



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 TiO₂ 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 CO₂-water solution into CH₃OH. 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 RuO₂, 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

TiO₂, 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/TiO₂ 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/TiO₂ 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 TiO₂, 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 $Cr_{2-x}Fe_xO_3$ 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 (Eg = 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 H₂ 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 TiO₂ (C_{70} -TiO₂) 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 TiO₂ nanoparticles not only generate point-to-point interfaces between the functionalized C_{70} and TiO₂, but also slightly reduce the crystallite size of TiO₂, as well as extend absorption edge of TiO₂ to the visible light region. The photocatalytic degradation rate of sulfathiazole by using C_{70} -TiO₂ hybrid as photocatalysts is 1.6 times higher than that of C_{60} -TiO₂ hybrid due to the larger photo cross-sectional area, larger delocalization effect, and higher electron affinity of C_{70} (Figure 2).



Figure 2. SEM (**A**) and TEM (**B**) images of $0D C_{70}/0D \text{ TiO}_2$ nanocomposites; and (**C**) photocatalytic performance of the as-prepared nanocomposites for degrading sulfathiazole. Reprinted with permission from [38]. Copyright 2015, Royal Society of Chemistry.

2.2. 0D/1D

Long et al. [39] synthesized C_{60} nanoparticles incorporated TiO₂ nanorods. The photocatalytic activity of C_{60} /TiO₂ nanorods is about 3.3 times higher than that of TiO₂ nanorods. The high specific surface area plays an important role and the electronic interactions between C_{60} and TiO₂ enhance the absorption of visible light (Figure 3). Grandcolas et al. [40] reported that after the hybridization with C_{60} , the absorption capacity in the visible light region and photocatalytic activity of titania nanotubes (TiNTs) are all enhanced. It was found that C_{60} distributes both inside and outside of TiNTs. Photoinduced electrons are delivered from the 1D main photocatalyst to 0D C_{60} nanoparticles through the point-to-point interface, inhibiting the electron-hole recombination.



Figure 3. TEM (**A**) and HRTEM (**B**) images of 0D $C_{60}/1D$ TiO₂ nanorods heterostructures; and (**C**) kinetics of the RhB degradation under visible irradiation with different catalyst. Without any catalyst (**I**), in the presence of P25 (**A**), TiO₂ nanorods (**•**), and 0D $C_{60}/1D$ TiO₂ composites (**V**) in ambient atmosphere, and 0D $C_{60}/1D$ TiO₂ composites in N₂ atmosphere (**♦**). Reprinted with permission from [39]. Copyright 2009, American Chemical Society.

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_{60} uniformly. Li and coworkers [41] synthesized fullerene C_{60} -enhanced Bi₂TiO₄F₂ hierarchical microspheres and employed the obtained photocatalysts to degrade Rhodamine B (RhB) and Eosin Y (EY) under visible light irradiation. $C_{60}/Bi_2TiO_4F_2$ not only has higher photocatalytic activity than pure $Bi_2TiO_4F_2$, but also shows improved stability (Figure 4). The photocatalytic activity of $C_{60}/Bi_2TiO_4F_2$ is also higher than that of a physical mixture of C_{60} and $Bi_2TiO_4F_2$, further confirming the strong interaction between C_{60} and $Bi_2TiO_4F_2$.



Figure 4. (A) Schematic illustration of photogenerated electron-hole separation mechanism in 0D $C_{60}/2D$ Bi₂TiO₄F₂ heterostructure; and (B) photocatalytic performance of $C_{60}/Bi_2TiO_4F_2$ 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 agglomerate are universal [35], which induce poor interfacial contact between nanocarbon particles and main photocatalysts.

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 photocatalyts [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/TiO₂ composites and employed them to reduce CO₂ with H₂O. 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 TiO₂. 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 TiO₂/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 TiO₂, 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, TiO₂ 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 ($\lambda \ge 420$ nm) and full spectrum of the Xe lamp. Reaction conditions: 35 mg of photocatalyst, 0.35 M Na₂S and 0.25 M Na₂SO₃ 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@ZnIn₂S₄ composites by controlling the in situ growth of ZnIn₂S₄ nanosheets on carbon nanofibers (CNFs). This preparation process not only ensures the uniform growth of nanosheets, but also avoids the agglomeration of ZnIn₂S₄. It is believed that the stacking force between ZnIn₂S₄ nuclei and nanofibers promotes the in situ formation of ZnIn₂S₄ (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 ($\lambda \ge 420$ 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/ TiO_2 composites. TiO_2 with a size of about 7 nm fully cover both surfaces of the graphene nanosheets. The growth of TiO_2 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 ($\lambda \ge 420$ 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 nanocomposites 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 H_2 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 \cdot h⁻¹ \cdot g⁻¹, 10 times more than pure CdS nanorods, and even better than Pt-CdS composites. Shen et al. [101] chose $Zn_xCd_{1-x}S$ (ZCS) as main photocatalysts, whose band gap can be adjusted by changing the Cd/Zn ratio, and synthesized Zn_xCd_{1-x}S ultrathin nanorods/RGO sheets 1D/2D nanocomposites (ZCS/RGO). The presence of RGO can avoid the agglomeration of $Zn_xCd_{1-x}S$ 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 ($\lambda \ge 420$ 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

RGO. Liu and coworkers [103] fabricated N-doped TiO₂ nanowires/N-doped graphene (N-TiO₂/NG) nanocomposites. N-TiO₂/NG nanocomposites exhibit higher photocatalytic performance than TiO₂ nanowire/graphene composites and N-doped TiO₂ nanowire/graphene composites for degradation of MB under visible light irradiation. N-doped graphene restrains the recombination of photogenerated holes and electrons and N doping extends the absorpton spectrum of TiO₂ to the visible light region.

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 Ta₃N₅ [104], GaN [105,106], and graphitic carbon nitride (g-C₃N₄/g-CN) [107,108]. g-C₃N₄ 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-C₃N₄ is generally synthesized by nitrogen-rich precursors such as dicyandiamide, urea, melamine, and so forth [113,114], so g-C₃N₄ 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_3N_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-C₃N₄. GO sheets contained versatile oxygen-containing groups [85], pre-absorb melamine molecules and, thus, possess a compact structure with $g-C_3N_4$ 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_3N_4 composite is 451 μ mol·h⁻¹·g⁻¹, 3.07 times more than pure g-C₃N₄. Toing's group [120] employed a photocatalytic reduction method to produce RGO/g-C3N4 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 $g-C_3N_4$ and RGO, the RGO can interact with g-C₃N₄ via π - π stacking, which can promote the electron-hole separation and improve the interfacial charge transfer. Although g- C_3N_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 $g-C_3N_4/RGO$ (CN/RGO) nanocomposites with a tunable band structure (Figure 9). They demonstrated that the band gap of $g-C_3N_4/RGO$ 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 $g-C_3N_4/RGO$ composites and enhance the photocatalytic performance [119,122]. Most explanations attribute those phenomena to the interactions between graphene and $g-C_3N_4$. 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 $g-C_3N_4/RGO$ 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 $g-C_3N_4/GO$ composites by anchoring $g-C_3N_4$ nanosheets on GO sheets. Different from $g-C_3N_4/RGO$ composites, $g-C_3N_4/GO$ composites display the same absorption edge with pure $g-C_3N_4$, 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 $g-C_3N_4$ powder. Compared with these systems which required complicated processes, Yu [117] employed a one-step calcination method and synthesized GO-modified porous $g-C_3N_4$ (porous $g-C_3N_4/GO$). Due to the porous structure and heterojunction formed between $g-C_3N_4$ and GO, the photocatalytic performance of porous $g-C_3N_4/GO$ for MB degradation is six times higher than that of pure $g-C_3N_4$.



Figure 9. (A) Schematic illustration of the reaction process and the formation of 2D CN/2D RGO nanocomposites; (B) photocatalytic activities of the $g-C_3N_4$ 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 TiO_2 to get the more intimate connection between TiO_2 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 TiO_2 nanosheets with exposed (001) facets formed on the surface of RGO sheets with face-to-face orientation. The TiO_2/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 TiO_2 . 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-C₃N₄ nanosheets/nitrogen-doped graphene/layered MoS₂ (CNNS/NRGO/MoS₂) ternary nanocomposites. They pointed out that the layered structure of MoS₂ can shorten the charge transport distance and time by promoting charge separation and transfer at CNNS/MoS₂ interfaces (sheet to sheet); the porous structure of g-C₃N₄ 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.

Dimension of Nanocarbons/ Photocatalyst	Nanocarbon Co-Catalysts	Semiconductor Photocatalysts	Content of Co-Catalysts (wt%)	Evaluation	Reference
0D/0D	C ₆₀	TiO ₂	-	Degrade of MB	[31]
	C ₆₀	ZnO	1.5%	Degrade of MB	[35]
	C ₆₀	Cr _{1.3} Fe _{0.3} O ₃	3%	H ₂ evolution rate of 220.5 µmol· h ⁻¹ · g ⁻¹ (Xe lamp, $\lambda \ge 420$ nm, 10 vol% triethanolamine as sacrificial reagent)	[36]
	C ₇₀	TiO ₂	18%	Degrade of sulfathiazole	[38]
0D/1D	C ₆₀	TiO ₂ nanorods	0.5%	Degrade of RhB	[39]
	C ₆₀	TiO ₂ nanotubes	5%	Degrade of organic molecule	[40]
0D/2D	C ₆₀	Bi2TiO4F2	1%	Degrade of RhB and EY	[41]
1D/0D	MWCNTs	CdS	10%	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)	[51]
	CNT	ZnO	60%	Degrade of methyl red	[52]
	MWCNTs	TiO ₂	-	Reduction of CO ₂	[53]
	CNT	Mo+TiO ₂	-	Degrade of MB	[59]
1D/1D	MWCNTs	TiO ₂ nanotubes	10%	Degrade of RhB-6G dye	[<mark>61</mark>]
1D/2D	CNFs	ZnIn ₂ S ₄ nanosheets	15%	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)	[62]
2D/0D	Graphene	CdS	5%	Selective oxidation of alcohols	[72]
	RGO	CdS	5%	Reduction of aromatic nitro organics	[71]
	GO	CdS	5%	H ₂ evolution rate of 314 μ mol· h ⁻¹ . (Xe lamp, $\lambda \ge 420$ nm, 0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃ as sacrificial reagent)	[75]
	Graphene	CdS cluster	1%	H ₂ evolution rate of 1.12 mmol· h ⁻¹ . (Xe lamp, $\lambda \ge 420$ nm, 10 vol % lactic acid as sacrificial reagent and 0.5 wt% Pt as a cocatalyst)	[78]

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

Dimension of Nanocarbons/ Photocatalyst	Nanocarbon Co-Catalysts	Semiconductor Photocatalysts	Content of Co-Catalysts (wt%)	Evaluation	Reference
2D/0D	N-doped G	CdS	2%	H ₂ evolution rate of 210 μ mol·h ⁻¹ . (Xe lamp, $\lambda \ge 420$ nm, 0.1 Na ₂ S and 0.1 M Na ₂ SO ₃ as sacrificial reagent)	[79]
	Graphene	TiO ₂	-	Photocurrent response.	[76]
	Graphene	TiO ₂	5%	H_2 evolution rate of 8.6 µmol·h ⁻¹ . (Xe lamp, UV-vis light, 0.1 Na ₂ S and 0.04 M Na ₂ SO ₃ as sacrificial reagent)	[74]
	Graphene	TiO ₂	5%	Selective transformation of alcohols to aldehydes	[73]
	N-doped G	TiO ₂	5%	Degrade of MO and Phenol aqueous	[83]
	Graphene	MoS ₂ +TiO ₂	5%	H_2 evolution rate of 165.3 µmol· h ⁻¹ . (Xe lamp, 25 vol % ethanol as sacrificial reagent)	[88]
	Graphene	MCM41+TiO ₂	0.15%	Degrade of 2-propanol	[87]
	Graphene	CdS+TiO ₂	5%	Selective oxidation of benzylic alcohols and allylic alcohols	[91]
2D/1D	RGO	CdS nanowires	5%	Selective reduction of nitro organics	[97]
	RGO	CdS nanorods	0.5%	Reduction of CO ₂	[98]
	RGO	Zn _{0.5} Cd _{0.5} S ultrathin nanorods	2%	H ₂ evolution rate of 30.8 μ mol· h ⁻¹ . (Xe lamp, $\lambda \ge 420$ nm, 0.1 Na ₂ S and 0.02 M Na ₂ SO ₃ as sacrificial reagent)	[101]
	GO	TiO ₂ nanorods	-	Degrade of MB	[102]
	RGO	V-doped TiO ₂ nanorods	10%	H ₂ evolution rate (Xe lamp, AM 1.5 Global, 20 vol % methanol as sacrificial reagent)	[94]
	N-dopedG	N-doped TiO ₂ nanowires	7%	Degrade of MB	[103]
2D/2D	RGO	g-C ₃ N ₄	0.1%	Degrade of phenol	[120]
	RGO	g-C ₃ N ₄	2.5%	Degrade of RhB and 4-nitrophenol	[122]
	GO	g-C ₃ N ₄	5%	Degrade of MB	[124]
	GO	g-C ₃ N ₄	-	Degrade of MB	[117]
	graphene	TiO ₂	1%	H_2 evolution rate of 36.8 µmol· h ⁻¹ . (Xe lamp, 20 mW· cm ⁻² , 25 vol % methanol as sacrificial reagent)	[125]
	N-doped graphene	$MoS_2+g-C_3N_4$	-	Degrade of MB and reduction of Cr(VI)	[128]

Table 1. Cont.

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 photocatalystic performance than 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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References

- Fujishima, A. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972, 238, 37–38. [CrossRef] [PubMed]
- 2. Halmann, M. Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells. *Nature* **1978**, 275, 115–116. [CrossRef]
- 3. Ma, G.; Hisatomi, T.; Domen, K. Semiconductors for photocatalytic and photoelectrochemical solar water splitting. *Chem. Soc. Rev.* 2014, *43*, 7520–7535.
- Li, C.; Yuan, J.; Han, B.; Jiang, L.; Shangguan, W. TiO₂ nanotubes incorporated with CdS for photocatalytic hydrogen production from splitting water under visible light irradiation. *Int. J. Hydrog. Energy* 2010, 35, 7073–7079. [CrossRef]
- 5. Zhuang, Z.; Peng, Q.; Li, Y. Controlled synthesis of semiconductor nanostructures in the liquid phase. *Chem. Soc. Rev.* **2011**, 40, 5492–5513. [CrossRef] [PubMed]
- Zhao, L.; Geng, F.; Di, F.; Guo, L.H.; Wan, B.; Yang, Y.; Zhang, H.; Sun, G. Polyamine-functionalized carbon nanodots: a novel chemiluminescence probe for selective detection of iron(iii) ions. *RSC Adv.* 2014, 4, 45768–45771. [CrossRef]
- Preethi, V.; Kanmani, S. Photocatalytic hydrogen production using Fe₂O₃-based core shell nano particles with ZnS and CdS. *Int. J. Hydrog. Energy* 2014, *39*, 1613–1622. [CrossRef]
- 8. Xiang, Q.; Yu, J.; Jaroniec, M. Graphene-based semiconductor photocatalysts. *Chem Soc. Rev.* 2012, 41, 782–796. [CrossRef] [PubMed]
- 9. Kołacz, K.; Gajewska, M.; Komornicki, S.; Radecka, M. The effect of GO deposition on the photoelectrochemical properties of TiO₂ nanotubes. *Int. J. Hydrog. Energy* **2016**, *41*, 7538–7547. [CrossRef]
- Su, J.; Zhu, L.; Chen, G. Ultrasmall graphitic carbon nitride quantum dots decorated self-organized TiO₂ nanotube arrays with highly efficient photoelectrochemical activity. *Appl. Catal. Environ.* 2016, 186, 127–135. [CrossRef]

- Zeng, R.; Sun, Z.; Cao, S.; Shen, R.; Liu, Z.; Xiong, Y.; Long, J.; Zheng, J.; Zhao, Y.; Shen, Y.; Wang, D. Facile synthesis of Ag-doped ZnCdS nanocrystals and transformation into Ag-doped ZnCdSSe nanocrystals with Se treatment. *RSC Adv.* 2015, *5*, 1083–1090. [CrossRef]
- 12. Liu, R.; Wang, P.; Wang, X.; Yu, H.; Yu, J. UV- and Visible-Light Photocatalytic Activity of Simultaneously Deposited and Doped Ag/Ag(I)-TiO₂ Photocatalyst. *J. Phys. Chem.* **2012**, *116*, 17721–17728.
- 13. Moniz, S.J.; Shevlin, S.A.; Martin, D.J.; Guo, Z.X.; Tang, J. Visible-light driven heterojunction photocatalysts for water splitting-a critical review. *Energy Env. Sci.* **2015**, *8*, 731–759. [CrossRef]
- Aazam, E.S. Photocatalytic oxidation of cyanide under visible light by Pt doped AgInS₂ nanoparticles. *J. Ind. Eng. Chem.* 2014, 20, 4008–4013. [CrossRef]
- 15. Ampelli, C.; Perathoner, S.; Centi, G. Carbon-based catalysts: opening new scenario to develop next-generation nano-engineered catalytic materials. *Chin. J. Catal.* **2014**, *35*, 783–791. [CrossRef]
- Zhang, F.; Li, C. Semiconductor-Based Photocatalytic Water Splitting. In *Solar to Chemical Energy Conversion*; Masakazu, S., Katsushi, F., Shinichiro, N., Eds.; Springer International Publishing: Cham, Switzerland, 2016; pp. 299–317.
- 17. Tan, L.L.; Chai, S.P.; Mohamed, A.R. Synthesis and applications of graphene-based TiO₂ photocatalysts. *ChemSusChem.* **2012**, *5*, 1868–1882. [CrossRef] [PubMed]
- Stankovich, S.; Dikin, D.A.; Dommett, G.H.; Kohlhaas, K.M.; Zimney, E.J.; Stach, E.A.; Piner, R.D.; Nguyen, S.T.; Ruoff, R.S. Graphene-based composite materials. *Nature* 2006, 442, 282–286. [CrossRef] [PubMed]
- Haddon, R. Chemistry of the fullerenes: The manifestation of strain in a class of continuous aromatic molecules. *Science* 1993, 261, 1545–1550. [CrossRef] [PubMed]
- 20. Meng, Z.D.; Zhu, L.; Choi, J.G.; Chen, M.L.; Oh, W.C. Effect of Pt treated fullerene/TiO₂ on the photocatalytic degradation of MO under visible light. *J. Mater. Chem.* **2011**, *21*, 7596. [CrossRef]
- 21. Virovska, D.; Paneva, D.; Manolova, N.; Rashkov, I.; Karashanova, D. Photocatalytic self-cleaning poly (L-lactide) materials based on a hybrid between nanosized zinc oxide and expanded graphite or fullerene. *Mater. Sci. Eng. C* 2016, *60*, 184–194. [CrossRef] [PubMed]
- Wakimoto, R.; Kitamura, T.; Ito, F.; Usami, H.; Moriwaki, H. Decomposition of methyl orange using C₆₀ fullerene adsorbed on silica gel as a photocatalyst via visible-light induced electron transfer. *Appl. Catal. Environ.* 2015, 166, 544–550. [CrossRef]
- 23. Cho, E.C.; Ciou, J.H.; Zheng, J.H.; Pan, J.; Hsiao, Y.S.; Lee, K.C.; Huang, J.H. Fullerene C₇₀ decorated TiO₂ nanowires for visible-light-responsive photocatalyst. *Appl. Surf. Sci.* **2015**, *355*, 536–546. [CrossRef]
- 24. Kim, K.H.; Ko, J.W.; Ko, W.B. Preparation and kinetics of nanocomposites using WO₃ with carbon nanomaterials for photocatalytic degradation of organic dyes. *Asian J. Chem.* **2016**, *28*, 194. [CrossRef]
- 25. Qi, K.; Selvaraj, R.; Al Fahdi, T.; Al-Kindy, S.; Kim, Y.; Wang, G.C.; Tai, C.W.; Sillanpää, M. Enhanced photocatalytic activity of anatase-TiO₂ nanoparticles by fullerene modification: A theoretical and experimental study. *Appl. Surf. Sci.* **2016**, *22*, 1498–1504.
- 26. Zhang, X.; Wang, Q.; Zou, L.H.; You, J.-W. Facile fabrication of titanium dioxide/fullerene nanocomposite and its enhanced visible photocatalytic activity. *J. Colloid Interface Sci.* **2016**, *466*, 56–61. [CrossRef] [PubMed]
- Liu, E.; Kang, L.; Yang, Y.; Sun, T.; Hu, X.; Zhu, C.; Liu, H.; Wang, Q.; Li, X.; Fan, J. Plasmonic Ag deposited TiO₂ nano-sheet film for enhanced photocatalytic hydrogen production by water splitting. *Nanotechnology* 2014, 25, 165401. [CrossRef] [PubMed]
- Li, L.; Yan, J.; Wang, T.; Zhao, Z.J.; Zhang, J.; Gong, J.; Guan, N. Sub-10 nm rutile titanium dioxide nanoparticles for efficient visible-light-driven photocatalytic hydrogen production. *Nat. Commun.* 2015, 6, 5881. [CrossRef] [PubMed]
- Wang, C.C.; Hsueh, Y.C.; Su, C.Y.; Kei, C.C.; Perng, T.P. Deposition of uniform Pt nanoparticles with controllable size on TiO₂-based nanowires by atomic layer deposition and their photocatalytic properties. *Nanotechnology* 2015, 26, 254002. [CrossRef] [PubMed]
- Wang, S.; Pan, L.; Song, J.J.; Mi, W.; Zou, J.J.; Wang, L.; Zhang, X. Titanium-defected undoped anatase TiO₂ with p-type conductivity, room-temperature ferromagnetism, and remarkable photocatalytic performance. J. Am. Chem. Soc. 2015, 137, 2975–2983. [CrossRef] [PubMed]
- 31. Oh, W.C.; Jung, A.R.; Ko, W.-B. Preparation of fullerene/TiO₂ composite and its photocatalytic effect. *J. Ind. Eng. Chem.* **2007**, *13*, 1208–1214.

- 32. Huang, X.; Li, Z.; Wang, S.; Chi, D.; Chua, S.J. Solution-grown ZnO films towards transparent and smart dual-color light-emitting diode. *ACS Appl. Mater. Interfaces* **2016**, *8*, 15482–15488. [CrossRef] [PubMed]
- 33. Qi, J.; Zhang, H.; Lu, S.; Li, X.; Xu, M.; Zhang, Y. High performance indium-doped ZnO gas sensor. J. Nanomater. 2015, 2015, 74. [CrossRef]
- 34. Ghosh, M.; Ghosh, S.; Seibt, M.; Rao, K.Y.; Peretzki, P.; Rao, G.M. Ferroelectric origin in one-dimensional undoped ZnO towards high electromechanical response. *Crystengcomm* **2015**, *18*, 622–630. [CrossRef]
- 35. Fu, H.; Xu, T.; Zhu, S.; Zhu, Y. Photocorrosion Inhibition and Enhancement of Photocatalytic Activity for ZnO via Hybridization with C₆₀. *Environ. Sci. Technol.* **2008**, *42*, 8064–8069. [CrossRef]
- 36. Song, T.; Huo, J.; Liao, T.; Zeng, J.; Qin, J.; Zeng, H. Fullerene [C₆₀] modified Cr_{2-x}Fe_xO₃ nanocomposites for enhanced photocatalytic activity under visible light irradiation. *Chem. Eng. J.* **2016**, *287*, 359–366. [CrossRef]
- 37. Scuseria, G.E. The equilibrium structure of C₇₀. An ab initio Hartree-Fock study. *Chem. Phys. Lett.* **1991**, *180*, 451–456. [CrossRef]
- 38. Wang, S.; Liu, C.; Dai, K.; Cai, P.; Chen, H.; Yang, C.; Huang, Q. Fullerene C₇₀-TiO₂ hybrids with enhanced photocatalytic activity under visible light irradiation. *J. Mater. Chem. A* **2015**, *3*, 21090–21098. [CrossRef]
- Long, Y.; Lu, Y.; Huang, Y.; Peng, Y.; Lu, Y.; Kang, S.Z.; Mu, J. Effect of C₆₀ on the photocatalytic activity of TiO₂ nanorods. *J. Phys. Chem. C* 2009, 113, 13899–13905. [CrossRef]
- 40. Grandcolas, M.; Ye, J.; Miyazawa, K. Titania nanotubes and fullerenes C₆₀ assemblies and their photocatalytic activity under visible light. *Ceram. Int.* **2014**, *40*, 1297–1302. [CrossRef]
- 41. Li, G.; Jiang, B.; Li, X.; Lian, Z.; Xiao, S.; Zhu, J.; Zhang, D.; Li, H. C₆₀/Bi₂TiO₄F₂ heterojunction photocatalysts with enhanced visible-light activity for environmental remediation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7190–7197. [CrossRef] [PubMed]
- 42. Han, M.; Zhao, Q.; Zhu, Z.; Hu, Y.; Tao, Z.; Chen, J. The enhanced hydrogen storage of micro-nanostructured hybrids of Mg(BH₄)2-carbon nanotubes. *Nanoscale* **2015**, *7*, 18305–18311. [CrossRef] [PubMed]
- Fu, L.; Lai, G.; Zhang, H.; Yu, A. One-pot synthesis of multipod ZnO-carbon nanotube-reduced graphene oxide composites with high performance in photocatalysis. *J. Nanosci. Nanotechnol.* 2015, 15, 4325–4331. [CrossRef] [PubMed]
- 44. Zhang, F.; Xie, F.; Xu, H.; Liu, J.; Oh, W.C. Characterization of Pd/TiO₂ embedded in multi-walled carbon nanotube catalyst with a high photocatalytic activity. *Kinet. Catal.* **2013**, *54*, 297–306. [CrossRef]
- 45. Koziol, K.; Vilatela, J.; Moisala, A.; Motta, M.; Cunniff, P.; Sennett, M.; Alan, W. High-performance carbon nanotube fiber. *Science* 2007, *318*, 1892–1895. [CrossRef] [PubMed]
- 46. Wang, S.G.; Zhang, Q.; Yang, D.J.; Sellin, P.J.; Zhong, G.F. Multi-walled carbon nanotube-based gas sensors for NH₃ detection. *Diamond Related Mater.* **2004**, *13*, 1327–1332. [CrossRef]
- 47. Filleter, T.; Espinosa, H.D. Multi-scale mechanical improvement produced in carbon nanotube fibers by irradiation cross-linking. *Carbon* **2013**, *56*, 1–11. [CrossRef]
- 48. Zhang, L.L.; Zhao, X. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* 2009, *38*, 2520–2531. [CrossRef] [PubMed]
- Chen, P.; Wang, L.; Wang, P.; Kostka, A.; Wark, M.; Muhler, M.; Beranek, R. CNT-TiO₂-δ composites for improved co-catalyst dispersion and stabilized photocatalytic hydrogen production. *Catalysts* 2015, *5*, 270–285. [CrossRef]
- 50. Woan, K.; Pyrgiotakis, G.; Sigmund, W. Photocatalytic carbon-nanotube-TiO₂ composites. *Adv. Mater.* **2009**, *21*, 2233–2239. [CrossRef]
- 51. Peng, T.; Zeng, P.; Ke, D.; Liu, X.; Zhang, X. Hydrothermal preparation of multiwalled carbon nanotubes (MWCNTs)/CdS nanocomposite and its efficient photocatalytic hydrogen production under visible light irradiation. *Energy Fuels* **2011**, *25*, 2203–2210. [CrossRef]
- 52. Wang, X.; Yao, S.; Li, X. Sol-gel Preparation of CNT/ZnO nanocomposite and its photocatalytic property. *Chin. J. Chem.* **2009**, *27*, 1317–1320. [CrossRef]
- 53. Xia, X.H.; Jia, Z.J.; Yu, Y.; Liang, Y.; Wang, Z.; Ma, L.L. Preparation of multi-walled carbon nanotube supported TiO₂ and its photocatalytic activity in the reduction of CO₂ with H₂O. *Carbon* **2007**, *45*, 717–721. [CrossRef]
- Tanaka, A.; Sakaguchi, S.; Hashimoto, K.; Kominami, H. Preparation of Au/TiO₂ with Metal Cocatalysts Exhibiting Strong Surface Plasmon Resonance Effective for Photoinduced Hydrogen Formation under Irradiation of Visible Light. ACS Catal. 2013, 3, 79–85. [CrossRef]

- 55. Seery, M.K.; George, R.; Floris, P.; Pillai, S.C. Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis. *J. Photochem. Photobiol. Chem.* **2007**, *189*, 258–263. [CrossRef]
- Wang, X.; Ling, D.; Wang, Y.; Long, H.; Sun, Y.; Shi, Y.; Chen, Y.; Jing, Y.; Sun, Y.; Dai, Y. N-doped graphene quantum dots-functionalized titanium dioxide nanofibers and their highly efficient photocurrent response. *J. Mater. Res.* 2014, 29, 1408–1416. [CrossRef]
- Yu, K.; Song, M.; Gao, X.; Hou, C.; Liang, J. Preparation and Photocatalytic Property of Nickel-Doped Titanium Dioxide Nanotubes. *Synth. React. Inorg. Metal.-Org. Nano-Metal. Chem.* 2014, 45, 1576–1579. [CrossRef]
- 58. Venditti, F.; Cuomo, F.; Ceglie, A.; Avino, P.; Russo, M.V.; Lopez, F. Visible light caffeic acid degradation by carbon-doped titanium dioxide. *Langmuir* **2015**, *31*, 3627–3634. [CrossRef] [PubMed]
- 59. Zhang, F.J.; Oh, W.C. Visible light photocatalytic properties of novel molybdenum treated carbon nanotube/titania composites. *Bull. Mater. Sci.* 2011, *34*, 543–549. [CrossRef]
- 60. Liu, B.; Xu, Y.; Cui, J.; Wang, S.; Wang, T. Carbon nanotubes-dispersed TiO₂, nanoparticles with their enhanced photocatalytic activity. *Mater. Res. Bull.* **2014**, *59*, 278–282. [CrossRef]
- 61. Natarajan, T.S.; Lee, J.Y.; Bajaj, H.C.; Jo, W.K.; Tayade, R.J. Synthesis of multiwall carbon nanotubes/TiO₂ nanotube composites with enhanced photocatalytic decomposition efficiency. *Catal. Today* **2016**. [CrossRef]
- Chen, Y.; Tian, G.; Ren, Z.; Pan, K.; Shi, Y.; Wang, J.; Fu, H. Hierarchical core-shell carbon nanofiber@ZnIn₂S₄ composites for enhanced hydrogen evolution performance. *ACS Appl. Mater. Interfaces* 2014, *6*, 13841–13849. [CrossRef] [PubMed]
- Bonaccorso, F.; Colombo, L.; Yu, G.; Stoller, M.; Tozzini, V.; Ferrari, A.C.; Ruoff, R.S.; Pellegrini, V. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* 2015, 347, 1246501. [CrossRef] [PubMed]
- 64. Perreault, F.; de Faria, A.F.; Elimelech, M. Environmental applications of graphene-based nanomaterials. *Chem. Soc. Rev.* **2015**, *44*, 5861–5896. [CrossRef] [PubMed]
- 65. Xiang, Q.; Lang, D.; Shen, T.; Liu, F. Graphene-modified nanosized Ag₃PO₄ photocatalysts for enhanced visible-light photocatalytic activity and stability. *Appl. Catal. B Environ.* **2015**, *162*, 196–203. [CrossRef]
- 66. Liu, J.; Xue, Y.; Zhang, M.; Dai, L. Graphene-based materials for energy applications. *MRS Bull.* **2012**, *37*, 1265–1272. [CrossRef]
- 67. Huang, X.; Qi, X.; Boey, F.; Zhang, H. Graphene-based composites. *Chem. Soc. Rev.* 2012, 41, 666–686. [CrossRef] [PubMed]
- 68. An, X.; Yu, J.C. Graphene-based photocatalytic composites. RSC Adv. 2011, 1, 1426. [CrossRef]
- 69. Iwashina, K.; Iwase, A.; Ng, Y.H.; Amal, R.; Kudo, A. Z-schematic water splitting into H₂ and O₂ using metal sulfide as a hydrogen-evolving photocatalyst and reduced graphene oxide as a solid-state electron mediator. *J. Am. Chem. Soc.* **2015**, *137*, 604–607. [CrossRef] [PubMed]
- 70. Zhang, G.; Li, G.; Wang, X. Surface Modification of Carbon Nitride Polymers by Core-Shell Nickel/Nickel Oxide Cocatalysts for Hydrogen Evolution Photocatalysis. *ChemCatChem* **2015**, *7*, 2864–2870. [CrossRef]
- 71. Chen, Z.; Liu, S.; Yang, M.Q.; Xu, Y.J. Synthesis of uniform CdS nanospheres/graphene hybrid nanocomposites and their application as visible light photocatalyst for selective reduction of nitro organics in water. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4309–4319. [CrossRef] [PubMed]
- 72. Zhang, N.; Zhang, Y.; Pan, X.; Fu, X.; Liu, S.; Xu, Y.J. Assembly of CdS nanoparticles on the two-dimensional graphene scaffold as visible-light-driven photocatalyst for selective organic transformation under ambient conditions. *J. Phys. Chem. C* 2011, *115*, 23501–23511. [CrossRef]
- 73. Zhang, Y.; Zhang, N.; Tang, Z.R.; Xu, Y.J. Improving the photocatalytic performance of graphene-TiO₂ nanocomposites via a combined strategy of decreasing defects of graphene and increasing interfacial contact. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9167–9175. [CrossRef] [PubMed]
- Zhang, X.Y.; Li, H.P.; Cui, X.L.; Lin, Y. Graphene/TiO₂ nanocomposites: Synthesis, characterization and application in hydrogen evolution from water photocatalytic splitting. *J. Mater. Chem.* 2010, 20, 2801. [CrossRef]
- 75. Peng, T.; Li, K.; Zeng, P.; Zhang, Q.; Zhang, X. Enhanced photocatalytic hydrogen production over graphene oxide–cadmium sulfide nanocomposite under visible light irradiation. *J. Phys. Chem. C* **2012**, *116*, 22720–22726. [CrossRef]
- 76. Zhu, C.; Guo, S.; Wang, P.; Xing, L.; Fang, Y.; Zhai, Y.; Dong, S. One-pot, water-phase approach to high-quality graphene/TiO₂ composite nanosheets. *Chem. Commun.* **2010**, *46*, 7148–7150. [CrossRef] [PubMed]

- 77. Guo, C.X.; Yang, H.B.; Sheng, Z.M.; Lu, Z.S.; Song, Q.L.; Li, C.M. Layered graphene/quantum dots for photovoltaic devices. *Angew. Chem. Int. Ed.* 2010, *49*, 3014–3017. [CrossRef] [PubMed]
- Li, Q.; Guo, B.; Yu, J.; Ran, J.; Zhang, B.; Yan, H.; Gong, J.R. Highly efficient visible-light-driven photocatalytic hydrogen production of CdS-cluster-decorated graphene nanosheets. *J. Am. Chem. Soc.* 2011, 133, 10878–10884. [CrossRef] [PubMed]
- Jia, L.; Wang, D.H.; Huang, Y.X.; Xu, A.W.; Yu, H.Q. Highly durable N-doped graphene/CdS nanocomposites with enhanced photocatalytic hydrogen evolution from water under visible light irradiation. *J. Phys. Chem. C* 2011, 115, 11466–11473. [CrossRef]
- Soin, N.; Sinha Roy, S.; Roy, S.; Hazra, K.S.; Misra, D.S.; Lim, T.H.; Hetherington, C.J.; McLaughlin, J.A. Enhanced and stable field emission from in situ nitrogen-doped few-layered graphene nanoflakes. *J. Phys. Chem. C* 2011, 115, 5366–5372. [CrossRef]
- Mou, Z.; Wu, Y.; Sun, J.; Yang, P.; Du, Y.; Lu, C. TiO₂ nanoparticles-functionalized N-doped graphene with superior interfacial contact and enhanced charge separation for photocatalytic hydrogen generation. *ACS Appl. Mater. Interfaces* 2014, *6*, 13798–13806. [CrossRef] [PubMed]
- 82. Wu, M.; Cao, C.; Jiang, J.Z. Light non-metallic atom (B, N, O and F)-doped graphene: A first-principles study. *Nanotechnology* **2010**, *21*, 505202. [CrossRef] [PubMed]
- Xu, Y.; Mo, Y.; Tian, J.; Wang, P.; Yu, H.; Yu, J. The synergistic effect of graphitic N and pyrrolic N for the enhanced photocatalytic performance of nitrogen-doped graphene/TiO₂ nanocomposites. *Appl. Catal. B Environ.* 2016, *181*, 810–817. [CrossRef]
- 84. Yan, J.; Ye, Q.; Wang, X.; Yu, B.; Zhou, F. CdS/CdSe quantum dot co-sensitized graphene nanocomposites via polymer brush templated synthesis for potential photovoltaic applications. *Nanoscale* **2012**, *4*, 2109–2116. [CrossRef] [PubMed]
- 85. Park, W.I.; Lee, C.H.; Lee, J.M.; Kim, N.-J.; Yi, G.-C. Inorganic nanostructures grown on graphene layers. *Nanoscale* **2011**, *3*, 3522–3533. [CrossRef] [PubMed]
- Manga, K.K.; Wang, J.; Lin, M.; Zhang, J.; Nesladek, M.; Nalla, V.; Ji, W.; Loh, K.P. High-performance broadband photodetector using solution-processible PbSe-TiO₂-graphene hybrids. *Adv. Mater.* 2012, 24, 1697–1702. [CrossRef] [PubMed]
- 87. Kamegawa, T.; Yamahana, D.; Yamashita, H. Graphene coating of TiO₂ nanoparticles loaded on mesoporous silica for enhancement of photocatalytic activity. *J. Phys. Chem. C* **2010**, *114*, 15049–15053. [CrossRef]
- Xiang, Q.; Yu, J.; Jaroniec, M. Synergetic effect of MoS₂ and graphene as cocatalysts for enhanced photocatalytic H₂ production activity of TiO₂ nanoparticles. *J. Am. Chem. Soc.* 2012, 134, 6575–6578. [CrossRef] [PubMed]
- Bai, S.; Wang, L.; Chen, X.; Du, J.; Xiong, Y. Chemically exfoliated metallic MoS₂ nanosheets: A promising supporting co-catalyst for enhancing the photocatalytic performance of TiO₂ nanocrystals. *Nano Res.* 2015, *8*, 175–183. [CrossRef]
- Lang, D.; Shen, T.; Xiang, Q. Roles of MoS₂ and graphene as cocatalysts in the enhanced visible-light photocatalytic H₂ production activity of multiarmed CdS nanorods. *ChemCatChem* 2015, 7, 943–951. [CrossRef]
- Zhang, N.; Zhang, Y.; Pan, X.; Yang, M.Q.; Xu, Y.J. Constructing ternary CdS-graphene-TiO₂ hybrids on the flatland of graphene oxide with enhanced visible-light photoactivity for selective transformation. *J. Phys. Chem. C* 2012, *116*, 18023–18031. [CrossRef]
- Xiao, F.X.; Liu, B. 1D TiO₂, Nanotube-Based Photocatalysts. Heterogeneous Photocatalysis. In *Heterogeneous PhotoCatal*; Colmenares, J.C., Xu, Y.J., Eds.; Springer: Berlin, Germany; Heidelberg, Germany, 2016; pp. 151–173.
- 93. Tien, H.N.; Hur, S.H. Fabrication of 3D structured ZnO nanorod/reduced graphene oxide hydrogels and their use for photo-enhanced organic dye removal. *J. Colloid Interface Sci.* **2015**, 437, 181–186.
- 94. Agegnehu, A.K.; Pan, C.-J.; Tsai, M.-C.; Rick, J.; Su, W.-N.; Lee, J.-F.; Hwang, B.J. Visible light responsive noble metal-free nanocomposite of V-doped TiO₂ nanorod with highly reduced graphene oxide for enhanced solar H₂ production. *Int. J. Hydrog. Energy* **2016**, *41*, 6752–6762. [CrossRef]
- Utterback, J.K.; Wilker, M.B.; Brown, K.A.; King, P.W.; Eaves, J.D.; Dukovic, G. Competition between electron transfer, trapping, and recombination in CdS nanorod-hydrogenase complexes. *Phys. Chem. Chem. Phys.* 2015, 17, 5538–5542. [CrossRef] [PubMed]

- 96. Zhang, J.; Wang, L.; Liu, X.; Li, X.A.; Huang, W. High-performance CdS-ZnS core-shell nanorod array photoelectrode for photoelectrochemical hydrogen generation. *J. Mater. Chem. A* **2015**, *3*, 535–541. [CrossRef]
- Liu, S.; Chen, Z.; Zhang, N.; Tang, Z.-R.; Xu, Y.J. An efficient self-assembly of CdS nanowires-reduced graphene oxide nanocomposites for selective reduction of nitro organics under visible light irradiation. *J. Phys. Chem. C* 2013, *117*, 8251–8261. [CrossRef]
- Yu, J.; Jin, J.; Cheng, B.; Jaroniec, M. A noble metal-free reduced graphene oxide-CdS nanorod composite for the enhanced visible-light photocatalytic reduction of CO₂ to solar fuel. *J. Mater. Chem. A* 2014, 2, 3407. [CrossRef]
- 99. Zhang, K.; Liu, X. One step synthesis and characterization of CdS nanorod/graphene nanosheet composite. *Appl. Surf. Sci.* **2011**, 257, 10379–10383. [CrossRef]
- 100. Cao, M.; Wang, P.; Ao, Y.; Wang, C.; Hou, J.; Qian, J. Investigation on graphene and Pt co-modified CdS nanowires with enhanced photocatalytic hydrogen evolution activity under visible light irradiation. *Dalton Trans.* 2015, 44, 1507–1508. [CrossRef] [PubMed]
- 101. Shen, S.; Ma, A.; Tang, Z.; Han, Z.; Wang, M.; Wang, Z.; Zhi, L.; Yang, J. Facile synthesis of Zn_{0.5}Cd_{0.5}S ultrathin nanorods on reduced graphene oxide for enhanced photocatalytic hydrogen evolution under visible light. *ChemCatChem* 2015, 7, 609–615. [CrossRef]
- Liu, J.; Bai, H.; Wang, Y.; Liu, Z.; Zhang, X.; Sun, D.D. Self-assembling TiO₂, nanorods on large graphene oxide sheets at a two-phase interface and their anti-recombination in photocatalytic applications. *Adv. Funct. Mater.* 2010, 20, 4175–4181. [CrossRef]
- 103. Liu, C.; Zhang, L.; Liu, R.; Gao, Z.; Yang, X.; Tu, Z.; Yang, F.; Ye, Z.; Cui, L.; Xu, C.; Li, Y. Hydrothermal synthesis of N-doped TiO₂ nanowires and N-doped graphene heterostructures with enhanced photocatalytic properties. *J. Alloys Compd.* **2016**, 656, 24–32. [CrossRef]
- 104. Nurlaela, E.; Ouldchikh, S.; Llorens, I.; Hazemann, J.L.; Takanabe, K. Establishing efficient cobalt-based catalytic sites for oxygen evolution on a Ta₃N₅ photocatalyst. *Chem. Mater.* **2015**, *27*, 5685–5694. [CrossRef]
- 105. Akimov, A.V.; Muckerman, J.T.; Prezhdo, O.V. Nonadiabatic dynamics of positive charge during photocatalytic water splitting on GaN (10-10) surface: charge localization governs splitting efficiency. J. Am. Chem. Soc. 2013, 135, 8682–8691. [CrossRef] [PubMed]
- 106. Maeda, K.; Teramura, K.; Saito, N.; Inoue, Y.; Domen, K. Photocatalytic overall water splitting on gallium nitride powder. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1004–1010. [CrossRef]
- 107. Zhang, H.; Zhao, L.; Geng, F.; Guo, L.H.; Wan, B.; Yang, Y. Carbon dots decorated graphitic carbon nitride as an efficient metal-free photocatalyst for phenol degradation. *Appl. Catal. B Environ.* 2016, 180, 656–662. [CrossRef]
- 108. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J.M.; Domen, K.; Antonietti, M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* 2009, *8*, 76–80. [CrossRef] [PubMed]
- 109. Dong, G.; Zhao, K.; Zhang, L. Carbon self-doping induced high electronic conductivity and photoreactivity of g-C₃N₄. *Chem. Commun.* **2012**, *48*, 6178–6180. [CrossRef] [PubMed]
- Cao, S.; Low, J.; Yu, J.; Jaroniec, M. Polymeric photocatalysts based on graphitic carbon nitride. *Adv. Mater.* 2015, 27, 2150–2176. [CrossRef] [PubMed]
- Liu, Y.; Zhou, F.; Zhan, S.; Yang, Y.; Yin, Y. Significantly enhanced performance of g-C₃N₄/Bi₂MoO₆ films for photocatalytic degradation of pollutants under visible-light irradiation. *Chem. Res. Chin. Univ.* 2016, 32, 284–290. [CrossRef]
- 112. Chen, Y.; Wang, B.; Lin, S.; Zhang, Y.; Wang, X. Activation of n→π* transitions in two-dimensional conjugated polymers for visible light photocatalysis. *J. Phys. Chem. C* **2014**, *118*, 29981–29989. [CrossRef]
- Akhundi, A.; Habibi-Yangjeh, A. A simple large-scale method for preparation of g-C₃N₄/SnO₂ nanocomposite as visible-light-driven photocatalyst for degradation of an organic pollutant. *Mater. Express* 2015, *5*, 309–318. [CrossRef]
- 114. Chai, B.; Wang, X. Sonochemical Synthesis of CdS/C₃N₄ Composites with Efficient Photocatalytic Performance Under Visible Light Irradiat. *J. Nanosci. Nanotechnol.* **2016**, *16*, 2032–2041. [CrossRef] [PubMed]
- 115. Chen, D.; Wang, Z.; Yue, D.; Yang, G.; Ren, T.; Ding, H. Synthesis and Visible Photodegradation Enhancement of CdS/mpg-C₃N₄ Photocatalyst. *J. Nanosci. Nanotechnol.* **2016**, *16*, 471–479. [CrossRef] [PubMed]

- Vo, V.; Van Kim, N.; Nga, N.T. V.; Trung, N.T.; Van Hanh, P.; Hoang, L.H.; Kim, S.-J. Preparation of g-C₃N₄/Ta₂O₅ Composites with Enhanced Visible-Light Photocatalytic Activity. *J. Electron. Mater.* 2016, 45, 2334–2340. [CrossRef]
- 117. Yu, Q.; Guo, S.; Li, X.; Zhang, M. One-step fabrication and high photocatalytic activity of porous graphitic carbon nitride/graphene oxide hybrid by direct polymerization of cyanamide without templates. *Russ. J. Phys. Chem. A* 2014, *88*, 1643–1649. [CrossRef]
- 118. Xu, L.; Huang, W.Q.; Wang, L.L.; Tian, Z.A.; Hu, W.; Ma, Y.; Wang, X.; Pan, A.; Huang, G.-F. Insights into Enhanced Visible-Light Photocatalytic Hydrogen Evolution of g-C₃N₄ and Highly Reduced Graphene Oxide Composite: The Role of Oxygen. *Chem. Mater.* **2015**, *27*, 1612–1621. [CrossRef]
- 119. Xiang, Q.; Yu, J.; Jaroniec, M. Preparation and Enhanced Visible-Light Photocatalytic H₂-Production Activity of Graphene/C₃N₄ Composites. *J. Phys. Chem. C* **2011**, *115*, 7355–7363. [CrossRef]
- 120. Tiong, P.; Lintang, H.O.; Endud, S.; Yuliati, L. Improved interfacial charge transfer and visible light activity of reduced graphene oxide–graphitic carbon nitride photocatalysts. *RSC Adv.* **2015**, *5*, 94029–94039. [CrossRef]
- 121. Lee, J.S.; You, K.H.; Park, C.B. Highly photoactive, low bandgap TiO₂ nanoparticles wrapped by graphene. *Adv. Mater.* **2012**, *24*, 1084–1088. [CrossRef] [PubMed]
- 122. Li, Y.; Zhang, H.; Liu, P.; Wang, D.; Li, Y.; Zhao, H. Cross-linked g-C₃N₄/rGO nanocomposites with tunable band structure and enhanced visible light photocatalytic activity. *Small* **2013**, *9*, 3336–3344. [CrossRef] [PubMed]
- Park, S.; Ruoff, R.S. Chemical methods for the production of graphenes. *Nat. Nanotechnol.* 2009, *4*, 217–224.
 [CrossRef] [PubMed]
- 124. Dai, K.; Lu, L.; Liu, Q.; Zhu, G.; Wei, X.; Bai, J.; Xuan, L.; Wang, H. Sonication assisted preparation of graphene oxide/graphitic-C₃N₄ nanosheet hybrid with reinforced photocurrent for photocatalyst applications. *Dalton Trans.* **2014**, *43*, 6295–6299. [CrossRef] [PubMed]
- 125. Xiang, Q.; Yu, J.; Jaroniec, M. Enhanced photocatalytic H₂-production activity of graphene-modified titania nanosheets. *Nanoscale* **2011**, *3*, 3670–3678. [CrossRef] [PubMed]
- 126. Ding, S.S.; Huang, W.Q.; Yang, Y.C.; Zhou, B.X.; Hu, W.Y.; Long, M.Q.; Peng, P.; Huang, G.-F. Dual role of monolayer MoS₂ in enhanced photocatalytic performance of hybrid MoS₂/SnO₂ nanocomposite. *J. Appl. Phys.* **2016**, *119*, 205704. [CrossRef]
- 127. Weng, B.; Zhang, X.; Zhang, N.; Tang, Z.R.; Xu, Y.J. Two-dimensional MoS₂ nanosheet-coated Bi₂S₃ discoids: synthesis, formation mechanism, and photocatalytic application. *Langmuir* 2015, *31*, 4314–4322. [CrossRef] [PubMed]
- 128. Hou, Y.; Wen, Z.; Cui, S.; Guo, X.; Chen, J. Constructing 2D porous graphitic C₃N₄ nanosheets /nitrogen-doped graphene/layered MoS₂ ternary nanojunction with enhanced photoelectrochemical activity. *Adv. Mater.* 2013, 25, 6291–6297. [CrossRef] [PubMed]



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