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Journal Name

ARTICLE

Photocatalytic conversion of CO₂ over graphene-based composites: current status and future perspective

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The continuous rise in atmospheric CO₂ level and ever-increasing demand of energy have raised serious concerns about the ensuing effects on the global climate change and future energy supply. Photocatalytic conversion of CO₂, which uses solar light energy to recycle CO₂ into fuels and chemicals, provides a promising and straightforward strategy to simultaneously reduce the atmospheric CO₂ level and fulfill the future energy demand. However, the lack of substantial development of state-of-the-art materials remains a major bottleneck of this technology. In recent years, graphene-based composite photocatalysts have gained increasing interests in CO₂ conversion due to the introduction of graphene with a series of unique physicochemical properties, which has shown significant role for promoting the photocatalytic solar energy conversion efficiency. In this review, we comprehensively summarize the typical literature reports of graphene-based composites for photocatalytic conversion of CO₂ to produce solar fuels and chemicals. The main types of the reported graphene-based composites and the effect of graphene in the composites for improving the photocatalytic performance have been elaborated. In particular, we have highlighted the possible role of graphene in tuning the product selectivity of photocatalytic reduction of CO₂. Finally, perspectives on the existing problems and future research of graphene-based composites toward photocatalytic conversion of CO₂ are critically discussed.

1. Introduction

The rapid development of human society since the Industrial Revolution has resulted in a dramatically raise of global demand for energy, which has increased from the average energy consumption rate of 2.8 terawatt (TW) in 1950 to 15 TW in 2010, and is projected to increase to 25-27 TW by 2050. a,b Fossil fuels, as the most important global energy source with the advantages such as being freely provided by nature, high energy content, and ease of transportation and storage, have accounted for the largest proportion, more than 80 percent, of the energy supply of current world. a,b,c The heavy reliance on fossil fuels for the production of energy leads to an explosive growth of CO₂ emission into the atmosphere, which has disturbed the balance of natural cycle of CO₂ emission and uptake (fixation by terrestrial plants and microorganisms, plus underground inorganication), d and caused a severe global climate change, e,f resulting in a devastating impact on the living environment of humans. Additionally, the fast increase in combustion of fossil fuels also leads to an excessive exploitation and sharp depletion of the finite global fossil fuel reserves, causing serious energy shortage crisis throughout the world since the late 1970s. g The ever-increasing environmental issue and lack of natural energy resources have raised serious concerns about the ensuing effects on the global energy security, environmental security, and economic security etc. h Alleviating the environmental burden and seeking alternative sustainable energy supply have become the most urgent tasks of human society.

Fig. 1 Schematic diagram of a natural photosynthetic system, with four areas of artificial photocatalysis research highlighted in red and described in green text. The artificial photocatalytic systems are designed to perform similar functions to the different components of natural photosystems, which typically focuses on one or two of these topics at a time to reduce complexity. The goal of photocatalytic reduction of CO₂ is to mimic the natural photosynthetic system for generation of renewable fuels and chemicals such as CO₂, formic acid, methanol and methane from CO₂, H₂O, and sunlight. Reprinted with permission from ref 4. Copyright 2010 American Chemical Society. i

In this context, semiconductor photocatalysis, a wellorchestrated mimic of natural photosynthesis (Fig. 1) reported from 1960s j for direct converting solar energy to
chemical energy, is likely to kill these two birds with one stone. In particular, in 1979, Inoue et al. for the first time observed the photocatalytic reduction of CO$_2$ in aqueous suspensions of semiconductor photocatalysts such as TiO$_2$, ZnO, CdS, GaP and SiC for generation of methane, methanol, formaldehyde and formic acid, which are high energy density fuels (e.g., methane, methanol) compatible with current energy infrastructure and carbon feedstocks (e.g., formaldehyde and formic acid) available for chemical synthesis. The photocatalytic technique shows a fascinating potential of recycling CO$_2$ from a climate altering waste product into value-added chemicals, which has been regarded as a promising way to simultaneously address the global energy and environment issues.

Over the past decades, continuous efforts have been devoted to the photocatalysis research. A large number of new photocatalyst materials have been developed and studied for diverse photocatalytic processes, including the photocatalytic reduction of CO$_2$ to produce solar fuels and chemicals. However, despite the significant progresses made in this area, the state-of-the-art development of photocatalysis still suffers from some severe limitations such as inferior utilization of solar light, low quantum efficiency, instability of some photocatalysts (e.g., metal sulfides) and hard control of the product selectivity of some reactions (e.g., photocatalytic reduction of CO$_2$). To overcome these challenges, different strategies including metal loading, ion doping, crystal structure, particle size and morphology controlling, and carbonaceous nanomaterials modification, etc. have been explored.

In recent years, graphene, a two-dimensional (2D) single layer of graphite with exceptional electrical, thermal, optical, and mechanical properties, has triggered a surge of research interest in both scientific and technological communities. The fabrication of graphene-based composite materials has evolved into myriad fields, including nanoelectronics, bio-sensors, energy storage and conversion, optoelectronics and supercapacitors, etc. In particular, the past several years have witnessed the cornucopia of the fabrication of graphene-based composite photocatalysts for improving the solar energy conversion efficiency. The large specific surface area, good optical transmittance, high work function and excellent electronic conductivity of graphene make it to be a high performance candidate for catalyst support and electron acceptor/trapper. Up to date, more than 200 different kinds and over 2000 publications of graphene-based composite photocatalysts have been reported. In these literature reports, it is notable that the integration of graphene with the photoactive component obviously improves the efficiency of graphene-based composite photocatalysts toward the solar energy conversion, although the real state of graphene in the composite photocatalysts is different from that of the original defined single-layer and defect-free graphene due to the presence of defect, oxygenated functional groups and aggregation of the graphene sheets, which makes it hard to take full advantages of the excellent electronic, optical and physicochemical properties of graphene. Such situation strongly suggests that (i) the integration of graphene with photoactive ingredient (e.g., semiconductor) to form new multicomponent composite materials provides a promising way for constructing the next-generation artificial photosynthetic systems; (ii) there is still a large room to improve the performance of graphene-based composite photocatalysts by optimizing the physicochemical properties of the prepared graphene in the composites.

During the past years, some reviews have been published in literature pertaining to the preparation and/or application of graphene-based composites. However, most of them give little attention or even neglect to cover the reaction type of photocatalytic reduction of CO$_2$. Very recently, Low et al., have discussed the important advantages of coupling graphene with a photocatalyst for promoting the catalytic reduction of CO$_2$ with some selected reports, but the comprehensive summary of the literature results of graphene-based composites for photocatalytic conversion of CO$_2$ to produce solar fuels and chemicals is still unavailable in the literature. In particular, none of the previous reviews have highlighted the role of graphene in tuning the product selectivity for photocatalytic CO$_2$ conversion, which is of great significance for promoting the development of photocatalytic solar fuel production. Therefore, facing the increasing research interest of this field in recent years, it is desirable and necessary to present an up-to-date insightful review of photocatalytic reduction of CO$_2$ to produce solar fuels and chemicals over graphene-based photocatalysts, with the purpose of describing the current state and promoting further development in this area.

As such, in this critical review, we comprehensively summarize the results of graphene-based composites for photocatalytic conversion of CO$_2$ from the following aspects. Firstly, we briefly illustrate the fundamentals of photoactivity enhancement of graphene-based composites for catalytic conversion of CO$_2$ to solar fuels and chemicals. Secondly, after the collection of the literature reports of graphene-based composites for photocatalytic reduction of CO$_2$, the main types of these developed graphene-based composites and the effect of graphene in these composites for improving the photocatalytic performance are elaborated with selected typical examples. Thirdly, the significant effect of graphene in tuning product selectivity for photocatalytic reduction of CO$_2$ is discussed. Finally, the challenges and issues confronted by graphene-based photocatalysts for reduction of CO$_2$ and perspectives on future research have been presented.

2. Fundamentals of photoactivity enhancement of CO$_2$ reduction over graphene-based composites
As CO₂ is a thermodynamically stable and chemically inert molecule with σ- and π-bond characteristics and linear molecular structure of O=C=O, the reduction of CO₂ is energetically uphill and highly endothermic. As schematically illustrated in Fig. 2, the standard Gibbs free energies (ΔG°) for the reduction of CO₂ with water to carbon monoxide, methanol, methane, formaldehyde and formic acid are all highly positive, indicating that in order to convert CO₂ into value-added chemicals and fuels, large amount of external energy input is required, which is indispensable for overcoming the reaction barriers to break the C=O bond and promote the formation of C-H/C-C bond and then the final chemical products.

![Reaction type](image)

**Fig. 2** Energy diagram for conversion of CO₂ into chemical products.

In photocatalytic reduction of CO₂, solar light is adopted as the input energy source to trigger the CO₂ reduction with H₂O through the employment of appropriate robust and efficient photocatalysts. The primary processes of catalytic reduction of CO₂ over traditional photocatalysts have been shown in Fig. 3. Typically, under the light irradiation, the photoactive material (taking the most widely reported semiconductor as example) is excited to generate charge carriers (i.e. electron-hole pairs) upon the absorption of photons with energy equal to or higher than its band gap energy (Eg). Then, the spatially separated photogenerated electrons and holes would migrate to the catalytically active sites at the semiconductor surface (Pathway 1 and 2) and subsequently transfer to the adsorbed molecules (CO₂ and H₂O). The hole oxidizes the H₂O to O₂ and release H⁺, and the electrons reduce CO₂ by a sequence of reactions to produce chemicals and fuels such as CO, CH₃OH and CH₄ with the assistance of H⁺. However, it is notable that the photogenerated carriers would also recombine in the bulk of the semiconductor (Pathway 3, volume recombination) or on the semiconductor surface with their trapped counterparts of opposite charge (Pathway 4, surface recombination), which release the light energy in the form of heat or photon. Both of these recombination processes are detrimental to the efficiency of photocatalysis. They strongly compete with the processes of separation and transfer of photogenerated charge carriers, resulting in the low photocatalytic CO₂ reduction efficiency. Therefore, promoting the separation and transfer of photogenerated charge carriers and inhibiting their recombination are essential for improving the efficiency of photocatalytic solar fuels and chemicals production.

In the case of graphene-based composite photocatalysts, the integration of graphene with the photoactive ingredient (e.g., semiconductor, organics) has widely proven to be effective for enhancing the separation and inhibiting the recombination of charge carriers. Graphene with high work function is able to act as an electron acceptor/trapper to induce electrons transfer from the photoactive ingredient to it, leading to the formation of an additional non-radiative delay channel for the separation and migration of photogenerated charge carriers (Pathway 5), as depicted in the right of Fig. 3. Then, the good conductivity and high electron mobility of graphene promotes the transferred electrons to diffuse fast along its unique large 2D π-conjugated structure, which efficiently improves the probability and rate of the charge carriers (i.e. electron-hole pairs) transfer in the photocatalyst.

![Fig. 3 Schematic illustration of photocatalytic reduction of CO₂](image)

In addition, the graphene with large π-conjugated structure would enhance the adsorption of CO₂ due to that the CO₂ molecules also contain delocalized π-conjugation binding πⁿ⁻¹, which can form strong π-π conjugation with graphene and thus increase the local concentration of CO₂ on the surface of the photocatalyst. Especially, the strong π-π conjugation between CO₂ and graphene can result in the destabilization and activation of CO₂ molecules. Therefore, the integration of graphene with photoactive ingredient is not only able to enhance the separation and transfer of photogenerated charge carriers in the composite photocatalysts, but also can promote the photocatalytic reduction of CO₂ to be performed on the...
graphene surface with low external energy, thereby significantly increasing the reaction sites and likelihood of photogenerated electrons to interact with the adsorbed CO\(_{2}\) reactants. As a result, high photocatalytic activity of the graphene-based composite photocatalysts can be expected. Moreover, the 2D structured graphene with high surface area is excellent catalyst supports. When it is utilized to integrate with the photoactive material, it is possible to promote the dispersion and inhibit the aggregation of the nanostructured photoactive component. This would result in the short diffusion length of aggregation of the nanostructured photoactive component. The broad light absorption is also beneficial for enhancing the utilization of solar energy and improving the efficiency of photocatalytic CO\(_{2}\) conversion. Therefore, the integration of graphene with photoactive material is believed to provide a wide range of opportunities to prepare diverse new graphene-based composite materials with extraordinary properties for promoting the photocatalytic conversion of CO\(_{2}\).

3. Summary and Category of Graphene-Based Composite Photocatalysts

Table 1 has summarized the typical reports in literature of photocatalytic reduction of CO\(_{2}\) over graphene-based composite photocatalysts. An overview of the summary results shows that the graphene-based composites developed for photocatalytic reduction of CO\(_{2}\) are mainly consisted of graphene-semiconductor photocatalysts, for which the semiconductor acts as light harvesters and graphene as co-catalyst. In addition, the combination of graphene-organics composites with enzyme for photocatalytic conversion of CO\(_{2}\) to fuels and chemicals has also been reported, which forms the second type of graphene-organics/biomolecule photocatalysts. Moreover, some reports have shown that the graphene derivatives such as graphene oxide (GO) and nitrogen doped graphene are able to perform as semiconductors, which have proven to exhibit obvious photoactivity in reduction of CO\(_{2}\). Therefore, they can be regarded as another new type of graphene derivatives-based photocatalysts.

Consequently, in terms of different photoactive components, the as-reported graphene-based composites in literature for photocatalytic reduction of CO\(_{2}\) have been classified into three main groups: graphene-semiconductor photocatalysts, graphene-organics/biomolecule photocatalysts and graphene derivatives-based photocatalysts. In the following section, the typical examples of these different types of graphene-based composite photocatalysts and the effect of graphene in these composites for improving the photocatalytic performance have been discussed separately.

### Table 1. Summary of photocatalytic conversion of CO\(_{2}\) into solar fuels and chemicals over typical graphene-based composite photocatalysts.

<table>
<thead>
<tr>
<th>Composite photocatalyst</th>
<th>Light source</th>
<th>Reaction medium</th>
<th>Main products</th>
<th>Photocatalytic performance</th>
<th>Ref. (Year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO-P25; SEG-P25</td>
<td>UV light, 100 W mercury vapor lamp; Visible light, 60 W daylight bulb</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CH(_4)</td>
<td>UV light: 1.9 (\mu)mol m(^{-2})h(^{-1}); the photoactivity is close to that of TiO(_{2})</td>
<td>76 (2011)</td>
</tr>
<tr>
<td></td>
<td>UV light, 100 W mercury vapor lamp; Visible light, 60 W daylight bulb</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CH(_4)</td>
<td>UV light: 8.5 (\mu)mol m(^{-2})h(^{-1}); 4.5-fold of TiO(_{2})</td>
<td>77 (2012)</td>
</tr>
<tr>
<td>SEG-TiO(_{2})</td>
<td>UV light, 100 W mercury vapor lamp; Visible light, 60 W daylight bulb</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CH(_4)</td>
<td>UV light: 9.3 (\mu)mol m(^{-2})h(^{-1}); 3.5-fold of TiO(<em>{2}); Visible light: 1.5 (\mu)mol m(^{-2})h(^{-1}); 3.7-fold of TiO(</em>{2})</td>
<td>78 (2013)</td>
</tr>
<tr>
<td>G-TiO(_{2})</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CH(_4), C(_2)H(_4), H(_2)</td>
<td>CO(_{2}): 8.9 (\mu)mol h(^{-1})g(^{-1}); CH(<em>4): 1.1 (\mu)mol h(^{-1})g(^{-1}); the total solar fuel production rate is 1.7-fold of TiO(</em>{2})</td>
<td>79 (2012)</td>
</tr>
<tr>
<td>G-Ti(<em>{3})O(</em>{2})</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CO, CH(_4)</td>
<td>CO(_{2}): 8.9 (\mu)mol h(^{-1})g(^{-1}); CH(<em>4): 1.1 (\mu)mol h(^{-1})g(^{-1}); the total solar fuel production rate is 7.1-fold of TiO(</em>{2})</td>
<td>74 (2015)</td>
</tr>
<tr>
<td>RGO-(g-C(_3)N(_2))</td>
<td>Visible light, 15 W daylight bulb</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CH(_4)</td>
<td>CO(_{2}): 0.59 (\mu)mol h(^{-1})g(^{-1}); 2.3-fold of g-C(_3)N(_2)</td>
<td>75 (2014)</td>
</tr>
<tr>
<td>RGO-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CH(_4)</td>
<td>CO(_{2}): 2.5 (\mu)mol h(^{-1})g(^{-1}); 12-fold of CdS</td>
<td>80 (2014)</td>
</tr>
<tr>
<td>RGO-Cu(_{2})O</td>
<td>Visible light, 150 W xenon lamp</td>
<td>CO(_{2}) saturated Na(_2)S solution</td>
<td>CO</td>
<td>CO(<em>{2}): 50 ppm h(^{-1})g(^{-1}); 2-fold of Cu(</em>{2})O</td>
<td>81 (2014)</td>
</tr>
<tr>
<td>RGO-WO(_{3})</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO(_{2}) and H(_2)O vapor</td>
<td>CH(_3)OH</td>
<td>CO(<em>{2}): 4.2 (\mu)mol h(^{-1})g(^{-1}); 1.5-fold of Cu(</em>{2})O</td>
<td>82 (2014)</td>
</tr>
</tbody>
</table>
### 3.1 Graphene-semiconductor photocatalysts

Semiconductors as the most important type of photocatalysts have been intensively investigated to couple with graphene for obtaining graphene-based composites, which have been proven to display obviously improved photocatalytic performance for reduction of CO$_2$ than the corresponding bare semiconductors. For example, Hersam et al. have synthesized a series of graphene-TiO$_2$ P25 (solvent exfoliated graphene SEG-P25 and solvent-reduced graphene oxide SRGO-P25) composites by a vacuum filtration method for photo-reduction of CO$_2$ to methane (CH$_4$) $^{76}$ As shown in Fig. 4A, the results show that the SEG-P25 composites with the appropriate addition of SEG exhibit a significantly higher photocatalytic activity than bare P25 for CO$_2$ reduction in the presence of H$_2$O vapor under both UV and visible light illumination. The improved photocatalytic activity of SEG-P25 is ascribed to that SEG efficiently captures and transfers the photoelectrons from the valence band of TiO$_2$ to the conduction band of graphene, which improves the separation and transfer of photoelectrons that bare P25 for CO$_2$ reduction. The photoelectric activity of bare P25 for CO$_2$ reduction is 1.4-fold of SRGO-P25.

<table>
<thead>
<tr>
<th>Material</th>
<th>Photocatalyst Method</th>
<th>Photocatalyst Solution</th>
<th>Product</th>
<th>Photocatalytic Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO-ZnO</td>
<td>Simulated solar light, 500 W xenon lamp</td>
<td>CO$_2$ saturated NaHCO$_3$ solution</td>
<td>CH$_4$, 2.3 μmol h$^{-1}$ g$^{-1}$, 1.5-fold of ZnO</td>
<td>(2013) 83</td>
</tr>
<tr>
<td>G-TiO$_2$-M,M = $^{13}$Au, $^{10}$Ag, $^{10}$Pd, $^{10}$Pt</td>
<td>Visible light, 15 W daylight bulb</td>
<td>CO$_2$ and H$_2$O vapor</td>
<td>CH$_4$, 0.13 μmol h$^{-1}$ g$^{-1}$, 6;</td>
<td>(2015) 84</td>
</tr>
<tr>
<td>G-TiO$_2$-M,M = $^{13}$Au, $^{10}$Ag, $^{10}$Pd, $^{10}$Pt</td>
<td>Visible light, 15 W daylight bulb</td>
<td>CO$_2$ and H$_2$O vapor</td>
<td>CH$_4$, 0.17 μmol h$^{-1}$ g$^{-1}$, 7;</td>
<td>(2014) 85</td>
</tr>
<tr>
<td>G-Fe$^{2+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CO, CH$_4$</td>
<td>(2015) 86</td>
</tr>
<tr>
<td>G-Fe$^{2+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.29 μmol h$^{-1}$ g$^{-1}$, 1.6-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 87</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.28 μmol h$^{-1}$ g$^{-1}$, 1.3-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 88</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.26 μmol h$^{-1}$ g$^{-1}$, 1.1-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 89</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.24 μmol h$^{-1}$ g$^{-1}$, 1.0-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 90</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.22 μmol h$^{-1}$ g$^{-1}$, 0.9-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 91</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.20 μmol h$^{-1}$ g$^{-1}$, 0.8-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 92</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.18 μmol h$^{-1}$ g$^{-1}$, 0.7-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 93</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.16 μmol h$^{-1}$ g$^{-1}$, 0.6-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 94</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.14 μmol h$^{-1}$ g$^{-1}$, 0.5-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 95</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.12 μmol h$^{-1}$ g$^{-1}$, 0.4-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 96</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.10 μmol h$^{-1}$ g$^{-1}$, 0.3-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 97</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.08 μmol h$^{-1}$ g$^{-1}$, 0.2-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 98</td>
</tr>
<tr>
<td>G-Fe$^{3+}$O$_4$-CdS</td>
<td>Visible light, 300 W xenon lamp</td>
<td>CO$_2$, H$_2$O vapor</td>
<td>CH$_4$, 0.06 μmol h$^{-1}$ g$^{-1}$, 0.1-fold of Fe$^{2+}$O$_4$-CdS</td>
<td>(2015) 99</td>
</tr>
</tbody>
</table>

Note: MAQSP refers to multianthraquinone substituted porphyrin; TEA refers to triethanolamine; IP refers to 1,1’,1”-(2,2’:6’,2”-terpyridinyl)triphenylene; EU refers to 1,1’-((2R,5R)-2,5-dimethylcyclohexane-1,4-diyl)bis(2-methylbenzoic acid); BODIPY refers to 2,7-diisopropyl-3,4-dihydro-2H-benzo[1,4]diazepine-3,4-dione; THPP refers to tetrahydroxyphenyl porphyrin; CoTHPP refers to cobalt tetrahydroxyphenyl porphyrin; CoPc refers to cobalt phthalocyanine tetrabromide [Co-Pc·(SO$_3$Na)$_2$]; TEA refers to triethylamine; Ru refers to ruthenium trinuclear complex.
proven that (i) graphene is able to act as an efficient co-catalyst for improving the photocatalytic activity of TiO$_2$ for reduction of CO$_2$; (ii) the defect density and sheet resistance of graphene has significant influence on the photoactivity enhancement of the resulting graphene-semiconductor composite photocatalysts.

Additionally, Chai and co-workers have reported the synthesis of nitrogen doped-TiO$_2$-001/graphene (N-TiO$_2$-001/GR) composites by in situ growth of well-faceted N-TiO$_2$ with exposed (001) facets onto GR sheets for photocatalytic reduction of CO$_2$ to CH$_4$ in the presence of H$_2$O vapor.

Fig. 5 displays the photoactivity test results over the as-synthesized samples, from which it can be seen that under visible light irradiation, the N-TiO$_2$-001/GR composite exhibits the optimal CH$_4$ yield of 3.7 μmol g$^{-1}_{\text{catalyst}}$ after the reaction of 10 h, which is approximately 11-fold higher activity than that of TiO$_2$-001. In addition, the photoactivity of N-TiO$_2$-001/GR is also better than those of TiO$_2$-001/GR, N-TiO$_2$/GR, TiO$_2$/GR and N-TiO$_2$-001 counterparts. The high photocatalytic performance of N-TiO$_2$-001/GR is primarily attributed to the effective charge transportation of graphene, large exposure of catalytic active (001) facets relative to the (101) facets and high absorption of visible light of the composite, which strongly inhibit the recombination of electron-hole pairs, and simultaneously promote the activation of CO$_2$ and utilization of solar energy over N-TiO$_2$-001/GR, thereby enhancing the photocatalytic reduction of CO$_2$, as illustrated in Fig. 5B.

Apart from TiO$_2$, in a subsequent work of Chai et al., they have fabricated a series of sandwich-like graphene-(g-C$_3$N$_4$) (GCN) composites by one-pot impregnation-thermal reduction strategy for the conversion of CO$_2$ to CH$_4$ using H$_2$O vapor as a scavenger. Under visible light irradiation, the pure g-C$_3$N$_4$ without graphene displays low CH$_4$ production with a total yield of 2.55 μmol g$^{-1}_{\text{catalyst}}$ after reaction of 10 h due to rapid recombination of electron-hole pairs, as presented in Fig. 6A, B. By integrating g-C$_3$N$_4$ with graphene, the as-obtained GCN samples demonstrate obviously improved photoactivity for CH$_4$ formation. The optimal GCN-0.15 composite with the loading of 15 wt% graphene displays the maximum CH$_4$ production yield of 5.87 μmol g$^{-1}_{\text{catalyst}}$ among the GCN samples, which is 2.3-fold of the photoactivity of pure g-C$_3$N$_4$. The enhanced photocatalytic activity of GCN is accredited to the following concomitant factors. Firstly, the formation of C-O-C bond between graphene and g-C$_3$N$_4$ narrows the band gap of GCN and renders the GCN composites more sensitive to the visible light region, as reflected in Fig. 6C. Secondly, the coherent interface between graphene and g-C$_3$N$_4$ results in a more efficient electron transfer within the 2D layered composite structure (Fig. 6D). Finally, CO$_2$ molecules with delocalized π-conjugated binding π$^*$ can adsorb onto the graphene surface through π-π conjugation interaction, which is beneficial for the destabilization and activation of CO$_2$ molecules. These factors synergistically promote the photoactivity enhancement of GNS toward visible-light-driven CO$_2$ reduction.

Additionally, CdS as another important semiconductor has also been coupled with graphene for photocatalytic reduction of CO$_2$. Yu and co-workers have prepared a series of reduced...
graphene oxide-CdS nanorod (RGO-CdS) composites via a one-step microwave-hydrothermal method in ethanalamine-water solution. These composite samples have shown obviously improved visible light photocatalytic activity for reduction of CO2 with H2O vapor to CH4 as compared to blank CdS. As shown in Fig. 7, the 0.5%RGO-CdS (G0.5) composite with the optimal content of RGO exhibits the highest CH4 production rate of 2.51 µmol h⁻¹ g⁻¹, which exceeds the rate over blank CdS nanorod by more than 10 times (0.21 µmol h⁻¹ g⁻¹). Moreover, the value is also higher than that of the reference 0.5%Pt-CdS nanorod composite photocatalyst (1.52 µmol h⁻¹ g⁻¹) under identical reaction conditions. This high photocatalytic activity of the RGO-CdS composites has been ascribed to the deposition of CdS nanorod onto RGO sheets, which not only promotes the separation and transfer of the photogenerated charge carriers, but also enhances the adsorption and activation of CO2 molecules, thus resulting in the photoactivity enhancement for CO2 reduction over the RGO-CdS composites. However, in spite of the effectiveness of RGO-CdS composites for photocatalytic reduction of CO2 to CH4, the photostability of the composites is still unclear. Given that the photocatalytic reduction of CO2 over RGO-CdS composites is performed in gaseous phase without sacrificial reagent, it is natural to raise the question about the photocorrosion of semiconductor CdS in the composite, which would cause detrimental effect on the photoactivity and stability of the RGO-CdS composite photocatalysts.

Moreover, Tang and co-workers have reported the photocatalytic reduction of CO2 to CO in water over Cu2O/reduced graphene oxide (Cu2O/RGO) composites synthesized via one-step microwave-assisted hydrothermal method. Before the photoactivity measurements, a thermal pretreatment of the photocatalysts in Ar or air has been performed to remove possible trace organic contaminants on the samples. Fig. 8A, B has shown the visible-light-driven catalytic reduction of CO2 over blank Cu2O and Cu2O/RGO composites in the presence of sodium sulfite as hole scavenger. The result demonstrates that by coupling with RGO, the photoreduction activity of Cu2O has been efficiently enhanced. As for the lower photoactivity of Cu2O (Air) and Cu2O/RuOx (Air) than that of Cu2O (Ar), it is attributed to the partial oxidation of Cu2O to CuO upon heating, which causes harmful effect on the photoactivity of Cu2O. In addition, the photoactivity test also shows that the Cu2O/0.5% RGO composite produce CO stably with an average rate of 50 ppm g⁻¹ h⁻¹ for 20 h, showing a potential for photocatalytic conversion of CO2 over Cu2O/RGO in a sustainable manner.
The high photocatalytic activity and stability of Cu₂O/RGO composites are ascribed to the electron acceptor role of RGO, which efficiently promotes charge carriers transfer and retards the electron-hole recombination (Fig. 8C). Moreover, to further clarify the origin of the CO generated during the reaction, the photoreduction of CO₂ has been conducted, as shown in Fig. 8D. The dominant peak of ¹³C-labeled CO (m/z = 29) clearly indicates that the evolved CO originates from the photoreduction of CO₂ rather than the photodecomposition of RGO or organic contaminants that might be adsorbed on the photocatalyst surface/reactor.

Besides the reported binary graphene-semiconductor composites, some multinary (i.e., ternary and quaternary) graphene-semiconductor-based photocatalysts with further improved photoactivity as compared with their binary counterparts have also been fabricated for catalytic reduction of CO₂ into solar fuels and chemicals.

Additionally, Zou and co-workers have designed an all-solid-state Z-scheme system array consisting of Fe₃V₄O₁₃ nanoribbon (NR)/reduced graphene oxide (RGO)/CdS nanoparticle grown on the stainless-steel mesh (SSM) for photocatalytic conversion of CO₂ with H₂O vapor into CH₄. As shown in Fig. 10A, the SEM image shows that the as-prepared Fe₃V₄O₁₃ NRs with a length of 10-20 mm are perpendicularly grown on the entire SSM surface. With the GO coating and subsequent annealing treatment, the RGO-coated surface of the Fe₃V₄O₁₃ NR appears obviously a crumpled-layer structure (Fig. 10B). Then, after chemical vapor deposition of CdS, large numbers of the tiny CdS particles are observed on the surface of the Fe₃V₄O₁₃/RGO (Fig. 10C). The SEM analysis clearly demonstrates the ordered structure and intimate interfacial contact of the three components in the resulting Fe₃V₄O₁₃/RGO/CdS composite.
oxidized by holes than that of H₂O. Therefore, the photostability of this Z-schematic Fe₃V₂O₁₃/RGO/CdS composite photocatalysts should be concerned.

Very recently, Hou and co-workers have developed a novel quaternary three-dimensional bimetal-graphene- semiconductor (Au-Cu/graphene/CuO) integrated system for solar-light-driven conversion of CO₂ into methanol,⁸⁷ in which the CuO nanowire array on a Cu mesh substrate are encapsulated by ultrathin graphene layers and then decorated with optimized combination of Au-Cu nanoalloys, as displayed by the SEM and TEM images in Fig. 11A-E. The photocatalytic reduction of CO₂ over the as-synthesized composites has been performed in CO₂ saturated H₂O. As shown in Fig. 11F, under visible light irradiation of 6 h, the methanol yield over graphene/CuO array is 46.3 ppm cm⁻² h⁻¹, which is 3-fold of the photoactivity of CuO array (15.4 ppm cm⁻² h⁻¹). Especially, the Au-Cu/graphene/CuO array exhibits the highest methanol yield of 120.0 ppm cm⁻² h⁻¹, which is 7.8 times higher than that of CuO array. The recycle test of Au-Cu/graphene/CuO shows that the yield rate of methanol from CO₂ conversion maintains 92% of its original activity after five runs, implying the high photostability of the composite. Moreover, the photoactivity of Au-Cu/graphene/CuO has also been proven to be much higher than that of the graphene/CuO array decorated with Au, Cu and Au + Cu prepared by step-by-step deposition of metal on the support.⁸⁷ The significantly improved photocatalytic activity of Au-Cu/graphene/CuO is attributed to that (1) the introduction of graphene as an electron conductive platform with lower energy level than the conduction band (CB) of CuO leads to the photogenerated electrons migration from CB of CuO to the graphene layer;⁸⁷ (2) the formation of Schottky junction in 3D Au-Cu/graphene/CuO system results into the further migration of electrons from graphene to Au-Cu nanoalloys.⁸⁷ Furthermore, the electromagnetic field induced from the surface plasmonic resonance effect of Au-Cu also promotes the migration of electrons through the harness charge flow of CuO nanowire array→graphene layer→Au-Cu nanoalloys (Fig. 11G). Consequently, the electron-hole pairs are readily separated and the lifetime of the charge carriers is efficiently prolonged (Fig. 11H, I) in the quaternary 3D Au-Cu/graphene/CuO composites, which become readily available to drive the multi-electron CO₂ reduction process.

3.2 Graphene-organics/biomolecule photocatalysts

Organic compounds and metal organic complexes with suitable light absorption property is another important class of promising materials that are capable of participating in photochemical charge transfer and energy transfer processes.⁹⁸-¹⁰² The integration of graphene with organics and metal organic complexes, such as porphyrins, phthalocyanines iron complex and ruthenium complex have also been employed to improving the efficiency for harvesting solar energy.⁹³-¹⁰⁶ Especially, some recent reports have proven that with the assistance of biological enzyme, the graphene-organics/biomolecule photocatalysts composite system are able to catalytic conversion of CO₂ to target products efficiently and selectively.⁹⁸-⁹⁹
For instance, Baeg and co-workers have designed a graphene-based photocatalyst-biocatalyst coupled system, which is consisted of chemically converted graphene coupled multianthraquinone substituted porphyrin (CCGCMAQSP), organometallic rhodium complex, nicotinamide adenine dinucleotide (NADH) and formate dehydrogenase, for photocatalytic reduction of CO\textsubscript{2} to formic acid (HCOOH) in sodium phosphate buffer solution with triethanolamine (TEOA) as hole scavenger.\textsuperscript{90} As shown in Fig. 12A, the HCOOH yield increases linearly with the reaction time when CCGCMAQSP is used as the photocatalyst. The yield for the production of HCOOH over CCGCMAQSP within 2 h is 110.55 μmol, which is much higher than the values of the reference photocatalysts of W\textsubscript{2}Fe\textsubscript{4}Ta\textsubscript{2}O\textsubscript{17} (14.25 μmol) and blank MAQSP (46.53 μmol). The working mechanism of the as-prepared graphene-based photocatalyst-biocatalyst coupled system for production of formic acid from CO\textsubscript{2} has been schematically illustrated in Fig. 12B. Under visible light irradiation, the MAQSP firstly absorbs photons through the transition between localized orbitals around chromophore to generate electrons and transfer to the organometallic rhodium complex via graphene. Then, the reduced rhodium complex abstract protons from aqueous solution and further transfer electrons and hydrides to NAD\textsuperscript{+}, which converts NAD\textsuperscript{+} to NADH and finishes the photocatalysis cycle. During this process, the rhodium complex shuttles as an electron mediator between CCGMAQSP photocatalyst and NAD\textsuperscript{+}, which facilitates the regeneration of the NADH. Finally, NADH is consumed by the CO\textsubscript{2} substrate for its enzymatic (formate dehydrogenase) conversion to HCOOH. The NAD\textsuperscript{+} released from the enzyme can undergo photocatalysis cycle in the same way, leading to the photoregeneration of NADH. These two catalysis cycles thus couple integrally to work together, ultimately yielding HCOOH from CO\textsubscript{2}.\textsuperscript{89}

In a following work of Baeg et al., they have further reported the photocatalytic reduction of CO\textsubscript{2} to methanol over another new graphene-based photocatalyst-biocatalyst integrated system, which is derived from the covalent attachment of isatin-porphyrin (IP) chromophore onto chemically converted graphene (CG) forming CCG-IP photocatalyst, and then coupling with enzymes.\textsuperscript{90} The production of methanol over the as-synthesized photocatalysts has been performed in CO\textsubscript{2}-saturated sodium phosphate buffer solution with the addition of rhodium complex, mixed enzymes (formate dehydrogenase, formaldehyde dehydrogenase and alcohol dehydrogenase) and hole scavenger of TEOA. The photoactivity test results in Fig. 13A have shown that the methanol yield of CCG-IP photocatalyst is 11.21 μM after visible light irradiation of 1 h, which is much higher than that of the reference CCGMAQSP photocatalyst (5.62 μM). In addition, the photoactivity test of the IP chromophore generates trace amount of methanol which could not be quantified, while CCG fails to produce any methanol. Fig. 13B has displayed the transient photocurrent study of IP and CCG-IP. The CCG-IP presents significantly higher photocurrent than the IP electrode. The prompt photocurrent response of CCG-IP is well accordance with its improved photoactivity, indicating significant co-catalytic role of CCG for enhancing the electron transfer from IP to CCG upon visible light irradiation. Furthermore, the control experiments in the absence of CO\textsubscript{2}, CCG-IP photocatalyst (but with enzymes) or visible light irradiation show that no methanol is formed in all these cases, which further confirm the photocatalytic nature of converting CO\textsubscript{2} to methanol over the CCG-IP composite.

The above discussed works clearly demonstrate the possibility of using photoactive graphene-organics to construct photocatalyst-biocatalyst coupled system for catalytic reduction of CO\textsubscript{2} to value-added chemicals and fuels. More importantly, the works have shown the great potential of controlling the product with high selectivity through choosing appropriate biological enzymes. For example, in the presence of formate dehydrogenase alone, the photocatalytic conversion of CO\textsubscript{2} over the CCGMAQSP composite produces formic acid,\textsuperscript{89} whereas in the case of adding mixed enzymes of formate dehydrogenase, formaldehyde dehydrogenase and alcohol dehydrogenase, methanol is detected as the exclusive products for photocatalytic conversion of CO\textsubscript{2} over the same CCGMAQSP photocatalyst under identical reaction condition.\textsuperscript{90} Therefore, the design and fabrication of graphene-based photocatalysts/biomolecule composite system would be a promising strategy for selectively photocatalytic conversion of CO\textsubscript{2} to target products.

3.4 Graphene derivates-based photocatalysts

In addition to the above discussed graphene-semiconductor and graphene-organics/biomolecule photocatalysts, graphene oxide (GO), the most regularly used precursor of graphene for the synthesis of graphene-based composite photocatalysts,\textsuperscript{29, 60} recently has also been proven to be able to perform as photocatalysts for solar energy conversion.\textsuperscript{107-111} In particular, the GO has demonstrated to display obvious photoactivity that comparable with traditional semiconductors such as TiO\textsubscript{2} for catalytic reduction of CO\textsubscript{2} to produce solar chemicals and fuels.

For example, Chen et al. have reported the photocatalytic reduction of CO\textsubscript{2} with H\textsubscript{2}O vapor to CH\textsubscript{3}OH using GO as a promising photocatalyst under simulated solar light
irradiation.\textsuperscript{95} They have synthesized a series of GO samples under different oxidation conditions and found that the GO-3 obtained via the Hummers’ oxidation with excess KMnO$_4$ and H$_2$PO$_4$ exhibits the highest photocatalytic efficiency. As shown in Fig. 14A, the photocatalytic conversion rate of CO$_2$ to CH$_3$OH on GO-3 achieves up to 0.172 $\mu$mol g$^{-1}$cat$^{-1}$h$^{-1}$, which is 6-fold higher than the pure TiO$_2$ P25. The isotopic tracer analysis of GO with $^{13}$CO$_2$ demonstrates that CH$_3$OH is produced directly from the photocatalytic reduction of CO$_2$ instead of any photo-dissociation of the GO photocatalyst. Besides, the origin of the photoactivity has been described by the band structure of GO, as illustrated in Fig. 14B. In the GO photocatalyst, the oxygenated functional groups provide a 2D network of sp$^3$ and sp$^3$ bonded atoms, leading to the presence of a finite band gap depending on the isolated sp$^3$ domains. During the photocatalytic reduction process, the GO with surplus oxygenated components is photoexcited to generate electron-hole pairs, which then migrate to the GO surface to react with absorbed CO$_2$ reactants and produce CH$_3$OH.\textsuperscript{95}

![Fig. 14 Photocatalytic methanol formation (R$_{CH_3OH}$) on different GO samples (GO-1, GO-2, GO-3) and TiO$_2$ using a simulated solar-light source (A); schematic illustration of the photocatalytic CO$_2$ reduction mechanism on GO (B). Reprinted with permission from ref. 95. Copyright 2013, Royal Society of Chemistry.](image)

In a subsequent work of Chen et al., they have further synthesized a series of copper nanoparticles decorated GO photocatalysts with different weight ratios of Cu via a one-step microwave method.\textsuperscript{96} The as-synthesized GO-Cu composites display significantly enhanced photocatalytic activity for reduction of CO$_2$ to methanol and acetaldehyde in the presence of H$_2$O vapor under visible light irradiation, as shown in Fig. 15A. The solar fuel (methanol and acetaldehyde) formation rate over the optimal Cu/GO-2 (10 % Cu) composite (6.4 $\mu$mol g$^{-1}$cat$^{-1}$h$^{-1}$) is 60 times higher than that of pristine GO and 240 times higher than that of commercial P25 under visible light irradiation. The characterization results demonstrate that the incorporation of Cu effectively tunes the work function of GO due to the spontaneous transfer of electrons from GO to Cu nanoparticles.\textsuperscript{96} As a result, the charge separation at the GO-Cu interface and suppression of carrier recombination is more efficient than that of GO (Fig. 15B), which thus leads to the enhanced photocatalytic CO$_2$ reduction activity of GO-Cu composites. In addition, the variation in the production rate of different products is suggested to be determined by the band positions of these samples, as displayed in Fig. 15C. The plot shows that the conduction band (CB) of Cu/GO-1 (5 % Cu) and Cu/GO-2 (10 % Cu) is feasible for the multi-electron reduction of CO$_2$ to methanol and acetaldehyde. In contrast, the position of CB in Cu/GO-3 Cu/GO-2 (15 % Cu) is slightly lower than the CO$_2$/CH$_3$OH reduction potential at around -0.35 V, which leads to the absence of methanol in the product.\textsuperscript{96}

Additionally, Jain et al. have reported the immobilization of light responsive metal-organic complexes onto the GO support,\textsuperscript{97, 98, 112} which also significantly improves the photocatalytic CO$_2$ reduction activity of GO. For example, they have immobilized ruthenium trinuclear polyzine complexes on phenanthroline modified GO through the complex formation between them.\textsuperscript{98} The as-synthesized Ru-(phen-GO) composite displays higher visible light photoactivity than GO for catalytic reduction of CO$_2$ to CH$_3$OH in DMF/H$_2$O solution with the addition of triethylamine as sacrificial agent, as shown in Fig. 16A. After 48 h illumination, the CH$_3$OH yield of about 3978 $\mu$mol g$^{-1}$cat$^{-1}$ is obtained, which is much higher than the yield of CH$_3$OH over blank GO (2201 $\mu$mol g$^{-1}$cat$^{-1}$) under identical reaction conditions. The isotopic labeling experiment performed with $^{13}$CO$_2$ confirms that the methanol formation through CO$_2$ reduction. In addition, the recycle test of continuous five runs demonstrates that the Ru-(phen-GO) composite is stable as well as efficient for the photocatalytic reduction of CO$_2$ under the current experimental conditions. The enhanced photocatalytic performance of Ru-(phen-GO) composites is ascribed to the significant sensitization role of the synthesized ruthenium complex. It is able to strongly absorb visible light and be excited to inject electrons into the conduction band (CB) of

![Fig. 15 Photocatalytic Solar fuel production rate for GO, and Cu/GO-1, Cu/GO-2, and Cu/GO-3 (production rate was derived following 2 h of light irradiation) (A); schematic photocatalytic reaction mechanism (B); and band-edge positions of pristine GO and Cu/GO hybrids in compared with CO$_2$/CH$_3$OH and CO$_2$/CH$_3$CHO formation potential (C). Reprinted with permission from ref. 96. Copyright 2014 American Chemical Society.](image)
GO, which subsequently reduces the adsorbed CO₂ to methanol on the surface of GO. Meanwhile, the sacrificial agent of triethylamine provides electrons to the oxidized ruthenium for the continuation of the process (Fig. 16B).  

Besides the photocatalytic reduction of CO₂ over GO-based composite photocatalysts, recently, Jain et al. have reported that the nitrogen-doped graphene (GrN₀.₉₁) obtained from annealing dried GO-ethylenediamine material at 700 °C under argon flow is also efficient for CO₂ reduction in DMF/H₂O solvent. In particular, they have further grafted copper (II) complex ([Cu(bpy)₂(H₂O)]Cl₂•2H₂O) onto the nitrogen-doped graphene (GrN₀.₉₁) structure, which efficiently improves the photocatalytic CO₂ reduction activity by a factor of 2.05. As shown in Fig. 17A, after visible light irradiation of 24 h, the methanol production over bare copper (II) complex (CuCl₂·2H₂O), GO, GrN₀.₉₁, GrN₀.₉₁-CuC and GrN700-CuC (physical mixture) displays an total yield of 285, 420, 780, 971 and 1600 μmol g⁻¹, respectively. The GrN700-CuC has shown the highest photoactivity among these samples. The blank experiment performed in N₂ atmosphere demonstrates that no obvious methanol generation has been detected, confirming that the CH₃OH is produced directly from the photocatalytic reduction of CO₂. Moreover, the recycling experiment after five runs shows that methanol yield over GrN₀.₉₁-CuC is about 90% of its original photoactivity (Fig. 17B). These results indicate that the synthesized GrN₀.₉₁-CuC photocatalyst is quite stable and can be efficiently used for catalytic reduction of CO₂. The possible photocatalytic mechanism over GrN₀.₉₁-CuC has been illustrated as following. In the GrN₀.₉₁-CuC composite system, the N-doped graphene performed like a semiconductor, and the copper complex with good visible light absorbance works like a photosensitizer. Under visible light irradiation, the copper bipyridine complex would photoexcited to generate electrons and then transfer the conduction band of N-doped graphene, while the holes are scavenged by the solvent. Due to the high electrical conductivity and large surface for the attachment of CO₂ of N-doped graphene, the electrons in the conduction band of GrN₀.₉₁ efficiently reduce the CO₂ molecules to CH₃OH. 

According to the above discussed examples reported by different research groups, it is certain that the modification of graphene such as oxidation and doping would enable the as-obtained graphene derivates to be photocatalysts for catalytic conversion of CO₂. However, the origin of the light driven photoactivity of the graphene oxide and nitrogen doped graphene for catalytic reduction of CO₂ is still not well understood. In addition, the photostability of the graphene derivates-based photocatalyst, especially for the graphene oxide, is another important issue that should be carefully concerned. Because some previous works has proven that the light irradiation of GO during the photocatalytic process would result in an obvious decrease of oxygenated functional groups and thus narrows the band-gap of GO.  

4. Tuning the product selectivity of photocatalytic conversion of CO₂ over graphene-based photocatalysts

In addition to the photocatalytic activity, the selectivity toward target products is another important concern related to the photocatalytic conversion of CO₂ to produce solar fuels and chemicals. Recently, some reports have proven that in addition to improving the photoactivity, the integration of graphene with photoactive ingredient is also able to tune the product selectivity for photocatalytic reduction of CO₂.  

For example, Zou et al. have reported the fabrication of G-Ti₆.₉₁O₂ hollow spheres consisting of molecular-scale alternating Ti₆.₉₁O₂ nanosheets and G nanosheets for photocatalytic reduction of CO₂. As shown in Fig. 18, the total conversion of CO₂ to renewable fuels (CO and CH₄) in the presence of H₂O vapor over G-Ti₆.₉₁O₂ hollow spheres is five-times higher than blank Ti₆.₉₁O₂ hollow spheres and nine-times higher than commercial P25. The higher photoactivity of G-Ti₆.₉₁O₂ hollow spheres is attributed to that: (i) the ultrathin nature of Ti₆.₉₁O₂ nanosheets favors the rapid transportation of photoelectrons onto the surface to participate in the photoreduction; (ii) the sufficiently compact stacking of ultrathin Ti₆.₉₁O₂ nanosheets with G nanosheets leads to the spatial separation of the charge carriers; (iii) the hollow structure allows a more efficient, permeable absorption and scattering of light. Notably, the photoactivity result has also shown that CH₄ is the major product over Ti₆.₉₁O₂ photocatalyst, whereas CO is dominantly produced over G-Ti₆.₉₁O₂ composites. This photoactivity difference
indicates the significant role of graphene on determining the product for photocatalytic reduction of CO₂. The possible reason has been explained as following: the formation of CO and CH₄ follows the reaction route of CO₂→CO→C→CH₄, with the aid of two-electron and eight-electron transfer, respectively. The transferred electrons from TiO₂ to G diffuse quickly on a large area of G, benefiting from the enhanced electron mobility of G. This restrains the accumulation of the electrons and decreases local electron density, which is favorable for two-electron reaction to form CO.

Moreover, Wu et al. have also reported the control of photocatalytic products for reduction of CO₂ with H₂O vapor over graphene-based composites. They have synthesized two types of graphene-porphyrin composite films via a mist spray method, for which the cobalt tetrahydroxyphenyl porphyrin (CoTHPP) and meso-tetrahydroxyphenyl porphyrin (THPP) are chosen as the light harvester due to their suitable light absorption property and high photostability. Fig. 20A, B displays the photoactivities of the synthesized samples, which shows that THPP/G and CoTHPP/G both present higher photocatalytic CH₄ evolution amounts for (G-TiO₂) composites prepared by an in situ reduction-hydrolysis technique in a binary ethylenediamine (En)-H₂O solvent. The reduction of GO to G by En and the formation of TiO₂ nanoparticles loaded onto G through chemical bonds (Ti-O-C bond) are achieved simultaneously. In particular, owing to the reducing role of En, abundant Ti is formed on the surface of TiO₂. This journal is © The Royal Society of Chemistry 20xx
oxidized on the porphyrin of THPP and CoTHPP, by which realizes the spatially separation of photoredox processes. Moreover, the reaction intermediates such as CO$_2$• anion radical with a delocalized electronic structure can also be attached onto graphene through π-π non-covalent bonds and receive electrons uninterrupted. This would improve the stability of the reaction intermediates and enhances the coupling opportunities of them, thereby promoting the formation of C$_2$H$_4$. As for the different photoactivity between THPP/G and CoTHPP/G, the theoretical simulation result has proposed that the structure difference in central ring of the porphyrin molecule between THPP and CoTHPP is the main reason (Fig. 20C, D). The central ring of CoTHPP molecule is not a planar structure, which breaks the large π structure and is adverse for the transfer of electrons to graphene for the reduction of CO$_2$. Finally, the control experiments in the presence of N$_2$ and heating of the catalysts at 50 °C without light have been carried out. No CH$_4$ and C$_2$H$_4$ can be detected in these circumstances. The result confirms that the CH$_4$ and C$_2$H$_4$ products are generated by the photocatalytic reduction of CO$_2$ over the graphene-porphyrin composites.

The above reports have obviously demonstrated the important role of graphene on tuning the product selectivity for photocatalytic reduction of CO$_2$. With the incorporation of graphene, the synthesized graphene-based composite photocatalysts show great promise for converting CO$_2$ into more valuable high-grade multi-carbon compounds (such as C$_2$H$_4$, C$_3$H$_8$). However, currently, there is lack of direct and detailed experimental evidences to support the proposed reaction mechanism for controlling the CO$_2$ reduction product by graphene. In order to deeply exploit the potential application of graphene in promoting the photocatalytic conversion of CO$_2$ to produce high-energy-density multi-carbon compounds, more attention and efforts should be paid to this area.

5. Summary and perspectives

In this perspective review, we have summarized the literature results on exploring efficient graphene-based photocatalysts for catalytic conversion of CO$_2$ into solar fuels and chemicals. The progresses achieved by different research groups in this field demonstrate that coupling graphene with photoactive materials in a suitable manner and modification of graphene itself (e.g., oxidation and doping) hold great potential for improving the efficiency of photocatalytic conversion of CO$_2$. However, despite the considerable developments reported in this area, there are still some fundamental and essential issues that merit more research attention.

Firstly, the photocatalytic CO$_2$ reduction efficiencies of most of the graphene-based composite reported to date remain unsatisfactory (the rate of product formation is measured in μmol g$^{-1}$ h$^{-1}$). On-going efforts are still required to improve the overall efficiency of the CO$_2$ photoreduction process. In this respect, the construction of multinary graphene-based composite photocatalysts with the optimization of each component and the atomic charge carrier transfer pathway across the interface between the different components would be an effective strategy. In addition, the theoretical calculations of charge carrier dynamics within the photoactive ingredients and at their interfaces with graphene are also important.

Secondly, the photostability of the graphene-based composite photocatalysts is another important problem that should be considered. During the photocatalytic reaction process, the photoelectrons will be consumed to drive CO$_2$ reduction half-reaction, leaving the holes in the reaction system, which would be accumulated on the surface of the photocatalysts, and then decompose the photocatalyst component. This issue would be particularly prominent when the composite photocatalysts contain metal sulfide semiconductors, graphene oxide and organics/metal organic complexes. Given this issue, the integration of high-performance water oxidation co-catalyst into the graphene-based composite photocatalysts to promote the fast consumption of photogenerated holes would be an effective way for enhancing the photoactivity and stability of the graphene-based composite photocatalysts.

Thirdly, the origin of the photocatalytic generated products of CO$_2$ reduction over graphene-based composites should be identified, for example, by isotopic labeling experiment with $^{13}$CO$_2$. This is mainly because that the organic compounds in the reaction system, such as the residua obtained from the synthesis of photoactive materials with organic precursors, can be the origin of the observed products or at least can contribute in a certain percentage to the products. Moreover, considering the peculiar nature of the graphene-based composite photocatalysts with the carbon source of graphene, it is especially significant and necessary to confirm the origin of the products. However, a lot of the studies commented in this review have neglected this confirmation.

Finally, the underlying photocatalytic mechanism for reduction of CO$_2$ over graphene-based photocatalysts, and in particular, the reaction mechanism of graphene on tuning the
product selectivity of photocatalytic conversion of CO2 should be clarified in detail. In this regard, the experimental and computational methods, such as in situ time-resolved spectroscopy (time-resolved fluorescence spectroscopy and femtosecond transient absorption spectroscopy), electron paramagnetic resonance spectroscopy and density functional theory calculations20 should be integratively employed. The rational understanding of the mechanism would in turn offers guided information to design more efficient and highly selective graphene-based composites to promote the conversion of CO2 with sunlight.

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Notes and references

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A critical summary and insight of recent advances for photocatalytic reduction of CO$_2$ to produce solar fuels and chemicals over graphene-based photocatalysts has been presented, with the purpose of describing the current status and promoting further development in this area.
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