



## Review

## Structural diversity of graphene materials and their multifarious roles in heterogeneous photocatalysis

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## ABSTRACT

Recent years have seen the rocket rise of graphene as the unique two-dimensional carbon nanosheets and its outstanding promise in materials science. In particular, because of its diverse, tunable structural and electronic properties, graphene has been well recognized to be an ideal co-catalyst to optimize the photocatalytic performance of semiconductors. Given that the conductive, optical, chemical and mechanical performances of graphene are closely linked to its structural diversity, tremendous efforts have been devoted to designing and tailoring the graphene nanosheets to construct the desirable architecture. The tailored graphene materials (GMs), such as zero-dimensional graphene quantum dots, one-dimensional graphene nanoribbons and three-dimensional graphene frameworks show a variety of fascinating features, thereby offering a fertile and flexible ground for the further development of GMs-enhanced photocatalysis. This review aims to provide an overview on the structural diversity, tunable properties, and synthetic strategies of these GMs, followed by highlighting their multi-functionality in heterogeneous photocatalysis. Finally, the perspectives on future research trends and challenges in constructing more efficient GMs-enhanced systems for solar energy conversion are presented. The integral comprehension of GMs with all dimensions would further guide the fundamental processing-structure-properties-applications relationships of GMs.

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**Abbreviations:** GMs, graphene materials; GR, graphene; GO, graphene oxide; RGO, reduced graphene oxide; SEG, solvent exfoliated graphene; 0D, zero-dimensional; 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; GQDs, graphene quantum dots; GNRs, graphene nanoribbons; GFs, graphene frameworks; QDs, quantum dots; AGNRs, armchair graphene nanoribbons; ZGNRs, zigzag graphene nanoribbons; ZBNNRs, zigzag boron nitride nanoribbons; GAs, graphene aerogels; GHs, graphene hydrogels; MRGO, monomers functionalized graphene; AGQDs, alkylated graphene quantum dots; NTAs, nanotube arrays; EDC/NHS, ethyl(dimethylaminopropyl) carbodiimide/*N*-hydroxysuccinimide; UV, ultraviolet; Vis, visible; PL, photoluminescence; RhB, Rhodamine B; MB, methylene blue; 4-NA, 4-nitroaniline; UPCL, up-conversion luminescence; MO, methyl orange; CVD, chemical vapor deposition; PEG, polyethylene glycol; FET, field effect transistor; STM, scan tunneling microscopy; HIBL, helium ion beam lithography; MML, meniscus-mask lithography; PVA, poly(vinyl alcohol); APTES, 3-aminopropyltriethoxysilane; PVP, polyvinylpyrrolidone; DMF, *N,N*-dimethylformamide; BPEI, branched polyethyleneimine; DAN, 1,5-diaminonaphthalene; DFT, density functional theory.

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## Introduction

Energy and environmental issues caused by utilization of fossil fuels have become increasingly acute, and thus developing the renewable energy resources represented by solar and wind energy to reduce our dependency on fossil fuels has been increasingly crucial [1–4]. In order to develop and utilize these renewable energy resources more effectively, various energy conversion and storage devices such as photovoltaic [5,6], photocatalysts [7–19], and supercapacitors [20–22], have been intensely studied in recent years. Since the photoelectrochemical splitting of water on TiO<sub>2</sub> in 1972 [23], capture and conversion of solar energy by semiconductors-based photocatalysts have received considerable attention in response to resolving energy and environmental crisis [11,24]. Nowadays, photocatalysis has been applied to nonselective processes for environmental remediation [12,13], selective organic transformations for synthesis of fine chemicals [14–16], reduction of CO<sub>2</sub> into hydrocarbon fuels [17–19], water splitting to hydrogen energy [7–9] and other photoelectrochemical processes [25–27]. However, one of the major obstacles associated with practical

applications of photocatalysis still is the lack of ideal semiconductor photocatalysts. It has been generally accepted that a perfect photocatalyst system should possess the following features: (1) an appropriate band gap (1.6–2.2 eV) and high absorption coefficient for efficiently harvesting sunlight; (2) suitable band alignment to satisfy the kinetic requirement of the targeted reaction; (3) high photocarriers mobility and long-lived charge separation; (4) chemical and photostability to anti-corrosion in reaction environments [10,28]. But it is extremely difficult to optimize single conventional semiconductors materials based on metal oxide constituent to meet all these requirements. Thus, it is still a challenge to design and construct a novel photocatalyst to surmount the incapacity to utilize visible light, insufficient quantum efficiency, and the possible photocorrosion of the conventional semiconductors-based photocatalysts [24].

Recently, synthesizing graphene (GR)-semiconductors composites toward specific photocatalytic reaction opens up a new promising pathway for the further development of photocatalysis [29–31]. As the first true two-dimensional (2D) material, GR has demonstrated many intriguing properties such as excellent transparency, high specific surface area, locally conjugated aromatic system, superior electron mobility, and high chemical and electrochemical stability [32–35]. Thanks to these extraordinary and superior properties, GR has already been regarded as an ideal co-catalyst to optimize the photocatalytic performance of semiconductors [28–32,36,37]. However, the poor dispersibility and irreversible agglomeration of primitive GR nanosheets in common solvents severely dilute its materials identification, which would further weaken the electrical conductivity, lower the surface area, optical transparency and mass transfer kinetics of GR [3,38–42]. Besides, as a zero-band gap semi-metal, GR cannot be directly used for fabrication of photoactive nanomaterials [43–46], where a suitable band gap is required. Given that the conductive, optical, absorptive, chemical, and mechanical properties of GR are closely linked to its architecture [47–49], designing and tailoring GR with desired size and morphology is of great importance to enrich its applications and enhance its performance in photocatalysis. Indeed, tremendous efforts have been devoted to this rapidly growing area, demonstrating that the tailored graphene materials (GMs) show a variety of fascinating features, which provide a fertile and flexible ground for the further development of GMs-enhanced photocatalysis [40,48,50–60].

There have been some excellent reviews on synthesis, physiochemical properties, functionalization and applications of individual GMs [3,8,28–36,38,45–48,60–80]. However, to the best of our knowledge, a more integral overview that focuses on their structural diversity of GMs in different dimensions and their tunable properties and multi-functionality in heterogeneous photocatalysis has not been available. In this review, we present a comprehensive overview of the recent progress in synthesis and photocatalytic applications of four typical GMs (Fig. 1), spanning from nanoscaled zero-dimensional graphene quantum dots (0D-GQDs), one-dimensional graphene nanoribbons (1D-GNRs), two-dimensional graphene nanosheets (2D-GR) to macroscaled three-dimensional graphene frameworks (3D-GFs) structure. At first, we provide an overview of these GMs in different dimensions, with particular emphasis placed on their structures, properties and synthesis methods. Then, we describe various strategies for controlled assembly of GMs with semiconductors to achieve composite photocatalysts, and subsequently summarize the multi-functionality played by GMs in diverse photocatalysis systems. At last, the perspectives on future research trends and challenges in the construction of GMs-enhanced systems for solar energy conversion are proposed. It is believed that the integral comprehension of GMs

with all dimensions and understanding their multi-functionality in photocatalysis would inspire sparking crossover contribution to precisely tailoring GR with desirable architecture and exploiting their full potential in heterogeneous photocatalysis.

## The structures and properties of GMs

### Initiation with 2D planar GR species

Graphene (GR), consisting of interconnected hexagons of carbon atoms as in graphite, has been considered to be the thinnest materials in the world [33], as well as the basic structural element of other graphitic carbon forms, including fullerenes, carbon nanotubes, and graphite [62]. It can be wrapped into zero-dimensional fullerenes with the introduction of pentagons, rolled along a specific direction into one-dimensional carbon nanotubes or stacked into three-dimensional graphite [62]. However, such a single layer of two-dimensional (2D) crystal structure of GR is also puzzling. This is remarkable because there has been a long-standing argument (Mermin–Wagner theorem) that the strictly 2D crystals are thermodynamically unstable and thus should not exist [81]. But the presence of GR can also reconcile this theory to some extent because GR structure studied so far usually has an intrinsic wrinkled surface and is deemed as an integral part of larger three-dimensional (3D) structures [62,63]. The corrugations in the third dimension and the strong  $sp^2$  C–C bonds existing in GR provide the possibility of thermodynamic stability for 2D-GR [64].

The unique long-range  $\pi$ -conjugation structure in GR yields some extraordinary physical properties, like high mechanical stiffness (1060 GPa) [65], excellent electrical ( $\sim 104 \Omega^{-1} \text{cm}^{-1}$ ) and thermal ( $\sim 3000 \text{ W/Mk}$ ) conductivity [66], and huge theoretical specific surface area ( $2630 \text{ m}^2/\text{g}$ ) [33,65]. Therefore, once appeared, GR has attracted much research attention from physicists, chemists and engineers [34,62]. The earlier works on GR include observations of ambipolar field effect [82], quantum Hall effect at room temperature [83], measurements of extremely high carrier mobility [84], and even the first ever detection of single molecule adsorption experiments [85]. These findings greatly promote the implementations of GR in myriads of devices [67,86]. Nowadays, GR has become an exciting multidisciplinary platform and triggered enormous research activities ranging from nanoelectronics to nanobiotechnology [32]. Nevertheless, the applied research and development of GR are challenged by issues of production, storage and processing [68].

Graphene oxide (GO) is an intermediary product involving the solution-phase isolation of GR species from graphite. The 2D-GO nanosheets are strongly hydrophilic and can generate a stable aqueous suspension due to the cover with epoxy, hydroxyl, and carboxyl groups on its panel and edge [69]. Besides, these oxygen-containing functional groups offer great opportunities for access to functionalized GR-based materials [87]. Thus, GO is often used as the precursor of GR species to construct GR-based composites. However, compared to semi-metallic pristine GR, GO is an insulator due to the formation of  $sp^3$  hybridized carbon atoms, which disrupt the extended  $sp^2$  conjugated network of the pristine GR nanosheets [88]. Although the intrinsic structural and electronic properties of graphene can be partially restored upon reduction of GO to yield reduced graphene oxide (RGO), the quick re-aggregation of RGO nanosheets into graphite while removing oxygen-containing functional groups is still the main problem [3]. Recent advances in the design and fabrication of tailored GMs offer great possibilities to offset these shortages [89,90]. In this context, a more comprehensive description for these GM is very urgent and desirable.

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