Review

Nanocarbons with Different Dimensions as Noble-Metal-Free Co-Catalysts for Photocatalysts

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Abstract: In this review, we provide an overview of recent progress in nanocarbons with different dimensions as noble-metal-free co-catalysts for photocatalysts. We put emphasis on the interface engineering between nanocarbon co-catalysts and various semiconductor photocatalysts and the novel properties generating of nanocarbon co-catalysts, also including the synthesis and application of nanocarbon-based photocatalyst composites.

Keywords: nanocarbon co-catalysts; dimensionality; interface engineering; photocatalysis

1. Introduction

In the last decades, many techniques have been developed for solving energy crises and environmental pollution problems. However, most of the techniques have shortcomings of low efficiency, difficulty of complete removal of pollutants, production of secondary pollution, and high energy consumption. More economical and effective techniques are desired. In 1972, Fujishima and Honda [1], for the first time, found that the single crystal TiO$_2$ electrode could produce hydrogen by splitting water under UV irradiation. In 1978, Halmann [2] used a P-type semiconductor of GaP as a photoelectric electrode to reduce CO$_2$-water solution into CH$_3$OH. These two pioneering works revealed the potential capability of solar photocatalysis technology in solving the problems of energy crises and environmental pollution [3–5]. However, it is a long way for solar photocatalysis techniques in large scale industrial applications because of the low solar energy utilization, and high recombination rate of photoinduced electrons and holes of photocatalysts [6–8].

Various strategies have been developed for improving the photocatalytic performance of photocatalysts, such as morphology control, band gap engineering, and loading of co-catalysts on semiconductor photocatalysts [9,10]. Loading of co-catalysts on semiconductor photocatalysts and forming interfacial heterostructures has been proved an effective way for absorbing a broader spectrum of solar energy and gaining efficient charge separation and migration [11–13]. Here, co-catalyst means a certain substance which, itself, is a rather weak catalyst, but which greatly increases the activity of a given catalyst; also called a promoter. Noble metals and their compounds are frequently selected as co-catalysts. Noble metal co-catalysts, including Pt, Pd, Rh, or RuO$_2$, can significantly enhance the photocatalytic performance of semiconductor photocatalysts [14]. However, noble metals are rare and expensive, which hinder their practical application. Efficient and noble metal-free cocatalysts are urgently required. Nanocarbon materials with low dimension and specific morphology, such as zero dimensional (0D) fullerene and nano-onions, one dimensional (1D) nanofibers and nanotubes, and two dimensional (2D) graphene, exhibit unique physical and chemical properties including high...
electrical conductivity, high surface area, and chemical stability [15]. Thus, nanocarbon materials can be employed as excellent co-catalysts for semiconductor photocatalysts.

Different dimensional nanocarbon co-catalysts can form various dimensional interfaces with different dimensional semiconductor photocatalysts as shown in Figure 1. Three modes of interface will form including point-to-point, line-to-line and surface-to-surface in nanocarbon co-catalysts/semiconductor photocatalysts heterostructures. In photocatalytic reactions, such as H$_2$ evolution from photocatalytic water splitting, when photocatalysts absorb suitable light, the electrons will be excited and transfer from the valence band to the conduction band and positive holes are left in the valence band. Water molecules are reduced by the electrons to form H$_2$ and are oxidized by the holes to form O$_2$. However, negative electrons and positive holes have a tendency to recombine. The photocatalytic activity depends on the ability of the photocatalyst to create electron–hole pairs and the separation efficiency of photogenerated electron-hole pairs [16]. For nanocarbon-based photocatalysts, photogenerated electrons can transfer from the conduction band of semiconductor photocatalysts to nanocarbon materials through the intimate interface between them, which greatly inhibit the recombination of photoinduced electrons and holes. So, as the channel for electron transfer, the dimensions of the interface will be critical for effective separation of photoinduced electrons and holes.

Figure 1. Schematic illustration of different dimensional nanocarbon co-catalysts combining with different dimensional semiconductor photocatalysts.
Some reviews about nanocarbon-based materials for photocatalysis have been published [17,18]. However, most of them only focused on TiO$_2$ photocatalysts or graphene-based photocatalytic composites. In this short review, we provide an overview of recent progress in nanocarbons with different dimensions as noble-metal-free co-catalysts for photocatalysts. We put emphasis on the interface engineering between nanocarbon co-catalysts and various semiconductor photocatalysts, and the novel properties generating of nanocarbon co-catalysts.

2. 0D Carbon Materials as Cocatalysts

Fullerenes, as typical 0D nanocarbon materials, possess some special properties and have attracted much attention [19]. C$_{60}$ and C$_{70}$ are the most common fullerenes. It has been reported that fullerenes with unique electronic properties can be used as co-catalysts for improving transfer efficiency of photoinduced electrons and actually enhance photocatalytic activities [20–26].

2.1. 0D/0D

TiO$_2$, as one of the most researched photocatalytic materials, has attracted much attention [3,27,28] due to its advantages of nontoxicity, low cost, and high photocatalytic activity [29,30]. Oh et al. [31] employed an improved oxidation method to synthesize the fullerene/TiO$_2$ composites. One of the advantages of these composites is that there are more reactive sites on the surface of oxidized fullerenes than non-oxidized fullerenes, which can be helpful for high-quality dispersion of TiO$_2$ particles. The photocatalytic activity of fullerene/TiO$_2$ composites was evaluated by photocatalytic decomposition of methylene blue (MB) under UV light irradiation. It is no doubt that the composites exhibit enhanced photocatalytic activity. Different from TiO$_2$, photocorrosion of ZnO during light irradiation hinders their practical application in the field of photocatalysis and its applications are limited to light-emitting diodes [32], gas sensors [33], and so forth. [34]. Fu et al. [35] synthesized C$_{60}$-coated ZnO photocatalysts. The coating of C$_{60}$ enhances the photocatalytic activity and inhibits the photocorrosion of ZnO. It was found that the coverage of C$_{60}$ on the surface of ZnO nanoparticles determined the enhancement degree of photocatalytic activity, indicating the crucial role of hybridized interaction between C$_{60}$ and ZnO. From the viewpoint of efficient utilization of solar energy, visible light-response photocatalysts with high photocatalytic activity are desired. Song et al. [36] synthesized C$_{60}$ modified Cr$_{2-x}$Fe$_x$O$_3$ heterostructured photocatalysts and employed them in photocatalytic H$_2$ evolution from water splitting under visible light irradiation. The C$_{60}$-Cr$_{1.3}$Fe$_{0.3}$O$_3$ with an optimized band structure (E$_g$ = 1.5 eV) exhibits strong visible light absorption capability. The good dispersion of C$_{60}$ on the surface of Cr$_{1.3}$Fe$_{0.3}$O$_3$ nanoparticles supplies more reactive sites and the point-to-point interface promotes the transfer of photoinduced electrons. Consequently, the H$_2$ evolution ability of C$_{60}$-Cr$_{1.3}$Fe$_{0.3}$O$_3$ is two times higher than that of pure Cr$_{1.3}$Fe$_{0.3}$O$_3$ nanoparticles.

Similar to C$_{60}$, another fullerene C$_{70}$ is a closed-shell configuration consisting of 35 bonding molecular orbital with 70 p-electrons [37]. Wang and coworkers [38] fabricated fullerene C$_{70}$-modified TiO$_2$ (C$_{70}$-TiO$_2$) by titanium sulfate and functionalized C$_{70}$. The covalent bonds (Ti-O-C = O or Ti-O-C) formed by C$_{70}$ and surface atoms of TiO$_2$ nanoparticles not only generate point-to-point interfaces between the functionalized C$_{70}$ and TiO$_2$, but also slightly reduce the crystallite size of TiO$_2$, as well as extend absorption edge of TiO$_2$ to the visible light region. The photocatalytic degradation rate of sulfathiazole by using C$_{70}$-TiO$_2$ hybrid as photocatalysts is 1.6 times higher than that of C$_{60}$-TiO$_2$ hybrid due to the larger photo cross-sectional area, larger delocalization effect, and higher electron affinity of C$_{70}$ (Figure 2).
2.2. 0D/1D

Long et al. [39] synthesized C\textsubscript{60} nanoparticles incorporated TiO\textsubscript{2} nanorods. The photocatalytic activity of C\textsubscript{60}/TiO\textsubscript{2} nanorods is about 3.3 times higher than that of TiO\textsubscript{2} nanorods. The high specific surface area plays an important role and the electronic interactions between C\textsubscript{60} and TiO\textsubscript{2} enhance the absorption of visible light (Figure 3). Grandcolas et al. [40] reported that after the hybridization with C\textsubscript{60}, the absorption capacity in the visible light region and photocatalytic activity of titania nanotubes (TiNTs) are all enhanced. It was found that C\textsubscript{60} distributes both inside and outside of TiNTs. Photoinduced electrons are delivered from the 1D main photocatalyst to 0D C\textsubscript{60} nanoparticles through the point-to-point interface, inhibiting the electron-hole recombination.

2.3. 0D/2D

To further extend the surface area of photocatalysts, two-dimensional nanosheets may be an ideal candidate and also act as a supporting matrix to disperse C\textsubscript{60} uniformly. Li and coworkers [41] synthesized fullerene C\textsubscript{60}-enhanced Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2} hierarchical microspheres and employed the obtained photocatalysts to degrade Rhodamine B (RhB) and Eosin Y (EY) under visible light irradiation. C\textsubscript{60}/Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2} not only has higher photocatalytic activity than pure Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2}, but also shows improved stability (Figure 4). The photocatalytic activity of C\textsubscript{60}/Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2} is also higher than that of a physical mixture of C\textsubscript{60} and Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2}, further confirming the strong interaction between C\textsubscript{60} and Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2}.
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Figure 4. (A) Schematic illustration of photogenerated electron-hole separation mechanism in 0D C$_{60}$/2D Bi$_2$TiO$_4$F$_2$ heterostructure; and (B) photocatalytic performance of C$_{60}$/Bi$_2$TiO$_4$F$_2$ composites with different content of C$_{60}$ for degrading RhB. Reprinted with permission from [41]. Copyright 2013, American Chemical Society.

Although many achievements have confirmed that the employment of 0D carbon materials as co-catalysts can actually enhance the photocatalytic performance of semiconductor photocatalysts, these materials are difficult to homogeneously disperse on the surface of main photocatalysts. Even though the 0D nanocarbon particles can be dispersed on the surface of main photocatalysts, only point-to-point interfaces may form regardless of the dimensions of the main photocatalysts. Furthermore, 0D nanoparticles have a tendency to agglomerate and some large clusters with irregular shape can prevent their agglomeration as well as favor the recovery of photocatalysts. Especially if the support possesses excellent conductivity and 1D structure make them an ideal candidate co-catalyst for photocatalysts [49]. Many researchers focused on this field and made some achievements.

3. 1D Nanocarbon Materials as Co-Catalysts

1D carbon materials including carbon nanotube (CNTs) and carbon nanofibers (CNFs) have been studied for many years due to their unique properties. For instance, CNTs are studied as hydrogen storage materials due to their large surface area, hollow and layered structure [42]. As a supporting matrix, CNTs can offer high surface area and specific functional groups for efficient adsorption of reactants [43,44]. CNTs are also famous for their high mechanical strength, making them suitable for a large number of applications [45–48]. Their properties of excellent conductivity and 1D structure make them an ideal candidate co-catalyst for photocatalysts [49]. Many researchers focused on this field and made some achievements.

3.1. 1D/0D

It is known that 0D particles have a tendency of agglomeration due to the high surface energy [50]. Loading 0D photocatalysts nanoparticles on the surface of supports with high specific surface area and confinement effect can prevent their agglomeration as well as favor the recovery of photocatalysts. Especially if the support possesses excellent conductivity, the transfer of photogenerated electrons will be promoted and recombination of electrons and holes can be inhibited efficiently.

Peng et al. [51] synthesized 1D multiwall carbon nanotubes (MWCNTs)/0D CdS composites. MWCNTs function as supporting matrix and also play a role of electron transfer channels due to their intrinsic conductive properties (Figure 5). The contact interface between MWCNTs and CdS can be responsible for the enhanced photocatalytic performance because it ensures the timely transfer of electrons and stabilizes CdS nanoparticles. The enhancement of photocatalytic performance for degrading methyl red was also observed for 1D CNT/0D ZnO nanocomposites [52]. Xia et al. [53] reported the fabrication of MWCNTs/TiO$_2$ composites and employed them to reduce CO$_2$ with H$_2$O. The improved photocatalytic performance and major product HCOOH demonstrated that the separation of photogenerated electron and hole pairs is remarkable due to the interaction between...
MWCNTs and TiO$_2$. Noble metals as co-catalysts can bring significant improvement during the photocatalytic reaction [14,54,55]. However, their high price inhibits the particle’s applications. Researchers hope to find some non-noble metals to replace novel metals [56–58]. Zhang et al. [59] reported the synthesis of Mo-decorated TiO$_2$/CNTs (Mo-CT) composites. In this system, three parts play their own duty, respectively, and the interaction between them dramatically enhances the photocatalytic activity. Mo clusters play the role of accepting photoinduced electrons came from the conduction band of TiO$_2$, achieving the separation of photoinduced electrons and holes. CNTs act as both visible light absorption sites and electron transfer channels and, at the same time, TiO$_2$ plays a role in electron excitation [60].

**Figure 5.** (A) HRTEM images of 1D MWCNTs/0D CdS nanocomposite; and (B) the amount of H$_2$ evolution over different photocatalysts under visible light ($\lambda \geq 420$ nm) and full spectrum of the Xe lamp. Reaction conditions: 35 mg of photocatalyst, 0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$ as sacrificial reagents. Reprinted with permission from [51]. Copyright 2011, American Chemical Society.

### 3.2. 1D/1D

Different from 0D photocatalysts, 1D photocatalysts can form 1D interface with 1D nanocarbon co-catalysts at the same direction, thus bringing stronger interaction, which is beneficial to the photocatalytic reaction. However, it is actually hard to control two kinds of 1D material to array on one direction and form a line-to-line interface homogeneously. Natarajan [61] recently reported the fabrication of MWCNT-loaded TiO$_2$ nanotube (TNT) composites by a hydrothermal method. They tried to obtain 1D/1D composites, but it was found that most of the junctions between MWCNTs and TiO$_2$ nanotubes are still shaped as points. The excellent durability and stability of the obtained composites for degrading dyes seem to be due to the point-to-point interface, but not the line-to-line interface.

### 3.3. 1D/2D

Different from the 1D/1D mode, an intimate and larger contacted line-to-line interface can form when 1D nanocarbon co-catalysts combine with 2D photocatalysts. Chen at al. [62] synthesized hierarchical core-shell carbon nanofiber@ZnIn$_2$S$_4$ composites by controlling the in situ growth of ZnIn$_2$S$_4$ nanosheets on carbon nanofibers (CNFs). This preparation process not only ensures the uniform growth of nanosheets, but also avoids the agglomeration of ZnIn$_2$S$_4$. It is believed that the stacking force between ZnIn$_2$S$_4$ nuclei and nanofibers promotes the in situ formation of ZnIn$_2$S$_4$ (Figure 6A). The synergistic effects formed by the increased active sites, electron-tunneling effect and junctions, leading to excellent photocatalytic activity (Figure 6B).
Figure 6. (A) Schematic illustration of photogenerated electron-hole separation and H₂ evolution mechanism in 1D CNFs/2D ZnIn₂S₄ composites; and (B) photocatalytic performance of ZnIn₂S₄/CNFs, and the 1D CNFs/2D ZnIn₂S₄ composites with different contents of CNFs for H₂ evolution from water splitting under visible light (λ ≥ 420 nm) irradiation. Reaction conditions: 30 mg of photocatalysts, 0.35 M Na₂S, and 0.25 M Na₂SO₃ as the sacrificial reagents, and a Xe lamp as light source. Reprinted with permission from [62]. Copyright 2014, American Chemical Society.

4. 2D Nanocarbon Materials as Co-Catalysts

Graphene, a new class of nanocarbon material with honeycomb network of monolayer carbon atoms, different from 0D fullerene and 1D CNTs or CNFs, has attracted increasing attention due to their excellent electrical conductivity, large surface area, and high chemical stability [63,64]. Graphene can be used as an electron-transport matrix due to its excellent electrical conductivity and perfect 2D feature, and then take the place of noble metals as co-catalysts for enhancing the photocatalytic performance by offering strong interaction, as shown in Figure 1. It has been extensively explored to improve the utilization of solar energy by introducing graphene into photocatalysts. [65–69].

4.1. 2D/0D

With smart design, 0D photocatalyst nanoparticles can be dispersed on 2D graphene nanosheets homogeneously or be wrapped into the nanosheets. The functional groups anchored on the surface of graphene nanosheets can form chemical bonding with photocatalyst particles to avoid their agglomeration during the photocatalytic reaction. It is well-known that the availability of charge carriers has a decisive role in photocatalytic activity. Therefore, any method which can improve the utilization of photogenerated carriers and lengthen the lifetime of charge carriers is desired [70].

As one of the most attractive visible light-response photocatalysts, CdS is prone to photocorrosion and aggregation during the photoreactions [71]. Zhang et al. [72] synthesized CdS/graphene composites by evenly spreading CdS nanoparticles on 2D graphene nanosheets. The introduction of graphene is helpful for increasing the light absorption intensity. However, excessive graphene (more than 5% of weight ratio) obscures the light illumination reaching the surface of the CdS nanoparticles and leads to a decrease of photocatalytic activity. An appropriate amount of graphene promotes not only the transfer of electrons but also the capacity of visible light absorption. In addition, the introduction of graphene could have influence on the crystallinity and the specific surface areas of CdS nanoparticles. However, graphene is not easy to be dispersed in water, which makes it difficult to contact semiconductor nanoparticles with graphene in aqueous solution. GO with hydrophilic oxygen-containing groups is easy to be dispersed in aqueous solution, so GO is usually used as a graphene precursor [73–75]. Zhu et al. [76] employed GO and TiCl₃ as starting materials and synthesized graphene/TiO₂ composites. TiO₂ with a size of about 7 nm fully cover both surfaces of the graphene nanosheets. The growth of TiO₂ on the surface of GO plays an important role in enhancing photocurrent response [77] and, thus, improving the photocatalytic ability. Li and coworkers [78] synthesized CdS cluster-decorated graphene nanosheets via a solvothermal method (Figure 7). In this system, GO and cadmium acetate (Cd(Ac)₂) were used as the graphene precursor
and CdS precursor, respectively. The composites with 1.0 wt% of graphene and 0.5 wt% of Pt exhibit the highest H₂-production rate of 1.12 mmol·h⁻¹. This value of H₂-production rate is much higher than other reports about CdS/graphene composite photocatalysts (as shown in Table 1), which may be due to the presence of 0.5 wt% of Pt in this photocatalytic reaction system. This means that for reaching the highest photocatalytic performance, graphene still cannot completely replace the noble metal co-catalyst.

**Figure 7.** (A) Schematic illustration of the generation, transfer, and reaction of electrons in the 2D graphene/0D CdS composites under visible light irradiation; and (B) photocatalytic activity of graphene/CdS composite photocatalysts with different content of graphene. Reaction conditions: 20 mg of photocatalyst, 10 vol % lactic acid aqueous solution as a sacrificial reagent and 0.5 wt% Pt as a co-catalyst; a Xe lamp with a UV-cutoff filter (λ ≥ 420 nm) as the light source. Reprinted with permission from [78]. Copyright 2011, American Chemical Society.

Recently, it has been demonstrated that doping graphene with hetero atoms can effectively modulate the electronic and catalytic properties of graphene. Jia et al. [79] synthesized N-doped graphene/CdS nanoparticles by annealing graphene in NH₃ gas and combining it with CdS nanoparticles. When N-graphene is ca. 2 wt%, the N-graphene/CdS composites display enhanced photocatalytic ability and stability for H₂ evolution from water splitting under visible light irradiation, which is higher than that of the physical mixture of N-graphene and CdS, as well as undoped-graphene/CdS composites. These results strongly suggest the crucial role of the intimate contact between 2D N-graphene nanosheets and 0D CdS nanoparticles in transferring of photogenerated carriers [80]. Mou et al. [81] also reported that N-doped graphene/TiO₂ exhibit a higher photocatalytic activity. The enhanced photocatalytic activity of N-doped graphene based photocatalysts is attributed to the higher electrical conductivity of N-doped graphene because, after nitrogen doping, the free carrier density of graphene is improved [82]. Xu’s group [83] further studied the synergistic effect of graphitic N and pyrrolic N in N-doped graphene/TiO₂ nanocomposites. It was suggested that the doped graphitic-N functions as an electron-transfer mediator for the photo-generated electrons while the doped pyrrolic-N serves as the oxygen-reduction active site to promote the following interfacial catalytic reaction. From the above research, N-doped graphene has been proved to be effective to enhance photocatalytic performance.

Graphene-based binary nanocomposite photocatalysts show that graphene coupled to another single component can improve the photocatalytic ability. In addition to binary nanocomposites, hybrid nanomaterials with multicomponents are expected to provide enhanced photocatalytic performance as well as multifunctional properties for photocatalysts. Some groups synthesized graphene-based ternary system to improve the photocatalytic performance further [84–88]. MoS₂ is often used as co-catalyst in photocatalytic reactions [89,90]. Xiang et al. [88] synthesized TiO₂/MoS₂/graphene composites by preparing the layered MoS₂ and graphene hybrid firstly. The layered MoS₂/graphene
co-catalysts function not only as active adsorption sites but also as photocatalytic reaction centers which are important for H₂ evolution. Zhang and coworkers [91] prepared the ternary CdS-graphene-TiO₂ hybrid photocatalysts. In the ternary system, the CdS nanoparticles evenly disperse on the surface of graphene nanosheets and the TiO₂ nanoparticles decorate the CdS-graphene base uniformly. Compared with matrix binary CdS-graphene, the ternary CdS-graphene-TiO₂ hybrid exhibit higher photocatalytic activity.

4.2. 2D/1D

1D photocatalysts with high aspect ratios have attracted attention [92,93]. Compared with 0D structures, 1D structures have fast and long-distance electron-transport capability, high surface area, and pore volume [94–96]. When 1D semiconductor photocatalysts are combined with graphene nanosheets, a line-to-line interface will form, which is the key factor for electron transfer.

CdS nanowires/RGO nanosheets 1D/2D nanocomposites were designed and synthesized by Liu [97]. Their photocatalytic performance was characterized by selectively reducing nitro-containing compounds in an aqueous phase. Compared with CdS nanowires, the CdS-nanowires/RGO nanocomposites exhibit significantly enhanced photocatalytic activity. Yu and coworkers [98] synthesized CdS nanorods/RGO nanocomposites. CdS nanorods evenly spread on the surface of RGO nanosheets. RGO plays as an ideal platform for the nucleation and growth of CdS nanorods and has no obvious influence on the morphology of the CdS nanorods [99,100]. For photocatalytic reduction of CO₂ to CH₄, RGO/CdS nanocomposite photocatalysts with an optimal RGO content of 0.5 wt% exhibit the highest CH₄-production rate of 2.51 mmol h⁻¹ g⁻¹, 10 times more than pure CdS nanorods, and even better than Pt-CdS composites. Shen et al. [101] chose ZnₓCd₁₋ₓS (ZCS) as main photocatalysts, whose band gap can be adjusted by changing the Cd/Zn ratio, and synthesized ZnₓCd₁₋ₓS ultrathin nanorods/RGO sheets 1D/2D nanocomposites (ZCS/RGO). The presence of RGO can avoid the agglomeration of ZnₓCd₁₋ₓS ultrathin nanorods and simultaneously improve the conductivity of photocatalysts. The strong contact line-to-line interface, as shown in Figure 8, is beneficial for fast collection and transfer of electrons thus enhances the photocatalytic performance and stability of ultrathin nanorod photocatalysts (Figure 8).

Figure 8. (A) TEM image of 1D ZCS/2D RGO nanocomposites; and (B) the cycling stability of ZCS and ZCS/RGO for photocatalytic H₂ evolution from water splitting. Reaction conditions: 40 mg of photocatalysts, 0.02 M Na₂SO₃/0.1 M Na₂S as sacrificial reagent with Xe lamp with a UV-cutoff filter (λ ≥ 420 nm) as light source. Reprinted with permission from [101]. Copyright 2015, Wiley-VCH.

Liu et al. [102] synthesized GO/TiO₂ 2D/1D composites with a configuration of TiO₂ nanorods with 2–3 nm diameter and 20–30 nm length on the whole large GO sheets. It was found that when using the composites as photocatalysts for the degradation of MB, the degradation rate in the second cycle is faster than that in the first cycle because GO in the composites is reduced to

4.3. 2D/2D

A larger intimate interface can provide higher photocatalytic activity because of the more effectively transfer of photoinduced electrons, and lower electrons and holes recombination rate. In view of graphene's two-dimensional structure, an ideal interface formed with photocatalysts should be face-to-face interface (Figure 1). However, in most cases, the structures of photocatalysts are 0D nanoparticles or 1D nanorods. To completely utilize 2D nature of graphene, a more efficient face-to-face contact between 2D photocatalysts and graphene nanosheets is highly desirable.

Nitrogenous compounds have been studied as photocatalysts for a few decades, such as Ta$_3$N$_5$ [104], GaN [105,106], and graphitic carbon nitride (g-C$_3$N$_4$/g-CN) [107,108]. g-C$_3$N$_4$ has attracted dramatically increasing interest for its unique properties of Earth-abundant elements (C and N) and suitable band gap (2.7 eV) [109–112]. g-C$_3$N$_4$ is generally synthesized by nitrogen-rich precursors such as dicyandiamide, urea, melamine, and so forth [113,114], so g-C$_3$N$_4$ is nontoxic and cheap. However, its drawback, the low charge carrier mobility, inhibits the separation of electrons and holes and restricts its photocatalytic applications [115,116]. Considering the unique properties of graphene, researchers attempted to combine those two materials [117–119] in pursuit of superior photocatalytic performance.

Xiang et al. [119] reported the fabrication of graphene/g-C$_3$N$_4$ composites by a combined impregnation-chemical reduction strategy with melamine and GO as precursors. During the reaction, GO is reduced to graphene and melamine is decomposed to g-C$_3$N$_4$. GO sheets contained versatile oxygen-containing groups [85], pre-absorb melamine molecules and, thus, possess a compact structure with g-C$_3$N$_4$ sandwiched between graphene sheets. Graphene sheets act as a conductive path for efficiently transferring photogenerated electrons. The H$_2$ production rate of the graphene/g-C$_3$N$_4$ composite is 451 µmol·h$^{-1}$·g$^{-1}$, 3.07 times more than pure g-C$_3$N$_4$. Toing’s group [120] employed a photocatalytic reduction method to produce RGO/g-C$_3$N$_4$ photocatalysts and evaluated its photocatalytic performance by degradation of phenol under visible light irradiation. They suggested that due to the presence of an aromatic network in both g-C$_3$N$_4$ and RGO, the RGO can interact with g-C$_3$N$_4$ via π-π stacking, which can promote the electron-hole separation and improve the interfacial charge transfer. Although g-C$_3$N$_4$, with the band gap of 2.7 eV, can be excited by visible light, the utilization of solar energy is still very low. Using RGO to narrow the photocatalyst band gap to achieve higher photocatalytic activities under visible light has been demonstrated by a number of groups [121]. Li et al. [122] synthesized cross-linked g-C$_3$N$_4$/RGO (CN/RGO) nanocomposites with a tunable band structure (Figure 9). They demonstrated that the band gap of g-C$_3$N$_4$/RGO composites can be readily controlled by changing the weight ratio of cyanamide to GO in precursor materials. A suitable RGO ratio can narrow the band gap, shift the valence band edge positively, and enhance electronic conductivity.

It has attracted intensive attention that combining with RGO can narrow the band gap of g-C$_3$N$_4$/RGO composites and enhance the photocatalytic performance [119,122]. Most explanations attribute those phenomena to the interactions between graphene and g-C$_3$N$_4$. However, why do the interactions between constituents bring those results? Which atom plays the key role during the photocatalytic processes? The theoretical understanding is lacking until Xu and coworkers reported their opinions [118]. Xu et al. demonstrated that the O atom plays a crucial role in the RGO-based composites. They believed that the interfacial interaction at the g-C$_3$N$_4$/RGO interface mainly depend on the density of O atom. Thus, it can be said that the narrowing of the band gap is dependent on the concentration of O atom. They also found the negatively-charged O atom in the RGO can act as
active sites during photocatalytic activities. Since the O atom plays the key role in the photocatalytic system can GO, with versatile oxygen-containing groups on the basal planes and the edges [123], bring comparable or even greater photocatalytic performance than graphene? Dai et al. [124] fabricated g-C3N4/GO composites by anchoring g-C3N4 nanosheets on GO sheets. Different from g-C3N4/RGO composites, g-C3N4/GO composites display the same absorption edge with pure g-C3N4, but it extends broader background absorption in the visible light region. GO is not only a simple matrix for dispersion, but it also acts as an electron acceptor and enhances light absorption. During the degradation test, the composites exhibit enhanced photocatalytic performance under visible light irradiation 27.4 times higher than P25 photocatalyst and 3.7 times higher than pure g-C3N4 powder. Compared with these systems which required complicated processes, Yu [117] employed a one-step calcination method and synthesized GO-modified porous g-C3N4 (porous g-C3N4/GO). Due to the porous structure and heterojunction formed between g-C3N4 and GO, the photocatalytic performance of porous g-C3N4/GO for MB degradation is six times higher than that of pure g-C3N4.

![Figure 9](image_url)

**Figure 9.** (A) Schematic illustration of the reaction process and the formation of 2D CN/2D RGO nanocomposites; (B) photocatalytic activities of the g-C3N4 and 2D CN/2D RGO photocatalysis system; and (C) recycle test of 2D CN/2D RGO nanocomposites for the degradation of RhB. Reprinted with permission from [122]. Copyright 2013, Wiley-VCH.

To date, research on changing the morphology of TiO2 to get the more intimate connection between TiO2 and graphene has been confirmed to be effective for enhancing the transfer of photogenerated electrons. Xiang et al. [125] synthesized graphene-modified titania nanosheets by a microwave-hydrothermal method. GO is reduced to RGO and TiO2 nanosheets with exposed (001) facets formed on the surface of RGO sheets with face-to-face orientation. The TiO2/RGO composites with an optimal graphene content of 1.0 wt% demonstrate a more than 41 times enhancement of H2 production activity compared with pure TiO2.
As a typical 2D metal sulfide photocatalyst, molybdenum disulfide (MoS$_2$) with a layered structure has been studied extensively [126,127]. Hou et al. [128] presented the fabrication of 2D porous g-C$_3$N$_4$ nanosheets/nitrogen-doped graphene/layered MoS$_2$ (CNNS/NRGO/MoS$_2$) ternary nanocomposites. They pointed out that the layered structure of MoS$_2$ can shorten the charge transport distance and time by promoting charge separation and transfer at CNNS/MoS$_2$ interfaces (sheet to sheet); the porous structure of g-C$_3$N$_4$ can provide a large surface area, thus, increasing the efficient light absorption; the nitrogen doping can enhance the electrical conductivity of graphene, thus, enhancing the transfer of photogenerated electrons and promote the separation of electrons and holes. The photocatalytic activities of this hybridization were evaluated by oxidation of MB and reduction of Cr (VI). The prolonged lifetime of photogenerated carriers, the extended absorption edge and the higher photocurrent density are all attributed to the unique ternary nanostructure.

**Table 1.** Representative summary of photocatalysts composed of nanocarbon co-catalysts and semiconductor photocatalysts with different dimensions.

<table>
<thead>
<tr>
<th>Dimension of Nanocarbons/Photocatalyst</th>
<th>Nanocarbon Co-Catalysts</th>
<th>Semiconductor Photocatalysts</th>
<th>Content of Co-Catalysts (wt%)</th>
<th>Evaluation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D/0D</td>
<td>C$_{60}$</td>
<td>TiO$_2$</td>
<td>-</td>
<td>Degrade of MB</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$</td>
<td>ZnO</td>
<td>1.5%</td>
<td>Degrade of MB</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$</td>
<td>Cr$<em>{1.3}$Fe$</em>{0.3}$O$_3$</td>
<td>3%</td>
<td>H$_2$ evolution rate of 220.5 µmol·h$^{-1}$·g$^{-1}$ (Xe lamp, λ ≥ 420 nm, 10 vol% triethanolamine as sacrificial reagent)</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>C$_{70}$</td>
<td>TiO$_2$</td>
<td>18%</td>
<td>Degrade of sulfathiazole</td>
<td>[38]</td>
</tr>
<tr>
<td>0D/1D</td>
<td>C$_{60}$</td>
<td>TiO$_2$ nanorods</td>
<td>0.5%</td>
<td>Degrade of RhB</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$</td>
<td>TiO$_2$ nanotubes</td>
<td>5%</td>
<td>Degrade of organic molecule</td>
<td>[40]</td>
</tr>
<tr>
<td>0D/2D</td>
<td>C$_{60}$</td>
<td>Bi$_2$TiO$_4$F$_2$</td>
<td>1%</td>
<td>Degrade of RhB and EY</td>
<td>[41]</td>
</tr>
<tr>
<td>1D/0D</td>
<td>MWCNTs</td>
<td>CdS</td>
<td>10%</td>
<td>H$_2$ evolution rate of 174.2 µmol·h$^{-1}$, (Xe lamp, λ ≥ 420 nm, 0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$ as sacrificial reagent)</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>CNT</td>
<td>ZnO</td>
<td>60%</td>
<td>Degrade of methyl red</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>TiO$_2$</td>
<td>-</td>
<td>Reduction of CO$_2$</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>CNT</td>
<td>Mo+TiO$_2$</td>
<td>-</td>
<td>Degrade of MB</td>
<td>[59]</td>
</tr>
<tr>
<td>1D/1D</td>
<td>MWCNTs</td>
<td>TiO$_2$ nanotubes</td>
<td>10%</td>
<td>Degrade of RhB-6G dye</td>
<td>[61]</td>
</tr>
<tr>
<td>1D/2D</td>
<td>CNFs</td>
<td>ZnIn$_2$S$_4$ nanosheets</td>
<td>15%</td>
<td>H$_2$ evolution rate of 95 µmol·h$^{-1}$, (Xe lamp, λ ≥ 420 nm, 0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$ as sacrificial reagent)</td>
<td>[62]</td>
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<tr>
<td></td>
<td>Graphene</td>
<td>CdS</td>
<td>5%</td>
<td>Selective oxidation of alcohols</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>RGO</td>
<td>CdS</td>
<td>5%</td>
<td>Reduction of aromatic nitro organics</td>
<td>[71]</td>
</tr>
<tr>
<td>2D/0D</td>
<td>GO</td>
<td>CdS</td>
<td>5%</td>
<td>H$_2$ evolution rate of 314 µmol·h$^{-1}$, (Xe lamp, λ ≥ 420 nm, 0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$ as sacrificial reagent)</td>
<td>[75]</td>
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<tr>
<td></td>
<td>Graphene</td>
<td>CdS cluster</td>
<td>1%</td>
<td>H$_2$ evolution rate of 1.12 mmol·h$^{-1}$, (Xe lamp, λ ≥ 420 nm, 10 vol % lactic acid as sacrificial reagent and 0.5 wt% Pt as a cocatalyst)</td>
<td>[78]</td>
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Table 1. Cont.

<table>
<thead>
<tr>
<th>Dimension of Nanocarbons/Photocatalyst</th>
<th>Nanocarbon Co-Catalysts</th>
<th>Semiconductor Photocatalysts</th>
<th>Content of Co-Catalysts (wt%)</th>
<th>Evaluation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D/0D</td>
<td>N-doped G</td>
<td>CdS</td>
<td>2%</td>
<td>H₂ evolution rate of 210 µmol·h⁻¹. (Xe lamp, λ &gt; 420 nm, 0.1 Na₂S and 0.1 M Na₂SO₃ as sacrificial reagent)</td>
<td>[79]</td>
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<tr>
<td></td>
<td>Graphene</td>
<td>TiO₂</td>
<td>-</td>
<td>Photocurrent response.</td>
<td>[76]</td>
</tr>
<tr>
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<td>Graphene</td>
<td>TiO₂</td>
<td>5%</td>
<td>H₂ evolution rate of 8.6 µmol·h⁻¹. (Xe lamp, UV-vis light, 0.1 Na₂S and 0.04 M Na₂SO₃ as sacrificial reagent)</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Graphene</td>
<td>TiO₂</td>
<td>5%</td>
<td>Selective transformation of alcohols to aldehydes</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>N-doped G</td>
<td>TiO₂</td>
<td>5%</td>
<td>Degrade of MO and Phenol aqueous</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td>Graphene</td>
<td>MoS₂+TiO₂</td>
<td>5%</td>
<td>H₂ evolution rate of 165.3 µmol·h⁻¹. (Xe lamp, 25 vol % ethanol as sacrificial reagent)</td>
<td>[88]</td>
</tr>
<tr>
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<td>Graphene</td>
<td>MCM41+TiO₂</td>
<td>0.15%</td>
<td>Degrade of 2-propanol</td>
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<tr>
<td></td>
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<td>CdS+TiO₂</td>
<td>5%</td>
<td>Selective oxidation of benzylic and allylic alcohols</td>
<td>[91]</td>
</tr>
<tr>
<td>2D/1D</td>
<td>RGO</td>
<td>CdS nanowires</td>
<td>5%</td>
<td>Selective reduction of nitro organics</td>
<td>[97]</td>
</tr>
<tr>
<td></td>
<td>RGO</td>
<td>CdS nanorods</td>
<td>0.5%</td>
<td>Reduction of CO₂</td>
<td>[98]</td>
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<td>RGO</td>
<td>Zn₀.₅Cd₀.₅S ultrathin nanorods</td>
<td>2%</td>
<td>H₂ evolution rate of 30.8 µmol·h⁻¹. (Xe lamp, λ &gt; 420 nm, 0.1 Na₂S and 0.02 M Na₂SO₃ as sacrificial reagent)</td>
<td>[101]</td>
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<tr>
<td></td>
<td>GO</td>
<td>TiO₂ nanorods</td>
<td>-</td>
<td>Degrade of MB</td>
<td>[102]</td>
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<tr>
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<td>RGO</td>
<td>V-doped TiO₂ nanorods</td>
<td>10%</td>
<td>H₂ evolution rate (Xe lamp, AM 1.5 Global, 20 vol % methanol as sacrificial reagent)</td>
<td>[94]</td>
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<tr>
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<td>N-doped G</td>
<td>N-doped TiO₂ nanowires</td>
<td>7%</td>
<td>Degrade of MB</td>
<td>[103]</td>
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<td>2D/2D</td>
<td>RGO</td>
<td>g-C₃N₄</td>
<td>0.1%</td>
<td>Degrade of phenol</td>
<td>[120]</td>
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<td>RGO</td>
<td>g-C₃N₄</td>
<td>2.5%</td>
<td>Degrade of RhB and 4-nitrophenol</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>GO</td>
<td>g-C₃N₄</td>
<td>5%</td>
<td>Degrade of MB</td>
<td>[124]</td>
</tr>
<tr>
<td></td>
<td>GO</td>
<td>g-C₃N₄</td>
<td>-</td>
<td>Degrade of MB</td>
<td>[117]</td>
</tr>
<tr>
<td></td>
<td>graphene</td>
<td>TiO₂</td>
<td>1%</td>
<td>H₂ evolution rate of 36.8 µmol·h⁻¹. (Xe lamp, 20 mW·cm⁻², 25 vol % methanol as sacrificial reagent)</td>
<td>[125]</td>
</tr>
<tr>
<td></td>
<td>N-doped graphene</td>
<td>MoS₂+g-C₃N₄</td>
<td>-</td>
<td>Degrade of MB and reduction of Cr(VI)</td>
<td>[128]</td>
</tr>
</tbody>
</table>

5. Summary and Outlook

For enhancing the absorption capacity of visible light and the separation of photogenerated electrons and holes, co-catalysts are often considered in designing photocatalysts. Nanocarbon materials with low dimension and specific morphology, such as 0D fullerene and nano-onions, 1D nanofibers and nanotubes, and 2D graphene, possess unique physical and chemical properties, including high electrical conductivity, high surface area, and chemical stability. Thus, nanocarbon materials can be employed as excellent noble-metal free co-catalysts for semiconductor photocatalysts. Different dimensional nanocarbon co-catalysts can form different dimensional interface with different dimensional semiconductor photocatalysts including point-to-point, line-to-line, and face-to-face modes. The effective separation of electrons and holes pairs, prolonged photogenerated charge lifetime and shorten transfer channels which are beneficial to photocatalysis are bought by the junction between nanocarbon materials and photocatalysts. To maximize the photocatalytic performance,
reasonably designing the structure of nanocarbons/semiconductor nanocomposite photocatalysts is crucial. Diverse types of composite photocatalysts composed of different dimensional nanocarbons and main photocatalysts have been researched (as shown in Table 1) such as 0D nanocarbons with different dimensional main photocatalysts (0D/0D, 0D/1D, and 0D/2D), 1D nanocarbons with different dimensional main photocatalysts (1D/0D, 1D/1D, and 1D/2D), and 2D nanocarbons with different dimensional main photocatalysts (2D/0D, 2D/1D, and 2D/2D). Diverse synthesis approaches and techniques have been developed including directly decomposition of precursors, chemical deposition, microwave technique, hydrothermal/solvothermal techniques, and sol-gel processing. The obtained nanocomposites exhibited higher photocatalytic performance than main photocatalysts components due to the synergetic effects between nanocarbon co-catalysts and main photocatalysts. Heteroatom doping or multi-components photocatalysts were also adopted to further promote the separation of photogenerated electrons and holes.

Without any doubt, these nanocarbon materials with different dimensions and specific properties are promising co-catalysts for semiconductor photocatalysts. So far, the strategies for the synthesis of nanocarbon/main photocatalyst composites are still being explored and some intrinsic mechanisms are not fully understood. Therefore, more general synthesis method and advanced measurement approaches are needed for both scientific research and applications. It is still a long journey to develop general and simple synthetic strategies and understand the basic fundamental formation mechanisms, as well as the practical applications of nanocarbon-based photocatalysts.

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Conflicts of Interest: The authors declare no conflict of interest.

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