58 ultrasonic dispersion method,59
acidic solution impregnation,60,61 and chemical functionalization.62-66 As universally applied, methods mentioned
above were good as a proof-of-principle in tailoring the texture
and surface chemical properties, as well as the electronic properties.

2.2 Design considerations for g-C_{3}N_{4}-based nanocomposites
To develop effective g-C_{3}N_{4}-based nanocomposites working for
enhanced performance, several pivotal requirements must be
considered. First of all, the semiconductor light harvesting
antenna must have a narrow band gap to allow for efficient
absorption of the solar spectrum. Second, there must be a driving
force boosting charge separation and accelerating the transportation
process. Furthermore, the semiconductor should possess adequate redox potential for the desired photochemical
reactions. Ultimately, a mechanism should be accompanied to
guarantee the photochemical stability of the photocatalyst. It is
unlikely that a single material system could satisfy all these
requirements, while the nanocomposites photocatalysts may have
the potential to accomplish these goals. In general, nanocomposites photocatalysts could offer several potential
merits: (1) Cocatalyst effect. The integration with a proper
 cocatalyst can lower the redox overpotential at the respective
active sites; (2) Strengthened light absorption. For instance,
semiconductors with small band gap possessing high absorption
efficiency can be utilized to functionalize (or sensitize)
semiconductor materials with large band gaps; (3) Efficient
charge separation and transportation. A p-n
( semiconductor/semiconductor heterostructures) or the Schottky
junction (metal/semiconductor heterostructures) with built-in
electrical potential can be constructed in heterogeneous
photocatalysts to effectively expedite electron-hole pair
separation and transportation; (4) Decent stability. If the active
sites and function groups on the semiconductor surface can be
protected through proper surface passivation, it is possible to
improve the stability.

In consideration of the diverse mechanisms of different g-C_{3}N_{4}
-based nanocomposites in photocatalytic reactions, g-C_{3}N_{4} based
heterojunctions were summarized and classified into six main
different combination systems. Below we review the recent
progress on the g-C_{3}N_{4} based metal-free heterojunction, g-
C_{3}N_{4}/metal oxide (metal sulfide) heterojunction, g-
C_{3}N_{4}/inorganic acid salts composites, g-C_{3}N_{4}/halide
heterojunction, g-C_{3}N_{4}/metal heterostructures, and g-C_{3}N_{4}
based multi-component heterojunction for improved photocatalysis.

3. Categories of g-C_{3}N_{4} based nanocomposites
3.1 g-C_{3}N_{4} based metal-free layered heterojunction
To our knowledge, metal-free materials owing to various
advantages such as low-cost and environmentally amicable, have
stimulated multidistriubution attention because of their great potential
in solving environmental and energy problems. Hence, it is
extremely attractive to construct hybridized materials via
coupling two metal-free materials. For example, graphene, a two-
dimensional macromolecular sheet of carbon atoms, has
preferentially attracted much attention due to its outstanding
mechanical, thermal, easily-obtained, and electrical properties.
And it has been widely used in nanoelectronics, biosensing,
capacitors, and catalysis domains.67,68 In particular, it possesses
an extremely high specific surface area (~2600 m^{2}/g)69 and
marvelous thermal conductivity (~5000 W m^{-1}K^{-1}), guaranteeing
a superb mobility of charge carriers (200 000 cm^{2} V^{-1}s^{-1}).
Therefore, the merits mentioned above made graphene as the first
metal-free candidate, and preferentially used to construct layered
graphene/g-C_{3}N_{4} nanocomposites Sun et al prepared graphene/g-
C_{3}N_{4} nanoheterojunction by absorption-calculation method,
which demonstrated apparently enhanced conductivity and
electrocatalytic performance on oxygen reduction reaction
(ORR).70 Xiang et al also successfully obtained graphene/g-C_{3}N_{4}
nanocomposites by a combined impregnation-chemical reduction
strategy, and firstly utilized this graphene/g-C_{3}N_{4}
nanoheterojunction in visible-light photocatalytic H_{2}-production
containing Pt as a cocatalyst.72 Fig. 1a and 1b show a typical
TEM image of graphene oxide and graphene/g-C_{3}N_{4}
nanocomposites. In comparison to graphene oxide, the
graphene/g-C_{3}N_{4} composite possessed a more compact structure
due to the fact that g-C_{3}N_{4} was sandwiched between graphene
sheets through polymerization of melamine molecules pre-
adsorbed on the GO sheets. In the aforementioned trials, the high
H_{2}-production activity over the graphene/g-C_{3}N_{4} nanocomposites
under visible-light irradiation can be achieved. The mechanism of
the activity enhancement is illustrated in Fig. 1c.
Under visible-light illumination, electrons (e\textsuperscript{−}) of g-C\textsubscript{3}N\textsubscript{4} are excited from the valence band (VB) to the conduction band (CB), generating holes (h\textsuperscript{+}) in the VB. Generally, these charge carriers quickly recombine and only a section of electrons are injected into the Pt nanoparticles due to a Schottky barrier.\textsuperscript{71,72} The injected electrons accumulate on the Pt nanoparticles and can effectively reduce H\textsubscript{2}O (or H\textsuperscript{+}) to produce H\textsubscript{2}, while holes accumulate at the valence band of g-C\textsubscript{3}N\textsubscript{4} and can react with methanol as a sacrificial reagent. However, when g-C\textsubscript{3}N\textsubscript{4} is immobilized on the surface of graphene sheets to form the layered composites, these photogenerated electrons on the CB of g-C\textsubscript{3}N\textsubscript{4} could tend to transfer to graphene sheets due to their excellent electronic conductivity, restraining the electron-hole pair recombination.\textsuperscript{68} The transferred electrons will accumulate on the Pt nanoparticles loaded on the graphene sheets via a percolation mechanism\textsuperscript{73} and then participate in H\textsubscript{2} generation.

The major reaction steps in this photocatalytic water-splitting mechanism under visible-light illumination are summarized by the following Eqs. (1)-(4).

\[
\begin{align*}
\text{graphene/g-C}_3\text{N}_4 & \rightarrow \text{graphene (e\textsuperscript{−})/g-C}_3\text{N}_4 \text{ (h\textsuperscript{+})} \quad (1) \\
\text{graphene (e\textsuperscript{−}) + Pt} & \rightarrow \text{graphene + Pt (e\textsuperscript{−})} \quad (2) \\
\text{Pt (e\textsuperscript{−}) + 2H\textsuperscript{+}} & \rightarrow \text{Pt + H}_2 \quad (3) \\
\text{g-C}_3\text{N}_4 \text{ (h\textsuperscript{+}) + CH}_3\text{OH + 6OH} & \rightarrow \text{g-C}_3\text{N}_4\text{+CO}_3\text{+5H}_2\text{O} \quad (4)
\end{align*}
\]

And to date, a cross-linked g-C\textsubscript{3}N\textsubscript{4}/GO (reduced graphene oxide) nanocomposites with tunable band structure was synthesized by Li et al, which demonstrated well-enhanced visible light photocatalytic activity.\textsuperscript{74} Later, Wang et al noticed that a new class of ternary g-C\textsubscript{3}N\textsubscript{4}/Graphene/S nanoheterojunction was prepared by wrapping reduced graphene oxide and g-C\textsubscript{3}N\textsubscript{4} sheets on crystals of cyclooctasulfur (α-S\textsubscript{8}) in bacterial inactivation under visible-light.\textsuperscript{75} Except for the aforementioned achievement, a large numbers of attempts have been paid to explore novel materials coupling with g-C\textsubscript{3}N\textsubscript{4} for broadening the applications of g-C\textsubscript{3}N\textsubscript{4}-based coupling heterojunction. In summary, these excellent g-C\textsubscript{3}N\textsubscript{4} based non-metal nanoheterojunction are MWNTs (multi-walled carbon nanotubes)/g-C\textsubscript{3}N\textsubscript{4},\textsuperscript{76,77} polypyrrole/C\textsubscript{3}N\textsubscript{4},\textsuperscript{78} P/C\textsubscript{3}N\textsubscript{4},\textsuperscript{79} CN/CNS,\textsuperscript{80} g-C\textsubscript{3}N\textsubscript{4}(from thiourea)/g-C\textsubscript{3}N\textsubscript{4}(from urea),\textsuperscript{81} C\textsubscript{60}/g-C\textsubscript{3}N\textsubscript{4}, as shown in Table 1.\textsuperscript{82}

![Image](image_url)

**Table 1** Photocatalytic properties of g-C\textsubscript{3}N\textsubscript{4} based metal-free heterojunction composite photocatalysts

![Image](image_url)

**Fig. 1** (a) TEM images of graphene oxide and (b) the graphene/e-C\textsubscript{3}N\textsubscript{4} nanocomposites; (c) Proposed mechanism for the enhanced electron transfer in the graphene/e-C\textsubscript{3}N\textsubscript{4} composites (reprinted with permission from ref. 32. Copyright (2011) American Chemical Society).

**Fig. 2** Schematic illustration of organic heterojunction formed between CN and CNS. (CN refers to g-C\textsubscript{3}N\textsubscript{4}, CNS refers to sulfur-mediated CN, D=donor)

Significantly, Wang et al. obtained two types of host-guest CN/CNS heterojunctions (Fig. 2) with a facile band alignment by the surface-assisted polymerization: CNS–CN (CN serving as the host) and CN–CNS (CNS serving as the host).\textsuperscript{80} CN/CNS isotype heterojunctions were obtained based on the band alignment between CN and CNS, owing to the slight difference in their electronic band structures. As an amazing result, these two types of CN/CNS heterojunctions mentioned above demonstrated conspicuous enhancement in the photocatalytic activity and stability for hydrogen evolution.

Inspired by Wang’s work, the layered g-C\textsubscript{3}N\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} metal-free isotype heterojunction (Fig. 3a) was produced by treating the molecular composites precursors of urea and thiourea under the same thermal conditions. The molecular structure of this CN/T-CN-U heterojunction is illustrated in Fig. 3b. This isotype heterojunction was constructed on the basis that the g-C\textsubscript{3}N\textsubscript{4} prepared from separate urea and thiourea has different band structure. Upon visible light irradiation, the photogenerated electrons transfer from g-C\textsubscript{3}N\textsubscript{4} (thiourea) to g-C\textsubscript{3}N\textsubscript{4} (urea) driven by the conduction band offset of 0.10 eV, whereas the photogenerated holes transfer from g-C\textsubscript{3}N\textsubscript{4} (urea) to g-C\textsubscript{3}N\textsubscript{4} (thiourea) driven by the valence band offset of 0.40 eV.\textsuperscript{81} These two charge transfer processes are beneficial for overcoming the high dissociation barrier of the Frenkel exciton and stabilizing electrons and holes. The redistribution of electrons on one side of the heterojunction (CN-U) and holes on the opposite side (CN-T), could reduces the electron/hole pairs recombination as well as prolonged lifetime of charge carriers, resulting in exceptionally high photocatalytic capability. These two successful works demonstrated that rational design and construction of isotype heterojunction could open up a new avenue for the development of new efficient visible-light photocatalysts.

![Image](image_url)

**Fig. 3** (a) TEM images of CN-TU; (b) Schematic illustration of electron-hole separation and transport at the g-C\textsubscript{3}N\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} heterojunction interface and in both semiconductors: E\textsubscript{C} is the contact electric field for the two components; E\textsubscript{B} is the potential barrier in the interfacial depletion layer (E\textsubscript{A}<E\textsubscript{B} during the photocatalytic reaction); E\textsubscript{C} and E\textsubscript{T} are the internal electric fields induced by the redistribution of the spatial charges in CN-T and CN-U, respectively. CN-T refers to g-C\textsubscript{3}N\textsubscript{4} from thiourea and CN-U refers to g-C\textsubscript{3}N\textsubscript{4} from urea. (reprinted with permission from ref. 81. Copyright (2013) American Chemical Society).
<table>
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<tr>
<th>Composite photocatalyst</th>
<th>Mass or molar fraction of g-C₃N₄</th>
<th>Typical parameters of photocatalytic experiments</th>
<th>Photocatalytic activity</th>
<th>Reference photocatalyst; photocatalytic activity</th>
<th>Enhancement factor over the reference photocatalyst</th>
<th>Reference</th>
</tr>
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<tr>
<td>Graphene / g-C₃N₄</td>
<td>Mass: 99%</td>
<td>Photocatalytic H₂ evolution under visible light; co-catalyst: Pt; sacrificial reagent: methanol</td>
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<td>g-C₃N₄: 147 μmol h⁻¹</td>
<td>Graphene: no data</td>
<td>3.07</td>
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<td>reduced graphene oxide (rGO) / g-C₃N₄</td>
<td>Mass: 98.4%</td>
<td>Decomposing rhodamine B (RhB) under visible light</td>
<td>84%, in 75 min</td>
<td>g-C₃N₄: 80%</td>
<td>rGO: no data</td>
<td>1.05</td>
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<td>multi-walled carbon nanotubes (MWCNTs)/g-C₃N₄</td>
<td>Mass: 98%</td>
<td>Decomposing 4-nitrophenol under visible light</td>
<td>No data, in 150 min</td>
<td>g-C₃N₄: no data</td>
<td>rGO: no data</td>
<td>No data</td>
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<tr>
<td>multi-walled carbon nanotubes (CNT) /white C₃N₄</td>
<td>Mass: no data</td>
<td>Decomposing methyl orange (MO) under visible light</td>
<td>89.7%, in 3 h</td>
<td>white C₃N₄: no data</td>
<td>CNT: no data</td>
<td>No data</td>
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<tr>
<td>Polypyrrole (PPy) /g-C₃N₄</td>
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<td>Photocatalytic H₂ evolution under visible light; co-catalyst: Pt; sacrificial reagent: no mention</td>
<td>RH₂: 7.58 μmol h⁻¹</td>
<td>g-C₃N₄: 2.03 μmol h⁻¹</td>
<td>MWCNTs: no data</td>
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<td>Red phosphor (r-P)/g-C₃N₄</td>
<td>Mass: 5%</td>
<td>Photocatalytic H₂ evolution under visible light; co-catalyst: Ascorbic acid</td>
<td>RH₂: 310 μmol h⁻¹</td>
<td>g-C₃N₄: 340 μmol h⁻¹</td>
<td>r-P: 2.2 μmol h⁻¹</td>
<td>0.91; 14.09</td>
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<td>Red phosphor (r-P)/g-C₃N₄</td>
<td>Mass: 30%</td>
<td>Photocatalytic H₂ evolution under visible light; co-catalyst: Ascorbic acid</td>
<td>2.19 μmol h⁻¹</td>
<td>g-C₃N₄: 107 μmol h⁻¹</td>
<td>r-P: 145 μmol h⁻¹</td>
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<tr>
<td>RGO/ g-C₃N₄/ α-Si</td>
<td>Mass: 30%</td>
<td>Bacterial Inactivation (E.coli K-12) under Visible-Light</td>
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<td>g-C₃N₄: no data</td>
<td>RGO: no data</td>
<td>No data</td>
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<tr>
<td>g-C₃N₄/α-Si</td>
<td>Mass: 99.5%</td>
<td>Decomposing (RhB) under visible light</td>
<td>87%, in 60 min</td>
<td>g-C₃N₄: 54%</td>
<td>C₆₀: no data</td>
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<td>CN: no data</td>
<td>CNS: no data</td>
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<td>g-C₃N₄ / g-C₃N₄</td>
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<td>Decomposing NO under visible light</td>
<td>47.6%, in 30 min</td>
<td>g-C₃N₄: 73%</td>
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<td>g-C₃N₄: no data</td>
<td>graphene: no data</td>
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### 3.2 g-C₃N₄/single metal oxide (metal sulfide)

So far, various single metal oxides (metal sulfides) have been coupled with g-C₃N₄ to stability, appropriate band distribution for enhanced visible light photocatalysis. Among abundant metal oxides, TiO₂ (Eg: 3.2 eV) as a widely used photocatalyst, referentially acted as a candidate for constructing g-C₃N₄ based heterojunction. The work of Zhou et al., for example,
demonstrated that g-C3N4/TiO2 nanotube array heterojunction was successfully achieved by a simple electrochemical method, showing highly effective visible-light performance with respect to bare g-C3N4 and TiO2 nanotube. Zhao et al. obtained g-C3N4/TiO2 hybrid photocatalyst by facile hydrolysis approach, accompanied with a remarkable enhancement of photocatalytic capability in degradation of phenol both under visible and UV light irradiation. Sridharan et al. successfully fabricated g-C3N4/TiO2 composite with decent photocatalytic performance which was utilized in treatment of methylene blue (MB) and reduction of hazardous Cr(VI) ions. Very recently, a direct Z-scheme g-C3N4/TiO2 photocatalysts were successfully prepared via simple one-step calcinations with well photocatalytic response for formaldehyde decomposition in air, which was reported by Yu et al.

WO3 is another metal oxide that can be used to couple with g-C3N4. The band gap of WO3 is between 2.6 and 2.8 eV. For instance, Zang et al. obtained environmentally benign g-C3N4/WO3 composite via facile mixing-heating procedure, which showed superb performance in methyl orange (MO) degradation. A WO3/g-C3N4 heterojunction (Fig. 4a, and 4b) was prepared by a calcination process accompanied with marvelous visible-light-activity by degradation of MB and 4-chlorophenol, documented by Huang et al. Apparently, all of the WO3/g-C3N4 photocatalysts demonstrated higher photocatalytic performance than the pristine WO3, g-C3N4 as well as the mechanically blended WO3 and g-C3N4 sample under visible light irradiation (Fig. 4c). Equally important, Katsumata et al. have associated g-C3N4 with WO3 by a physical mixing method to decontaminate the organic gas pollution acetaldehyde (CH3CHO).

The remarkably highly-increased performance of WO3/g-C3N4 was mainly ascribed to the synergistic effects of the enhanced optical absorption in visible region, enlarged specific surface areas and the suitable band positions. A conceivable degradation mechanism was put forward as the Fig. 4d.

![HRTEM images of WO3/g-C3N4 (9.7%) composite](image)

**Table 2** Photocatalytic properties of g-C3N4/single metal oxide (metal sulfide) nanocomposite photocatalysts
<table>
<thead>
<tr>
<th>Composite photocatalyst</th>
<th>Mass fraction or molar of g-C₃N₄</th>
<th>Typical parameters of photocatalytic experiments</th>
<th>Photocatalytic activity</th>
<th>Reference photocatalyst; photocatalytic activity</th>
<th>Enhancement factor over the reference photocatalyst</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂/g-C₃N₄</td>
<td>No data</td>
<td>Decomposing methyl orange (MO) under visible light</td>
<td>100% degradation in 30 min</td>
<td>g-C₃N₄; no data TiO₂; no data</td>
<td>No data</td>
<td>45</td>
</tr>
<tr>
<td>TiO₂/g-C₃N₄</td>
<td>300 °C 500°C</td>
<td>Decomposing Methylene Blue (MB) under visible light; Photocatalytic reduction of Cr(VI) under visible light</td>
<td>93%, 75% degradation in 120 min; 72% in 100 min</td>
<td>g-C₃N₄; no data TiO₂; no data</td>
<td>No data</td>
<td>84</td>
</tr>
<tr>
<td>TiO₂/g-C₃N₄</td>
<td>300 °C 500°C</td>
<td></td>
<td></td>
<td>g-C₃N₄; no data TiO₂; no data</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>TiO₂/g-C₃N₄</td>
<td>Mass: 20%</td>
<td>Decomposing phenol under UV light</td>
<td>96.6% degradation in 60 min</td>
<td>g-C₃N₄; 79.5% TiO₂; 65.9%</td>
<td>1.2</td>
<td>83</td>
</tr>
<tr>
<td>TiO₂/g-C₃N₄</td>
<td>Mass: 20%</td>
<td>Decomposing phenol under visible light</td>
<td>67.7% degradation in 180 min</td>
<td>g-C₃N₄; 43.8% TiO₂; no data</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>TiO₂/g-C₃N₄</td>
<td>Mass: 16.7% 66.7% 83.3%</td>
<td>Decomposing phenol under UV light</td>
<td>69.1%; in 60 min 82.7%; in 60 min 96.6%; in 60 min 82.8%; in 60 min</td>
<td>g-C₃N₄; no data TiO₂; no data</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>TiO₂/g-C₃N₄ (Z-scheme)</td>
<td>Mass ratio: 100% (urea:P25)</td>
<td>Decomposing formaldehyde under UV light</td>
<td>94%; in 60 min apparent rate constant k: 7.36 x 10⁻⁷ min⁻¹</td>
<td>g-C₃N₄; no data TiO₂; no data P25: 5.53 x 10⁻⁷ min⁻¹</td>
<td>No data</td>
<td>85</td>
</tr>
<tr>
<td>WO₃/g-C₃N₄</td>
<td>Mass ratio: no data</td>
<td>Decomposing (MO) under visible light</td>
<td>No data</td>
<td>g-C₃N₄; no data WO₃; no data</td>
<td>No data</td>
<td>88</td>
</tr>
<tr>
<td>WO₃/g-C₃N₄</td>
<td>Mass: 80% 60% 40% 20%</td>
<td>Decomposing acetaldehyde (CH₃CHO) under visible light</td>
<td>No data</td>
<td>g-C₃N₄; no data WO₃; no data</td>
<td>No data</td>
<td>90</td>
</tr>
<tr>
<td>WO₃/g-C₃N₄</td>
<td>Mass: 90.3%</td>
<td>Decomposing MB under visible light</td>
<td>97% degradation in 2h</td>
<td>g-C₃N₄; 81.3% WO₃; 73.3%</td>
<td>1.2</td>
<td>89</td>
</tr>
<tr>
<td>WO₃/g-C₃N₄</td>
<td>Mass: 90.3%</td>
<td>Decomposing 4-chlorophenol (4-CP) under visible light</td>
<td>43% degradation in 6h</td>
<td>g-C₃N₄; 3.6% WO₃; no data</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td>a-Fe₃O₄/g-C₃N₄</td>
<td>precursors: [Bmim]FeCl₃ anhydrous FeCl₃</td>
<td>No data</td>
<td>Supercapacitive properties</td>
<td>g-C₃N₄; no data a-Fe₃O₄; 72 Fg⁻¹</td>
<td>No data</td>
<td>91</td>
</tr>
<tr>
<td>Fe₂O₃/g-C₃N₄</td>
<td>Mass: 97.2% 95.1% 93.5% 92% 88.4%</td>
<td>Decomposing rhodamine B (RhB) under visible light</td>
<td>100%; in 120 min 100%; in 160 min 95.7%; in 180 min 75.8%; in 180 min 52.5%; in 180 min</td>
<td>g-C₃N₄: 100%; 180 min Fe₂O₃: no data</td>
<td>No data</td>
<td>9</td>
</tr>
<tr>
<td>ZnO/g-C₃N₄</td>
<td>Mass: 95.1% 91.6% 84.4% 41.9%</td>
<td>Decomposing rhodamine B (RhB) under visible light</td>
<td>No data</td>
<td>g-C₃N₄; no data ZnO; no data</td>
<td>No data</td>
<td>100</td>
</tr>
<tr>
<td>ZnO/g-C₃N₄</td>
<td>Mass: 84.4%</td>
<td>Decomposing p-nitrophenol under visible light</td>
<td>No data</td>
<td>g-C₃N₄; 30%; 5h ZnO; no data</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>ZnO/g-C₃N₄</td>
<td>Mass: 5.0%</td>
<td>Decomposing (RhB) under visible light</td>
<td>97.4%; in 100 min</td>
<td>g-C₃N₄; no data ZnO; no data</td>
<td>No data</td>
<td>101</td>
</tr>
<tr>
<td>System</td>
<td>Mass (%)</td>
<td>Photocatalytic Activity</td>
<td>Yield (%)</td>
<td>Time</td>
<td>MO (%)</td>
<td>R (h)</td>
</tr>
<tr>
<td>---------------</td>
<td>----------</td>
<td>------------------------------------------------------------</td>
<td>-----------</td>
<td>-------------</td>
<td>-----------</td>
<td>--------</td>
</tr>
<tr>
<td>CeO₂/g-C₃N₄</td>
<td>87%</td>
<td>Decomposing MB under visible light</td>
<td>94%</td>
<td>120 min</td>
<td>g-C₃N₄: 75%,3h</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CeO₂: 28%,3h</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>94.1%,</td>
<td></td>
<td>30%,</td>
<td>5 h</td>
<td>g-C₃N₄: 2.3%</td>
<td>13.0/2.0</td>
</tr>
<tr>
<td>87.0%</td>
<td></td>
<td></td>
<td>45%,</td>
<td>5 h</td>
<td>CeO₂: 15.1%</td>
<td>19.6/3.0</td>
</tr>
<tr>
<td>77.6%</td>
<td></td>
<td></td>
<td>37%,</td>
<td>5 h</td>
<td>No data</td>
<td>16.1/2.5</td>
</tr>
<tr>
<td>MoO₃/g-C₃N₄</td>
<td>7.0%</td>
<td>Decomposing MB under visible light</td>
<td>93%</td>
<td>3 h</td>
<td>g-C₃N₄: no data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MoO₃: no data</td>
<td>No data</td>
</tr>
<tr>
<td>Fe₂O₃/g-C₃N₄</td>
<td>98%</td>
<td>Decomposing MO under visible light</td>
<td>No data</td>
<td></td>
<td>g-C₃N₄: no data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe₂O₃: no data</td>
<td>No data</td>
</tr>
<tr>
<td>Ni(OH)₂/g-C₃N₄</td>
<td>99.5%</td>
<td>Photocatalytic H₂ evolution under visible light; co-catalyst: no; sacrificial reagent: triethanolamine</td>
<td>RH₂: 7.6 mmol h⁻¹</td>
<td>3 h</td>
<td>g-C₃N₄: no data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td>99.9%</td>
<td></td>
<td>RH₂: 3.3 mmol h⁻¹</td>
<td>3 h</td>
<td>Ni(OH)₂: no data</td>
<td>No data</td>
</tr>
<tr>
<td>MoS₂/g-C₃N₄</td>
<td>99.5%</td>
<td>Photocatalytic H₂ evolution under visible light; co-catalyst: no; sacrificial reagent: lactic acid</td>
<td>RH₂: 20.6 mmol h⁻¹</td>
<td>1 h</td>
<td>g-C₃N₄: no data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MoS₂: no data</td>
<td>0.5 wt % Pt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g-C₃N₄: 4.8 mmol h⁻¹</td>
<td>No data</td>
</tr>
<tr>
<td>CdS/g-C₃N₄</td>
<td>70%</td>
<td>Decomposing (MO) under visible light</td>
<td>92%</td>
<td>20 min</td>
<td>g-C₃N₄: 16%, in 25 min</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CdS: no data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3CdS–0.7TiO₂: 19%, in 25 min</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7C₃N₄–0.3TiO₂: 22%, in 25 min</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₃N₄: 3%</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CdS: 38%</td>
<td>41.6</td>
</tr>
<tr>
<td>NiS/g-C₃N₄</td>
<td>99.5%</td>
<td>Photocatalytic H₂ evolution under visible light; co-catalyst: no; sacrificial reagent: triethanolamine</td>
<td>RH₂: 9.2 mmol h⁻¹</td>
<td>1 h</td>
<td>g-C₃N₄: 0.2 mmol h⁻¹</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td>98.75%</td>
<td></td>
<td>RH₂: 48.2 mmol h⁻¹</td>
<td>1 h</td>
<td>NiS: no data</td>
<td>46.0</td>
</tr>
<tr>
<td></td>
<td>98%</td>
<td></td>
<td>RH₂: 32.1 mmol h⁻¹</td>
<td>1 h</td>
<td>No data</td>
<td>241.0</td>
</tr>
<tr>
<td></td>
<td>97.5%</td>
<td></td>
<td>RH₂: 13.5 mmol h⁻¹</td>
<td>1 h</td>
<td>No data</td>
<td>160.5</td>
</tr>
<tr>
<td>TaON/g-C₃N₄</td>
<td>60%</td>
<td>Decomposing (RhB) under visible light</td>
<td>100%</td>
<td>50 min</td>
<td>g-C₃N₄: 100%, in 80 min</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TaON: 34%, in 80 min</td>
<td>No data</td>
</tr>
<tr>
<td>In₂O₃/g-C₃N₄</td>
<td>90%</td>
<td>CO₂ reduction into hydrocarbon fuels</td>
<td>CH₄ production yield: 7.67 ppm</td>
<td>40 h</td>
<td>g-C₃N₄: no data</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>In₂O₃: no data</td>
<td>4.0</td>
</tr>
<tr>
<td>WO₃/g-C₃N₄</td>
<td>50%</td>
<td>Oxidation of acetaldehyde into CO₂</td>
<td>at least 600 ppm of acetaldehyde had been removed in 48h</td>
<td>No data</td>
<td>g-C₃N₄: no data</td>
<td>No data</td>
</tr>
<tr>
<td>SiO₂/g-C₃N₄</td>
<td>No data</td>
<td>Decomposing RhB under visible light</td>
<td>Fully degraded in 60 min</td>
<td>No data</td>
<td>g-C₃N₄: no data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SiO₂: no data</td>
<td>No data</td>
</tr>
</tbody>
</table>

### 3.3 g-C₃N₄/composite oxide

During the past few years, many groups have reported different types of g-C₃N₄/composite oxide heterojunction photocatalysts. These research studies greatly improve the efficiencies of the photocatalysts and promote their applications in the energy production and environmental remediation.\(^\text{105, 106}\)

Table 3 summarizes and compares the g-C₃N₄/composite oxide heterojunction photocatalysts. Among these photocatalytic systems, Bi₂WO₆/g-C₃N₄ has been the most widely investigated. Ge et al prepared g-C₃N₄/Bi₂WO₆ heterostructured photocatalysts via mixing and heating methods.\(^\text{31}\) The g-C₃N₄/Bi₂WO₆ photocatalyst had a remarkably enhanced MO photodegradation activity than pure g-C₃N₄ and Bi₂WO₆ under visible light irradiation. This enhancement could be attributed to the enhanced visible-light utilization efficiency and accelerated transfer of photogenerated electron-hole pairs at the intimate interface of heterojunctions, which rationally can be ascribed to the well-aligned overlapping band-structures of g-C₃N₄ and Bi₂WO₆.\(^\text{20}\)

Subsequently, Wang et al prepared Bi₂WO₆ hybridized with g-C₃N₄ by facile chemisorptions, which exhibited enhanced photocatalytic performance in MB degradation.\(^\text{105}\) Tian et al hydrothermally synthesized a heterojunction by combining g-C₃N₄ with Bi₂WO₆ with enhanced visible light photocatalytic capability.\(^\text{106}\)

Li chose SmVO₄ (band gap 2.28eV) as a promising candidate for constructing g-C₃N₄ coupling heterojunction, and this g-C₃N₄/SmVO₄ composite photocatalyst exhibited high photocatalytic activity and stability for RhB decomposition under visible light irradiation.\(^\text{107}\) Moreover, earth abundant cobalt phosphate (Co–Pi) has been demonstrated to work effectively as oxygen-evolving electrocatalyst\(^\text{108-110}\) owing to its attractive characteristics such as the low cost and self-repairing behavior.\(^\text{111, 112}\) Recently, The Co–Pi species are presented as...
nanoparticles and well-distributed on the g-C$_3$N$_4$ surface, and the Co–Pi/g-C$_3$N$_4$ composites exhibit stronger visible light absorption. The Co–Pi/g-C$_3$N$_4$ composite samples show significantly enhanced H$_2$ and O$_2$ evolution activities.\textsuperscript{113}

It is well known that ZnWO$_4$ itself cannot be excited by visible light. On the contrary, C$_3$N$_4$ can absorb the visible light. Wang et al fabricated C$_3$N$_4$/ZnWO$_4$ coupling composite (Fig. 5a,b), i.e. the ZnWO$_4$ is a semiconductor without visible photocatalytic performance was successfully photo-sensitized by g-C$_3$N$_4$.\textsuperscript{114}

These composites possessed eminent and commendably durable photocatalytic activity in removal of Rh-B, as well as enhanced photocurrent responses under visible light irradiation (Fig. 5c). More importantly, a new mechanism of ZnWO$_4$ sensitized by carbon nitride was presented in Fig. 5d.

**Table 3 Photocatalytic properties of g-C$_3$N$_4$/composite oxide heterojunction photocatalysts**

<table>
<thead>
<tr>
<th>Composite photocatalyst</th>
<th>Mass or molar fraction of g-C$_3$N$_4$</th>
<th>Typical parameters of photocatalytic experiments</th>
<th>Photocatalytic activity</th>
<th>Reference photocatalyst; photocatalytic activity</th>
<th>Enhancement factor over the reference photocatalyst</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiPO$_4$g-C$_3$N$_4$</td>
<td>Mass:4%</td>
<td>Decomposing methyl blue (MB) under UV light</td>
<td>90% degradation in 5 min</td>
<td>BiPO$_4$; no data P25/TiO$_2$; no data</td>
<td>2.5</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>Mass:10%</td>
<td>Decomposing MB under visible light</td>
<td>apparent rate constant k : 0.31 h$^{-1}$</td>
<td>g-C$_3$N$_4$; k=0.06 h$^{-1}$</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Bi$_2$WO$_4$g-C$_3$N$_4$</td>
<td>Mass:2%</td>
<td>Decomposing (MB) under simulated solar irradiation</td>
<td>apparent rate constant: k : 1.0291 h$^{-1}$</td>
<td>Bi$_2$WO$_4$; k=0.6090 h$^{-4}$</td>
<td>1.67</td>
<td>105</td>
</tr>
<tr>
<td>Bi$_2$WO$_4$g-C$_3$N$_4$</td>
<td>Mass:50%</td>
<td>Decomposing methyl orange (MO) under visible light</td>
<td>93% degradation in 120 min</td>
<td>g-C$_3$N$_4$: 31% Bi$_2$WO$_4$: 0.6%</td>
<td>3</td>
<td>106</td>
</tr>
<tr>
<td>Bi$_2$WO$_4$g-C$_3$N$_4$</td>
<td>Mass:5% 10% 30% 50% 70% 90%</td>
<td>Decomposing (MO) under visible light</td>
<td>21.1%,3h 76.0%,3h 45.2%,3h 89.6%,3h 99.9%,3h 84.4%,3h</td>
<td>g-C$_3$N$_4$: 81.4%</td>
<td>0.26</td>
<td>31</td>
</tr>
<tr>
<td>Ag$_2$PO$_4$g-C$_3$N$_4$</td>
<td>Mass:16.7%</td>
<td>Decomposing RhB under visible light</td>
<td>No data</td>
<td>g-C$_3$N$_4$: no data Ag$_2$PO$_4$: no data</td>
<td>3.27</td>
<td>118</td>
</tr>
<tr>
<td>Ag$_2$PO$_4$g-C$_3$N$_4$</td>
<td>Mass:25%</td>
<td>Decomposing (MO) under visible light</td>
<td>No data</td>
<td>g-C$_3$N$_4$: no data Ag$_2$PO$_4$: no data</td>
<td>5</td>
<td>119</td>
</tr>
<tr>
<td>ZnWO$_4$g-C$_3$N$_4$</td>
<td>Mass:5%</td>
<td>Decomposing MB under UV light and visible light</td>
<td>No data</td>
<td>g-C$_3$N$_4$: no data g-C$_3$N$_4$: no data</td>
<td>1.8</td>
<td>114</td>
</tr>
</tbody>
</table>

Under visible light illumination, the excited-state electrons of the HOMO of the C$_3$N$_4$ would transport to the lower unoccupied molecular orbital (LUMO) of C$_3$N$_4$ ($\pi-\pi^*$ transition). Since the LUMO potential of C$_3$N$_4$ (-1.1 eV)\textsuperscript{115} is lower than the CB edge of ZnWO$_4$ (-0.8 eV),\textsuperscript{116} a chemical interaction occurs between them. Hence the excited-state electrons on C$_3$N$_4$ can directly inject into the CB of ZnWO$_4$. The electrons subsequently transfer to the photocatalyst surface to react with water and oxygen to generate hydroxyl and superoxide radicals.\textsuperscript{114} These reactive radicals are able to oxidize the pollutants. As a result, the CN polymer sensitized ZnWO$_4$ photocatalyst exhibits enhanced visible light photocatalytic performance. To further broaden the application, many groups have gained achievements on development of newly g-C$_3$N$_4$ based heterojunctions with superior performance in photocatalysis, such as C$_3$N$_4$/BiPO$_4$,\textsuperscript{117} g-C$_3$N$_4$/Ag$_3$PO$_4$,\textsuperscript{118,119} g-C$_3$N$_4$/N-In$_2$TiO$_4$,\textsuperscript{120} g-C$_3$N$_4$/GdVO$_4$,\textsuperscript{121} g-C$_3$N$_4$/NaTaO$_4$,\textsuperscript{122} g-C$_3$N$_4$/Rh-SrTiO$_3$,\textsuperscript{123} g-C$_3$N$_4$/Bi$_2$Nb$_2$O$_6$,\textsuperscript{124} and g-C$_3$N$_4$/Ag$_2$VO$_4$.\textsuperscript{125}
3.4 g-C3N4/BiOX (AgX)

Recently, as halide, BiOX (X = Cl, Br, I) with advantages of layered structure and indirect-transition band-gap were reported as an efficient photocatalysts.126-134 The layered structure can provide a large enough space to polarize the related atoms and orbitals, and then induce the presence of internal static electric fields perpendicular to the [Bi2O3] slabs and halogen anionic slabs in BiOX.135-137 It is interesting to couple BiOX with g-C3N4 to form layered nanojunctions.

Among the BiOX photocatalysts, BiOBr with an appropriate band-gap (2.75 eV) exhibits high photocatalytic activity. Ye et al synthesized BiOBr-g-C3N4 inorganic-organic composite photocatalysts by a one-step chemical bath method at low temperature.138 This heterojunction interacted by facets coupling contributes to the promoted photoinduced charges transfer between BiOBr and g-C3N4 and enhances the VLD photocatalytic activity for RhB degradation comparing with bare BiOBr and g-C3N4. Furthermore, Sun et al fabricated BiOBr-g-C3N4 heterojunction (Fig. 6a) by depositing BiOBr nanosheets onto the surface of C3N4 nanosheets at room temperature.139 The heterojunction possesses intimately contacted interfaces and well-alignment straddling band-structures, which are propitious to the effective separation and transfer of photogenerated charges, bringing an excellent performance. A schematic illustration of the band gap structures for the samples is shown in Fig. 6b.

\[ \text{Fig. 6 TEM of the as-synthesized BiOBr/C3N4 nanojunctions (a) and Schematic illustration of the band-gap matching and the crystal-plane coupling of C3N4/BiOBr nanojunctions (b). Reproduced with permission from ref. 139, copyright 2014, Elsevier.} \]

The band structures of the two components are well-matched and aligned with each other (Fig. 6b). Both C3N4 and BiOBr can be excited by visible light and then generate photo-induced electrons and holes. The relative CB and VB edge positions of C3N4 nanosheets and BiOBr nanosheets imply that the well-matched band energies and crystal planes can form heterojunctions at nanoscale level. The excited electrons in CB of C3N4 can transfer...
to CB of BiOBr, and excited holes in VB of BiOBr can transfer to VB of C$_2$N$_4$, which results in efficient separation and transport of photo-induced electrons and holes. The 2D BiOBr/C$_2$N$_4$ layered nanojunctions could effectively strengthen the photocatalytic activity. This work demonstrated that novel 2D nanojunction, accompanied with high visible light activity can be constructed by combining two visible-light-active 2D semiconductors with well-coupled crystal planes and well-matched band structure, which could provide a new approach for promoting the activity of current photocatalysts.

BiOI is an attractive p-type semiconductor with the strong photoresponse in the visible light region due to its narrow band gap energy (1.78 eV) and could act as a potential sensitizer to sensitize wide band gap semiconductors. Until now, Jiang et al. obtained novel p–n heterojunction photocatalyst constructed by porous graphite-like C$_2$N$_4$ and nanostructured BiOI. In fact, the coupling of p- and n-type semiconductors is believed to be helpful because an internal electric field is built up between them. As a result, the coupling of n-type C$_2$N$_4$ with a p-type narrow band gap BiOI semiconductor is a good strategy to enhance the visible light absorption capability and the photocatalytic performance of g-C$_3$N$_4$ under visible light irradiation. Besides, Wang and his group successfully used BiOCl as an alternative to prepare BiOCl/C$_2$N$_4$ heterojunction photocatalysts via an ionic-liquid-assisted solvent-thermal route, and this nanocomposites demonstrated significantly enhanced visible light performance in degradation of MO due the formation of well-matched heterostructure.

AgX based photocatalysts have attracted great attention as promising candidates for the development of highly efficient visible light photocatalysts. Some efforts were made to explore new-type g-C$_3$N$_4$ based heterojunction by coupling silver halide. Silver halide AgX (X = Br, I) is a photosensitive material extensively used in photography field. Up to now, Xu et al. successfully applied AgX (X = Br, I) developing novel visible-light-driven AgX/graphite-like C$_2$N$_4$(X=Br, I) hybrid materials and the photocatalytic activity dramatically improved, using methyl orange (MO) as a target pollutant. The high photocatalytic activity of the hybrid materials could be ascribed to the strong coupling between g-C$_3$N$_4$ and AgX, which facilitated interfacial charge transfer and inhibited electron-hole recombination. Table 4 summarizes the photocatalytic properties of different g-C$_3$N$_4$/BiOX (AgX) composite photocatalysts.

### Table 4 Photocatalytic properties of g-C$_3$N$_4$/BiOX (AgX) nanocomposite photocatalysts

<table>
<thead>
<tr>
<th>Composite photocatalyst</th>
<th>Mass or molar fraction of g-C$_3$N$_4$</th>
<th>Typical parameters of photocatalytic experiments</th>
<th>Photocatalytic activity</th>
<th>Reference photocatalyst; photocatalytic activity</th>
<th>Enhancement factor over the reference photocatalyst</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOBr/g-C$_3$N$_4$</td>
<td>Mass:50%</td>
<td>Decomposing rhodamine B (RhB) under visible light</td>
<td>95% degradation in 30 min</td>
<td>g-C$_3$N$_4$:15% BiOBr:35%</td>
<td>6.3</td>
<td>2.7</td>
</tr>
<tr>
<td>BiOBr/g-C$_3$N$_4$</td>
<td>Mass:50%</td>
<td>NO removal under visible light</td>
<td>32.7% degradation in 30 min</td>
<td>g-C$_3$N$_4$:22.9% BiOBr:21.2%</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>BiOCl/g-C$_3$N$_4$</td>
<td>Molar: 50%</td>
<td>Decomposing methyl orange (MO) under visible light</td>
<td>95% degradation in 80 min</td>
<td>g-C$_3$N$_4$:11% BiOCl:58%</td>
<td>8.6</td>
<td>1.6</td>
</tr>
<tr>
<td>BiOI/g-C$_3$N$_4$</td>
<td>Mass:77.5%</td>
<td>Decomposing methyl blue (MB) under visible light</td>
<td>99% degradation in 3h</td>
<td>g-C$_3$N$_4$:64% BiOCl:51%</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>AgBr/g-C$_3$N$_4$</td>
<td>Molar:70%</td>
<td>Decomposing MO under visible light</td>
<td>91% degradation in 10h</td>
<td>g-C$_3$N$_4$:low AgBr:23%</td>
<td>No data</td>
<td>4</td>
</tr>
<tr>
<td>AgI/g-C$_3$N$_4$</td>
<td>Molar: 97.5%, 95%, 90%, 70%, 50%</td>
<td>Decomposing MO under visible light</td>
<td>95% degradation in 10h</td>
<td>g-C$_3$N$_4$:low AgBr:23%</td>
<td>No data</td>
<td>4</td>
</tr>
<tr>
<td>AgBr/g-C$_3$N$_4$</td>
<td>Molar: 70%</td>
<td>Decomposing 4-chlorophenol under visible light</td>
<td>53%, 6h</td>
<td>g-C$_3$N$_4$:6.1% AgBr: no data</td>
<td>8.7</td>
<td>No data</td>
</tr>
<tr>
<td>AgI/g-C$_3$N$_4$</td>
<td>Molar: 70%</td>
<td>Decomposing 4-chlorophenol under visible light</td>
<td>53%, 6h</td>
<td>g-C$_3$N$_4$:6.1% AgBr: no data</td>
<td>8.7</td>
<td>No data</td>
</tr>
</tbody>
</table>

### 3.5 g-C$_3$N$_4$/noble metal

Semiconductor-metal junction is widely used to create a space-charge separation region (called the Schottky barrier). At the interface of the two components, electrons transfer from one component to the other to align the Fermi energy levels, preventing the charge recombination and enhancing photocatalytic performance. On the other hand, the surface plasmon renascence (SPR) endowed with noble metals could increase this visible light utilization and probably show special synergistic effects with g-C$_3$N$_4$. It is therefore feasible to couple noble metals with g-C$_3$N$_4$ in order to enhance the photocatalytic activity. The work of Di et al., for example, preferentially demonstrated that the deposition-precipitation method was successfully applied to prepare Au(III) nanoparticles on the surface of a structured polymeric g-C$_3$N$_4$. The as-synthesized nanosopic Au–semiconductor heterojunctions effectively accelerate charges transfer on the intimate interface between g-C$_3$N$_4$ and Au nanoparticles, enabling high photocatalytic hydrogen production. In addition, given that gold nanoparticles (AuNPs) can serve as photocatalysts for the degradation of dyes under visible-light irradiation through the surface plasmon effect, it is expected that AuNPs/g-C$_3$N$_4$ nanohybrids could show improved photocatalytic performance. Cheng et al proposed that Au nanoparticles (AuNPs) were successfully loaded on graphitic carbon nitride (g-C$_3$N$_4$), and the nanohybrids show superior photocatalytic activities for the...
decomposition of methyl orange under visible-light irradiation due to the facilitated separation of photogenerated electron-hole pairs, and the surface plasmon resonance excitation in AuNPs.\textsuperscript{157}

It is well-documented that Ag, a famous noble metal, was regarded as a decent co-catalyst in constructing heterojunctions with g-C$_3$N$_4$ in photocatalytic utilization.\textsuperscript{158-159} Yang et al. reported that an efficient visible-light plasmonic photocatalyst, Ag/g-C$_3$N$_4$ heterostructure, is facilely fabricated by a simple polymerization-photodeposition route.\textsuperscript{158} Compared with individual g-C$_3$N$_4$, the photocatalytic activity of Ag/g-C$_3$N$_4$ was sharply enhanced toward the degradation of MO and p-nitrophenol, which may be ascribed to the enhanced visible-light utilization efficiency due to the SPR absorption of silver nanoparticles as well as fast generation, separation and transportation of the photogenerated carriers. Bai and his groups have developed novel core-shell Ag@g-C$_3$N$_4$ plasmonic nanocomposites by facile reflux treating method, exhibiting superb capability in photodegradation of MB and H$_2$ evolution.\textsuperscript{159} Moreover, by embedding Pd nanoparticles on the g-C$_3$N$_4$, Pd@g-C$_3$N$_4$ metal-semiconductor heterojunction was constructed and demonstrated highly strengthened photocatalytic performance in bisphenol removal.\textsuperscript{160} Meanwhile, note that Li et al. have successfully obtained g-C$_3$N$_4$/noble metal by directly loading with Pt, Au and Pd NPs respectively via a conventional solution impregnation method.\textsuperscript{161} The functional catalyst/support system can unambiguously act as a tandem catalyst to effectively trigger the water reduction reaction to form H$_2$ and activation of the as-formed H$_2$ for further reduction of 4-nitrophenol to 4-aminophenol.

\textbf{Fig. 7} (a) Schematic diagram illustrating the photocatalytic degradation of organic contaminants over noble metal NPs/g-C$_3$N$_4$ hybrid under visible-light irradiation; (b) TEM image of AuNP/g-C$_3$N$_4$ nanohybrids. Reprinted with permission from ref. 157. Copyright (2013) American Chemical Society.

g-C$_3$N$_4$ could function as an effective solid stabilizer for chaperoning various ultrathin noble metal NPs.\textsuperscript{161} It is worthwhile to elucidate the function mechanisms of g-C$_3$N$_4$/noble metal nanohybrids with improved the photocatalytic performance. As an example of Au/g-C$_3$N$_4$ nanohybrids,\textsuperscript{157} a schematic diagram on the phorocatalytic mechanism of Au/g-C$_3$N$_4$ is presented in Fig. 7a. Owing to surface plasmon resonance of noble metal, the as-prepared Au/g-C$_3$N$_4$ nanocomposites exhibit highly enhanced visible-light photocatalytic activity. On the other hand, the SPR effect of Au nanoparticle causes the intense local electromagnetic fields, which can speed the formation rate of holes and electrons within g-C$_3$N$_4$.\textsuperscript{158-161} Additionally, the favorable Fermi level of noble metal facilitates the separation of electrons and holes, which in turn enhances the quantum efficiency of g-C$_3$N$_4$, due to the intimate combination of the noble metal/g-C$_3$N$_4$ nanohybrids (Fig. 7b).\textsuperscript{162} Moreover, the transfer of electrons shifts the Fermi level to more negative potential, and thereby improving the reducibility of electrons in the Fermi level close to the CB of g-C$_3$N$_4$.\textsuperscript{163} On the other hand, the efficient utilization of sunlight can be realized due to SPR absorption in the visible-light region as well as UV light response of the inter-band transition of noble metal nanoparticles. Table 5 shows the photocatalytic properties of different g-C$_3$N$_4$/noble metal nanocomposite photocatalysts.

\begin{table}[h]
\centering
\caption{Photocatalytic properties of g-C$_3$N$_4$/noble metal nanocomposite photocatalysts}  
\begin{tabular}{|l|c|c|c|c|c|}
\hline  
Composite photocatalyst & Mass fraction or mass of g-C$_3$N$_4$ & Typical parameters of photocatalytic experiments & Photocatalytic activity & Reference catalyst: photocatalytic activity & Reference factor over the reference catalyst & Reference \hline  
Au@g-C$_3$N$_4$ & Mass:4.5\% & Decomposing methyl orange (MO) under visible light & 92.6\% degradation in 150 min & g-C$_3$N$_4$: 28.7\% Au: no data & 3.2 & No data & 157 \hline  
Au@g-C$_3$N$_4$ & No data & Photocatalytic & RH$_2$: no data & Pt/g-C$_3$N$_4$: RH$_2$: No data & No data & 15 \hline  
Pt-Au@g-C$_3$N$_4$ & No data & H$_2$ evolution under visible light; co-catalyst: triethanolamine & RH$_2$: no data & No data & No data & 161 \hline  
Pd-Au@g-C$_3$N$_4$ & No data & no; sacrificial reagent: triethanolamine & RH$_2$: no data & No data & No data & 161 \hline  
Ru-Au@g-C$_3$N$_4$ & No data & Photocatalytic H$_2$ evolution Under a 300 W Xe lamp; co-catalyst: triethanolamine & >96\% in 5 min & No data & No data & 161 \hline  
Ag-Au@g-C$_3$N$_4$ & No data & reduction of 4-nitrophenol to 4-aminophenol under visible light; Photocatalytic H$_2$ evolution & >85\% H$_2$O conversion & No data & No data & 161 \hline  
m-CNR-Au(2nm) & No data & No data & No data & No data & No data & 161 \hline  
m-CNR-Pd(3nm) & No data & No data & No data & No data & No data & 161 \hline  
m-CNR-Pt(2 nm) & No data & No data & No data & No data & No data & 161 \hline  
m-CNR-Pt(2 nm) & No data & No data & No data & No data & No data & 161 \hline  
\end{tabular}
\end{table}
3.6 g-C3N4 based complex system

Although a number of g-C3N4-based two-component nanocomposites have been developed for enhanced visible light photocatalysis, there are still some shortages that needs to be further addressed. With this purpose, multicomponent complex heterojunction systems have been developed, in which two or more visible-light active components are integrated.164-167 For example, novel Ag/AgBr/g-C3N4 ternary composite photocatalysts were successfully constructed via deposition-precipitation method, presenting dramatically improved photocatalytic performance for degradation of MO as well as good stability under visible light.164

![Image](image_url)

**Fig. 8** (a) TEM image and (b) HRTEM image of 50% Ag/AgBr/g-C3N4; (c) Schematic diagram of electron-hole pairs separation and the possible reaction mechanism over Ag/AgBr/g-C3N4 photocatalyst under visible light irradiation. Reproduced with permission from ref. 164, copyright 2013, Elsevier.

The high photocatalytic activity and stability of Ag/AgBr/g-C3N4 mainly attributed to the synergetic effect of AgBr/g-C3N4 interface and metallic Ag (Fig. 8a and 8b). Namely, the matching energy band structure of AgBr/g-C3N4 and excellent electron trapping role of metallic Ag ensured the efficient separation of electron-hole pairs, i.e. metallic Ag quickly evacuated the electrons on the side of AgBr which guaranteed the stability of Ag/AgBr/g-C3N4, shown in Fig. 8c. Moreover, Chai et al. designed and prepared g-C3N4-TiO2 three components nanocomposites via a facile chemical adsorption-calcination process, accompanied with remarkably enhanced performance for hydrogen production under visible light irradiation.165 The cocatalyst Pt deposited on TiO2 surfaces in the g-C3N4-TiO2 heterojunction is beneficial for exerting the synergistic effect existing between TiO2 and g-C3N4, which can strengthen the photogenerated carrier separation in space. And inspiringly, a new-type Pt-TiO2/g-C3N4-MnOx quaternary composites were also fabricated by a impregnation method with extraordinarily enhanced H2 production capacity, firstly reported by S. Obregón and G. Colón.166 Such markedly increase in the photoactivity might be related the incorporation of Pt and g-C3N4-MnOx in the charge separation process, which is in favor of retarding the charge recombination and improving the photoactivity for H2 production. A novel complex g-C3N4/CoO/graphene hybrid, with g-C3N4 embedded CoO particles covalently supported on a two-dimensional graphene sheet, is synthesized through a facile and scalable method by Jin and his co-workers.167 Above all, these significant achievements can pave the way for constructing g-C3N4-based multi-component heterojunctions and it is highly possible to optimize the visible light absorption, the charge carriers separation and transfer by adequately tailoring the structure of the photocatalysts. Recent progress on g-C3N4 based complex nanocomposites is summarized in Table 6.

![Table 6](image_url)

<table>
<thead>
<tr>
<th>Composite photocatalyst</th>
<th>Mass or molar fraction of g-C3N4</th>
<th>Typical parameters of photocatalytic experiments</th>
<th>Photocatalytic activity</th>
<th>Reference photocatalyst; photocatalytic activity</th>
<th>Enhancement factor over the reference photocatalyst</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/g-C3N4</td>
<td></td>
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<tr>
<td>Ag: 0.1g</td>
<td>Decomposing MO under visible light</td>
<td>MO of 74% g-C3N4: 70%; P25 TiO2: 56%; 1: 1.3</td>
<td>158</td>
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<tr>
<td>Ag: 0.5g</td>
<td></td>
<td></td>
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<td>Ag: 1g</td>
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<td>Ag: 2g</td>
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<td>Ag: 5g</td>
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<td>Ag/g-C3N4</td>
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<tr>
<td>Ag: 2g</td>
<td>Decomposing p-nitrophenol(PNP) under visible light</td>
<td>PNP of 98% g-C3N4: 83%; P25 TiO2: &lt;10%; 1: 2</td>
<td>159</td>
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<tr>
<td>Ag/g-C3N4</td>
<td>Mass:99.5%</td>
<td>Decomposing MO methyl blue (MB) phenol under visible light</td>
<td>No data g-C3N4: no data</td>
<td>g-C3N4: no data</td>
<td>g-C3N4: no data</td>
<td>1.6</td>
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<tr>
<td>Ag/g-C3N4</td>
<td>Mass:90%</td>
<td>Photocatalytic H2 evolution Under visible light; co-catalyst: no; sacrificial reagent: triethanolamine</td>
<td>No data g-C3N4: no data</td>
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<tr>
<td>Pd/g-C3N4</td>
<td>No data</td>
<td>Decomposing bisphenol A under solar light</td>
<td>93.9% Degradation in 180 min Bulk g-C3N4: 6%</td>
<td>P25 TiO2: 6.7%</td>
<td>g-C3N4: 52.1%</td>
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4. Multifunctional applications

Semiconductor-mediated photocatalysis has attracted worldwide attention for its potential in environmental and energy-related applications.\textsuperscript{45,117-125} Nevertheless, the rapid recombination rate of photogenerated electron-hole pairs within photocatalytic materials results in low efficiency, thus limiting its practical applications. Therefore, the retardation of recombination of charge carriers is the key for the enhancement of photocatalytic performance of semiconductor photocatalysts. g-C\textsubscript{3}N\textsubscript{4}-semiconductor hybrid materials as a new class of photocatalysts recently has attracted wide research interests.\textsuperscript{38,141} In this regard, nanocomposites that combine g-C\textsubscript{3}N\textsubscript{4} and other components could potentially provide desirable efficiency for separating electron-hole pairs. As documented above, the g-C\textsubscript{3}N\textsubscript{4}-based semiconductor photocatalysts have been widely used for the degradation of pollutants, photocatalytic hydrogen generation and photocatalytic conversion of carbon dioxide to methane fuel, etc. In this section the multiple applications of g-C\textsubscript{3}N\textsubscript{4}-based nanocomposite are briefly summarized.

4.1 Photocatalytic degradation of pollutants

In recent years, a large quantity of efforts has been devoted to solving the widespread pollution of effluents and gaseous pollutants from urban and agricultural industries. Various catalytic techniques have been applied in environmental conservation. Photocatalysis has been widely used in environmental applications such as air purification,\textsuperscript{168-170} water disinfection,\textsuperscript{171,172} hazardous waste remediation\textsuperscript{173,174} and water decontamination.\textsuperscript{175}

Graphene carbon nitrogen, as a “rising star” material has many exceptional properties, such as environmentally benign, stable physicochemical property, large specific surface area and low bad-gap, etc.\textsuperscript{18,20} Hence, g-C\textsubscript{3}N\textsubscript{4}-based semiconductor photocatalysts have been extensively applied to photocatalytic degradation of environmental pollutants.\textsuperscript{89,90} These composites possess high dye adsorption capacity, extended light absorption boundary, and accelerated charge transportation and separation properties.

For instance, a novel, multi-walled carbon nanotubes (CNT) modified white C\textsubscript{3}N\textsubscript{4} composite (CNT/white C\textsubscript{3}N\textsubscript{4}) were fabricated by Xu et al.\textsuperscript{77} The CNT/C\textsubscript{3}N\textsubscript{4} nanocomposite was prepared by the hydrothermal method through electrostatically-driven self-assembly. The CNT/C\textsubscript{3}N\textsubscript{4} composite shows significantly enhanced photocatalytic performance in MB dye removal. A possible photocatalytic mechanism of CNT/white C\textsubscript{3}N\textsubscript{4} on the enhancement of visible light performance is proposed (Fig. 9a). Firstly, the electrons are motivated from the VB to the CB of C\textsubscript{3}N\textsubscript{4} under visible light irradiation. Secondly, the photo-excited electrons are effectively collected by CNT, hindering the recombination process of the electron-hole pairs. Thirdly, the O\textsubscript{2} adsorbed on the surface of catalyst can be reduced to active species. The holes and the generated ‘OH can react with the organic dye and generate degradation products. Furthermore, the photocatalytic stability of CNT/white C\textsubscript{3}N\textsubscript{4} was investigated through the repeated MB degradation experiments, as shown in Fig. 9b. It is clear that the MB dye can be completely bleached after each photocatalytic run, and CNT/C\textsubscript{3}N\textsubscript{4} is stable enough during the repeated experiments without significant loss of photocatalytic activity. Therefore, CNT/white C\textsubscript{3}N\textsubscript{4} can be used as an effective photocatalyst for organic compounds degradation with good stability.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9.png}
\caption{(a) Proposed photocatalytic mechanism of the CNT/white C\textsubscript{3}N\textsubscript{4}; (b) Recycling in the repeated MB degradation experiments with CNT/white C\textsubscript{3}N\textsubscript{4} under visible light irradiation. Reproduced with permission from ref. 77, Copyright (2013) The Royal Society of Chemistry.} 
\end{figure}
to the well-matched energy band structure. Therefore, the photo-generated electrons and holes can be separated effectively in this way, and the recombination rate of the photo-generated electrons and holes would be hampered, which contributed to the superior photocatalytic reactivity. Moreover, this coupling heterojunction could also be used to remove the poisonous gaseous pollutant acetaldehyde gas (CH₃CHO), which is a typical volatile organic compound (VOC) and exerts adverse effects on the health of humans. By incorporating g-C₃N₄ with different contents of WO₃, Katsumata et al. studied the photocatalytic performance of this composite in acetaldehyde gas removal. As a result, they found that as the WO₃ content increases, the photodegradation effect became more conspicuous, and the optimum mass ratio of g-C₃N₄ to WO₃ for photocatalysis is two to eight. What is more, Huang et al. further utilized this novel composite to treat another two organic pollutants of MB and 4-CP. The highest degradation efficiency was achieved for the WO₃/g-C₃N₄ (9.7%) sample, which induced 97% degradation of MB within 2h and 43% degradation of 4-CP within 6h under visible light irradiation, while pristine g-C₃N₄ only induced 81% degradation of MB within 3h and 3% degradation of 4-CP within 6h.

Apart from CNT/C₃N₄ and WO₃/g-C₃N₄ nanocomposites, composites of g-C₃N₄ and other semiconductor photocatalysts such as g-C₃N₄/TiO₂, CeO₂/g-C₃N₄, g-C₃N₄/Cds, g-C₃N₄/TaON, g-C₃N₄/Bi₂WO₆, BiOBr/g-C₃N₄, BiOI/g-C₃N₄, and Pd/g-C₃N₄ have been reported as efficient photocatalysts for decomposition of pollutants in water. Among these coupling systems, TiO₂ is a famous UV light-driven and g-C₃N₄ as a robust visible-light-driven photocatalyst, are favourably selected to be coupled for enhanced photocatalysis. Zhao et al. evaluated both the UV and visible-light photocatalytic activity of g-C₃N₄/TiO₂ for degradation of phenol in water, and found that these composites exhibited excellent photocatalytic performance. The pseudo-first-order kinetic constant of phenol degradation on g-C₃N₄/TiO₂ was 2.41 and 3.12 times higher than those on pristine g-C₃N₄ and TiO₂, respectively, which could be ascribed to the wide absorption wavelength range and effective photogenerated charge separation. Moreover, Fu and co-workers reported the g-C₃N₄ hybridized CdS composite as an efficient photocatalyst. The optimum activity of 0.7C₃N₄:0.3CdS photocatalyst is almost 20.5 and 3.1 times higher than those of individual C₃N₄ and CdS for methyl orange degradation, and 41.6 and 2.7 fold higher for 4-aminobenzoic acid removal, respectively. Moreover, its activity is also much higher than those of C₃N₄–TiO₂ and CdS–TiO₂ composites, as well as famous N-modified TiO₂. Of particular significance is that the present C₃N₄–CdS composites also demonstrate high stabilities under illumination, in contrast with CdS. The improvement in both performance and stability should be assigned to the effective separation and transfer of photogenerated charges originating from the well-matched overlapping band-structures and closely contacted interfaces.

Recently, the g-C₃N₄–Bi₂WO₆ composite photocatalysts were studied by Tian and co-workers for the photocatalytic degrading MO under visible light irradiation. Encouragingly, the resulting g-C₃N₄–Bi₂WO₆ heterojunctions own a strong absorption in the visible light region and have apparently enhanced photocatalytic performances. And this superior activity may be ascribed to the electronic interactions and charge equilibration between g-C₃N₄ and Bi₂WO₆, leading to the shift in the Fermi level and decreasing the conduction band potential of Bi₂WO₆. Simultaneously, the negative shift in the Fermi level of g-C₃N₄–Bi₂WO₆ and the high migration efficiency of photoinduced electrons can suppress the charge recombination effectively, resulting in the enhanced photocatalytic degradation of pollutants. Moreover, as bismuth subcarbonate ((BiO)₂CO₃) a novel photocatalyst, we achieved new g-C₃N₄/(BiO)₂CO₃ nanojunctions by a situ strategy depositing (BiO)₂CO₃ nanoflakes onto the surface of g-C₃N₄ nanosheets through efficiently capture atmospheric CO₂ (crude material of (BiO)₂CO₃) method at room temperature. These nanojunctioned photocatalysts showed excellent visible-light capability by degrading RhB and phenol, accompanied by well-stability.

Hitherto, arrays of successful efforts of g-C₃N₄-based heterojunctions have also been paid to degrading NOx, which have been regarded as a worldwide gaseous pollutant. Our groups have investigated the photocatalytic capability of novel 2D BiOBr/C₃N₄ nanojunctions in NOx removal. The NO removal ratios of BiOBr/C₃N₄ can be achieved to 32.7%, which is much higher than that of the pristine BiOBr (21.2%) and C₃N₄ (21.2%). The enhancement of photocatalytic performance of BiOBr/C₃N₄ could be ascribed to the synergistic effect of well-coupled crystal planes and band structure. To further boost the photocatalytic activities, we constructed the g-C₃N₄/g-C₃N₄ metal-free isotype heterojunction by a facile situ method. The CN-TU dramatically exhibited an improved NO removal ratio of 47.6%, compared to host substrates of CN-U and CN-T. Besides, this metal-free isotype heterojunction demonstrated well stability as well. The strengthened photocatalytic performance of g-C₃N₄/g-C₃N₄ isotype heterojunction can be directly ascribed to the efficiently accelerated charge separation across the heterojunction interface as well as prolonged lifetime of charge carriers.

4.2 Photocatalytic hydrogen generation

Hydrogen energy is regarded as an ultimate clean fuel in the near future because of its high-energy capacity, environmental benignity, and recycling utilization. Photocatalytic splitting water into hydrogen and oxygen using semiconductor photocatalysts has been regarded as an attractive and promising approach to produce hydrogen energy. A flock of semiconductor photocatalysts have been reported to catalyze the evolution of hydrogen from water. However, the practical applications of this strategy are limited on account of the prompt recombination of photogenerated electron-hole pairs within photocatalysts. Considering the visible-light-driven property and high specific surface area, g-C₃N₄ can be regarded as an efficient photocatalyst for enhancing the visible light utilization and accelerating the photo-induced charge transfer hampering the backward reaction, which will highly promote the photocatalytic H₂-production activity.
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Ni(OH)\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composites loaded with different contents of Ni(OH)\textsubscript{2}. Yu and co-workers\textsuperscript{96} studied their water splitting performance in triethanolamine aqueous solutions. The results demonstrated that Ni(OH)\textsubscript{2} was an efficient co-catalyst for g-C\textsubscript{3}N\textsubscript{4} photocatalytic producing H\textsubscript{2}. The optimal Ni(OH)\textsubscript{2} loaded on g-C\textsubscript{3}N\textsubscript{4} was found to be 0.5 mol\%, giving a H\textsubscript{2}-production rate of 7.6 mmol h\textsuperscript{-1} with quantum efficiency (QE) of 1.1% at 420 nm, depicted in Fig. 10a. The fact that the potential of Ni\textsuperscript{2+}/Ni is lower than that of the CB of g-C\textsubscript{3}N\textsubscript{4} and more negative than that of H\textsuperscript{+}/H\textsubscript{2} favors the electron transfer from CB of g-C\textsubscript{3}N\textsubscript{4} to Ni(OH)\textsubscript{2} and then reduce H\textsuperscript{+} to H\textsubscript{2} with decent performance (Fig.10b).

This work proved that Ni(OH)\textsubscript{2} was a very promising co-catalyst to combine with g-C\textsubscript{3}N\textsubscript{4} for visible-light photocatalytic hydrogen production. Very recently, Hong et al.\textsuperscript{90} systematically studied the efficiency of H\textsubscript{2} evolution for the NiS/g-C\textsubscript{3}N\textsubscript{4} composite constructed by a single hydrothermal method. This photocatalyst showed efficient hydrogen evolution (48.2 mmol h\textsuperscript{-1}) under visible light when using triethanolamine as a sacrificial reagent. The optimal ratios was 1.1 wt % of NiS loaded on g-C\textsubscript{3}N\textsubscript{4} and the rates of H\textsubscript{2} production can be enhanced by about 250 times compared with the native C\textsubscript{3}N\textsubscript{4}. The highest apparent quantum efficiency was recorded at 1.9 % induced by 440 nm light irradiation. In order to further explore the possible application of g-C\textsubscript{3}N\textsubscript{4}/single metal oxide (metal sulfide) composites in hydrogen production, Hou and co-workers\textsuperscript{99} constructed MoS\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} nanocomposites and found that visible-light performance of H\textsubscript{2} production of mpg-CN is significantly improved compared with bare MoS\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4}. Interestingly, the 0.5 wt % MoS\textsubscript{2}/mpg-CN performed better than 0.5 wt % Pt/mpg-CN under identical reaction conditions. The geometric similarity (layered morphology) of MoS\textsubscript{2} and g-CN (Fig.11), accompanied with the mesoporous architectures of mpg-CN facilitate to forming intimate planar MoS\textsubscript{2}/g-CN interface, which can significantly promote the photoactivity of MoS\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}. They also discovered that other layered transition metal dichalcogenides (such as WS\textsubscript{2}) are also efficient promoters for hydrogen production combined with g-C\textsubscript{3}N\textsubscript{4}. Herein they have presented not only an example of a catalyst made of abundant C, N, Mo and S elements for efficient H\textsubscript{2} photosynthesis, but also a conceptual advance to rationally design and fabricate a thin, effective interfacial 2D junctions between co-catalysts and semiconductors that have similar layered geometric architectures.
effective sensitizer of TiO₂ can be widely used to improve photocatalytic H₂ production, but also afforded various methods for developing novel, steady and visible-light-responsive photocatalysts.

Also, graphene, a two-dimensional macromolecular sheet of carbon atoms with a honeycomb structure, extremely high specific surface area and thermal conductivity, showed a good photocatalytic performance for hydrogen or oxygen production. After introduction of graphene sheets, g-C₃N₄ is also immobilized to form a layered composites, which will largely increase the BET and catalytic performance. In this system, graphene sheets act as conductive channels efficiently separating the photogenerated charge carriers as well as enhancing the visible-light capability of H₂-production. The optimal graphene content was found to be 1.0 wt %, and the corresponding H₂-production rate was 451 μmol h⁻¹g⁻¹, which exceeded that of pure g-C₃N₄ more than 3.07 times. The potential mechanism was illustrated in Scheme 1. Normally, when g-C₃N₄ is immobilized on the surface of graphene sheets to form the layered composites, these photogenerated electrons on the CB of g-C₃N₄ tend to transfer to graphene sheets due to their excellent electronic conductivity, favoring the hole-electron separation. Meanwhile, Sui et al. reported that they have successfully loaded highly-dispersed conductive polymer polypyrrole (PPy) nanoparticles on the surface of g-C₃N₄. Surprisingly, they found that the H₂ evolution rate of g-C₃N₄ loades with 1.5 wt% PPy can increase up to 50 times compared with that of pristine g-C₃N₄, and the reaction proceeded in a pure water system excluding the need of sacrificial agents. We believe that these work can provide an effective route for developing efficient photocatalysts for photocatalytic hydrogen evolution from pure water systems.

4.3 other applications

Solar fuels have been considered as one of the most important renewable clean energy resources and photocatalytically converting CO₂ into valuable hydrocarbon fuel (CH₄) is known as a challenging but promising application for sustainable energy resources. In g-C₃N₄ based composites, Yuan et al. significantly obtained red phosphor/g-C₃N₄ heterojunction with enhanced photocatalytic activities for solar fuels production. The introduction of g-C₃N₄ onto Red phosphor surface led to considerable improvement of the photocatalytic activity for CO₂ conversion into CH₄ in the presence of water vapor. The enhancement could be attributed to the effective separation of photogenerated electrons and holes across the red phosphor/g-C₃N₄ heterojunction. Owing to the advantages of non-toxicity, low cost and abundance in nature, this active heterostructural red phosphor/g-C₃N₄ would have great potential for efficient solar fuels production. Very recently, In₂O₃/g-C₃N₄ hybrid photocatalysts were fabricated by Cao and his group, and the resulting In₂O₃–g-C₃N₄ hybrid structures exhibited considerable photocatalytic activities for CO₂ reduction. After 4-h irradiation, the optimal In₂O₃/g-C₃N₄ (10 wt% In₂O₃) exhibited a CH₄ production yield of 76.7 ppm (over 20 mg samples) without any cocatalyst, which is more than three times higher than that of individual g-C₃N₄ and more than four times higher than that of pure In₂O₃. The enhanced activities were attributed to the enhanced interfacial transfer of photogenerated electrons and holes between g-C₃N₄ and In₂O₃, leading to effective charge separation on both parts.

Moreover, g-C₃N₄ based composites also were considered as a promising candidate in photocatalytic disinfection. A novel class of metal-free ternary heterojunction photocatalysts was prepared by wrapping reduced graphene oxide and g-C₃N₄ sheets on crystals of cyclooctasulfur (α-S₈), reported by Wang et al. Two distinctive structures were fabricated by wrapping reduced graphene oxide (RGO) and CN sheets in different orders. The first was RGO sheets sandwiched in heterojunction of CN sheets and α-S₈ (i.e., CNRGOS), while the second structure was the other way around (i.e., RGOCN₃S₈). And fascinatingly, both structures exhibited outstanding antibacterial activity in aerobic or anaerobic conditions irradiated with visible light (Fig. 12), which chose colibacillus as a representative microorganism to evaluate the photocatalytic water disinfection performances. This work not only provided new inroads into exploration and understanding the photocatalytic bacterial inactivation mechanisms, but also afforded developing suitable protocols for solar-driven photocatalytic water disinfection under different conditions.

![Fig. 12 Schematic illustration of the VLD photocatalytic bacterial inactivation mechanisms of (a) CNRGOS₃ and (b) RGOCN₃ in aerobic condition, and (c) CNRGOS₅ and (d) RGOCN₃ in anaerobic condition. (CNRGOSS was RGO sheets sandwiched in heterojunction of CN sheets and α-S₈, while RGOCN₃SS was the other way around (i.e.,)...](image-url)
for high-performance supercapacitors.

![Diagram of g-C3N4-based nanocomposites](image)

**Fig. 13** Schematic illustration of the g-C3N4 based heterojunction/heterostructure and their multifunctional applications.

We have made a summary of the design strategy, categories and their multifunctional applications of g-C3N4 based nanocomposites as illustrated in Fig. 13.

5. **Conclusion and perspectives**

In summary, various types of g-C3N4-based nanocomposites system have been designed and constructed. The incorporation of g-C3N4 into these nanocomposites can impart them with unique properties and induce enhanced performance, such as high adsorption capacity, extended light absorption range, and accelerated charge separation and transportation, which strengthen the overall photocatalytic performance. A wide range of heterostructures, including metal-free, metal/semiconductor, semiconductor/semiconductor, molecule/semiconductor, and multi-component heterostructures, have been explored for the improved photocatalysis by increasing the light absorption, improving the charge separation and transportation, enhancing the catalytic activity and prolonging the charge carriers lifetime. These nanocomposites photocatalysts have been widely used for photocatalytic degradation of pollutants, photocatalytic hydrogen generation, carbon dioxide storage and disinfection. The present review depicts the fabrication, microstructure and photocatalytic performance, as well as the photocatalytic mechanisms when g-C3N4 is coupled with an array of materials such as metal-free, single metal oxide (metal sulfide), composite oxide, halide, noble metal, etc. It is anticipated that the g-C3N4-based nanocomposites will receive ever increasing research interest in the future.

Although considerable progress has been achieved, the studies in this field are still at the primary stage and further systematic investigations are needed. Rational design of complex heterostructures that could simultaneously facilitate efficient optical absorption, carrier generation, separation, transportation and utilization is central for a new generation of highly efficient and robust photocatalysts. Significant challenges remain in the synthesis of such complex nanostructures with well designed architectures and optimized charge cascading processes.

First, a fundamental understanding of the charge transport process in the multi-heterostructure photocatalysts is critical for the optimization of the charge cascading process to maximize the utilization of photogenerated charge carriers for desirable redox chemistry. While it is relatively straightforward to understand electron/hole separation and transportation in a two component heterostructure, the understanding and control of charge transport in multi-component heterostructure become increasingly more complex, particularly on the nanometer scale. The interface properties of the photocatalysts determine the eventual efficiency of the photocatalytic system. To understand the charge generation, separation and transportation across these nanoscale interfaces is critical. Current investigations mainly focus on an overall apparent efficiency of the entire photocatalytic system. The detailed mechanism studies of the charge transfer process in photocatalysts integrating three or more components are scarce and will be necessary to further advance the field.

Secondly, the stability of g-C3N4-based nanocomposites is less addressed and will be one main challenge for photocatalyst development. A photocatalyst with very high efficiency is still useless if the lifetime of the catalyst is too short. For majority of systems, chemical corrosion and/or photodegradation of photocatalysts are difficult to avoid. The promoted photocatalyst stability has only been achieved in a few examples to date, which usually however, requires highly complicated synthetic processes. To develop a stable photocatalytic system with high efficiency at low-cost will be the central task to realize a practically viable photocatalyst for potential practical applications.

Thirdly, the mechanisms of photocatalytic enhancement by the g-C3N4-based semiconductor composite systems are partly unclear. And the explanation of photocatalytic activity by the g-C3N4 content in the composites is still controversial. Therefore, more studies are required to promote the general understanding of the enhancement mechanism of g-C3N4 based nanocomposites, especially employing advanced in situ techniques. Also, it is necessary to develop a uniform method to assess the photocatalytic performance as the current evaluation methods are diverse. A photocatalyst working better in water treatment may show poor performance in air purification.

Finally, the rapid development of material science and nanotechnology in the past few years has resulted in the creation of various advanced photocatalytic materials. Interesting properties may be explored by combining novel photocatalysts with g-C3N4. With a better understanding of the fundamental photocatalysis mechanism, assisted by the rapid development of advanced new nanomaterials, the bottleneck of environmental and energy-related global issues could be overcome in the near future. Overall, it is certain that there will be numerous exciting opportunities on g-C3N4 based nanocomposites, which require the combined efforts of scientists all over the world.

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