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Applications of Graphene in Catalysis

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Abstract

The extraordinary and unique physical, chemical, and mechanical properties of graphene have led to the development of graphene-based materials for a wide range of applications in different fields. Amongst, the use of graphene-based materials in the field of catalysis has attracted the interests of researchers in the last few years. Due to its extremely high surface area and adsorption capacities, graphene is expected to function as an excellent catalyst support material. Moreover, an ability to tune its structure using desired functionalities have added significant versatility for such materials in metal free catalyst systems. The interest is due to the activity and stability of graphene based catalysts through tailoring its structures/morphologies, catalytic performance, and design for synthesis, catalytic mechanisms. This editorial note summarizes the versatile applications of graphene-based catalysts in organic synthesis as a carbocatalyst, metal free catalysis, in photocatalysis, and as a catalyst support and provides an outlook on future trends and perspectives for graphene applications in sustainable catalysis.

Introduction

Graphene, the amazing two-dimensional carbon nanomaterial, has attracted extensive interest in recent years and emerged as the most intensively studied material [1]. In 2004, Geim and Nosovelov at Manchester University successfully isolated single layer graphene by the mechanical cleavage of graphite crystal [2]. This "thinnest" known material exhibits extraordinary electronic, chemical, mechanical, thermal and optical properties which bestowed graphene as a miracle material of the 21st Century. From applicative perspectives, graphene holds a great promise with the potential to be used as energy-storage materials, in nanoelectronics, in **catalysis**, biomedical, in polymer composites and many more [3-5].

Structurally, graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The high versatility of properties and numerous projected applications have triggered the development of graphene synthesis using various methodologies and substrates. Several production techniques for mass production of graphene encompassing bottom-up and top-down methods ranging from the mechanical exfoliation of high quality graphite to the direct growth on carbides or suitable metal substrates and from the chemical routes using graphene oxide have been developed [5]. Amongst, graphene derivatives i.e graphene oxide (GO) and reduced graphene oxide (RGO) obtained from chemical oxidation process contains substantial oxygenated functional groups that even after sufficient reduction, cannot be completely removed [6]. The resulting graphene oxide contains abundant oxygen functional groups on both the basal planes and edges (Figure 1). Similar to carbon nanotubes, these functional groups can offer a platform for various chemical reactions [7]. Hence, graphene offers a wide range of possibilities to synthesize graphene-based functional materials with potential in numerous applications including catalysis.

Recently, owing its surface decorated myriad oxygenated functions and conductivity with very high surface area, use of graphene materials either as metal-free catalysts or as supports for immobilizing active species for facilitating synthetic transformations is emerging as an area of great potential [8,9]. The boundless growth of graphene in catalysis has been evidenced by the number of annual publications on "graphene" and "graphene and Catalysis" as depicted in figure 2 which shows the annual number of publications using "Graphene" and "Graphene and Catalysis" provided using Scopus database. These numbers indicate the very rapid growth of graphene publications and the parallel growth of publications related to catalysis applications of graphene which accounts about a quarter of all graphene publication.

This advancement underlines the colossal potential of graphene to replace the precious metals used in common catalysts, and can be increasingly used in organic synthesis for various selective transformations of simple and complex molecules in time to come.

In the following sections we briefly shed light on applications of graphene materials in different field of catalysis and also discussed the current trends in the field.

Graphene as a Carbocatalyst

The use of heterogeneous carbon materials for the transformation or synthesis of organic or inorganic substrates are often termed as carbocatalysts. Recently, the use of metal free catalysts based on carbonaceous materials attracting a great deal of interest. Graphene based materials such as graphene oxide (GO) are considered as a new class of carbocatalysts and opened a series of novel application possibilities in chemical synthesis. Since, Bielawski and co-workers [10] demonstrated the ability of graphene-based materials to facilitate a number of synthetically useful transformations, the concept of "carbocatalysis" being widely explored and considered as an intriguing new direction in chemistry and materials science. The surface bound oxygenated functional groups on the aromatic scaffold of GO is believed to allow ionic and nonionic interactions with a wide range of molecules. Numerous transformation, including the oxidation of alcohols and alkenes into their respective aldehydes and ketones, as well as the hydration of alkynes have carried out using graphene as a carbocatalyst. Recent reviews by Garcia et al. [8] (Figure 3) and Loh et al. [11] comprehensively accounted a recent progress in the

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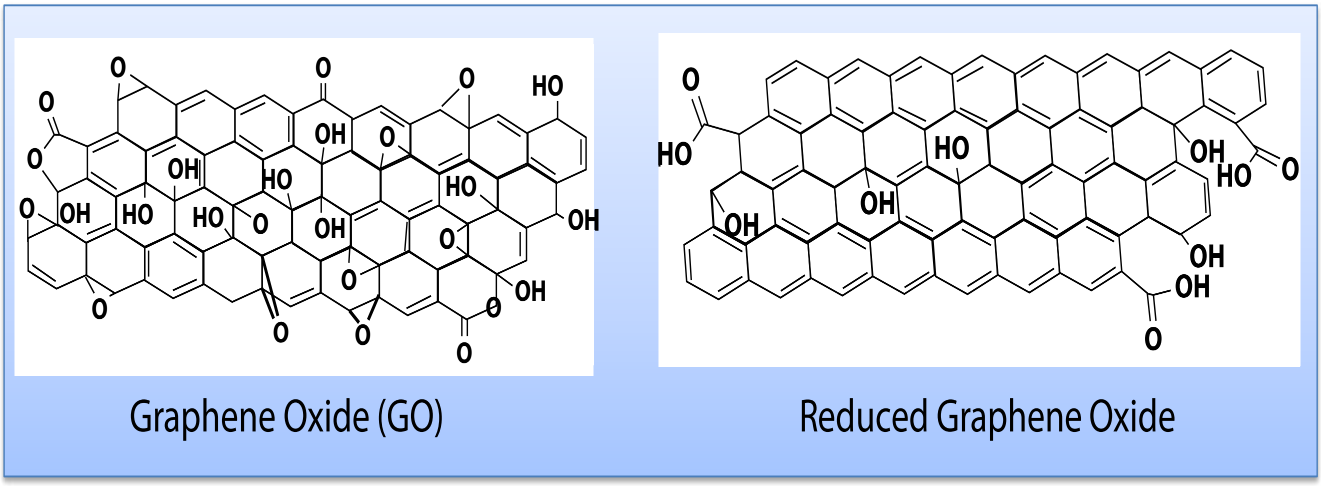

Figure 1: Structural model of single layer graphene oxide and reduced graphene oxide.

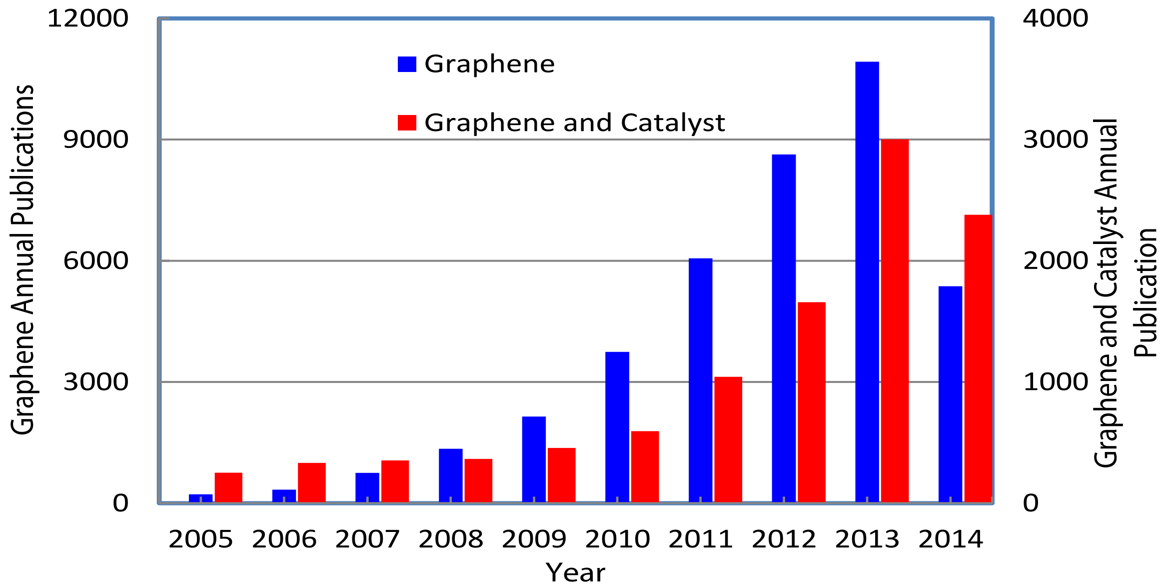

Figure 2: Annual Number of Publication returned from a Scopus Search using “Graphene” and “Graphene and Catalysis” as keywords.

field of graphene enabled carbocatalysis. It is observed that the GO with myriad oxygen atoms on its surface can function as an efficient oxidant during anaerobic oxidation and undergo reduction at the end of the first catalytic cycle. Moreover, reduced graphene oxides with its residual oxygenated species continue to activate molecular oxygen during aerobic oxidation.

Bielawski and co-workers have significantly contributed on use of graphene materials in various catalytic applications [12], including the oxidation of sulfides and thiols, C–H oxidation, Claisen–Schmidt condensation, polymerization of various olefin monomers, ring opening polymerization of various cyclic lactones and lactams, and dehydration polymerization in the synthesis of carbon reinforced poly (phenylene methylene) composites [13]. These contributions opened a fascinating and new catalytic approach, inspiring many researchers to explore graphene materials for catalytic performance in added catalytic transformations.

The demonstrated activity of graphene as a carbocatalyst can be further extended towards other methodologies by the exploitation of surface modifications and edge defects of GO. The structural features of graphene may offer a wide array of conversion and selectivity by tailoring the morphology and functionalities on the surface.

Doped Graphene in Catalysis

Graphene materials doped with different heteroatoms are also being explored as effective metal-free catalysts in various reactions [14]. Amongst, nitrogen (N) doped graphene have been extensively studied, the introduction of N considered to modify the local electronic structures of graphene which in turn facilitate the catalytic processes.

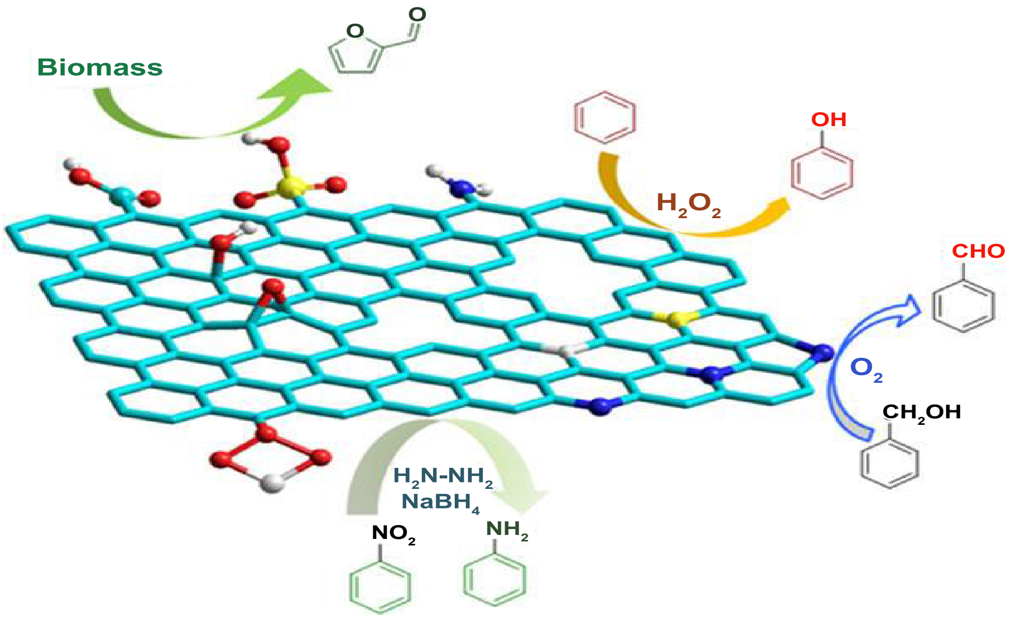

Figure 3: Various organic transformations catalyzed by graphene based carbocatalyst. Reprinted with permission from ref. [8]. Copyright 2014, American Chemical Society.

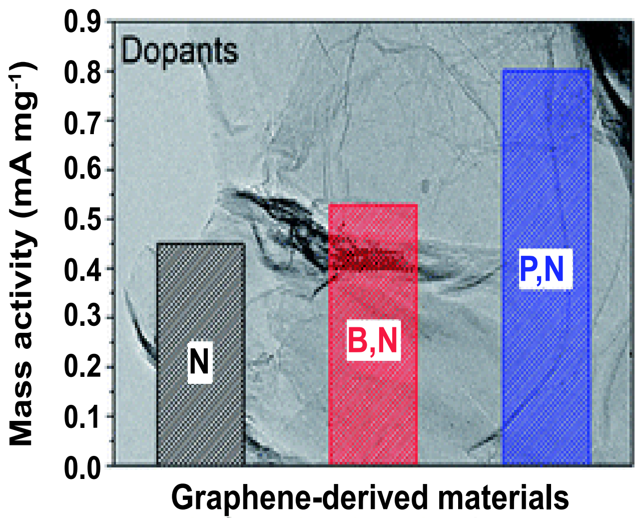

Figure 4: B, N- and P, N-doped graphene as highly active catalysts for oxygen reduction reactions in acidic media. Reprinted with permission from ref. [36]. Copyright 2013, Royal Scociety of Chemistry.

The N doping was commonly achieved by reacting GO with ammonia [15], aniline, lithium nitrides [16] or by direct CVD [17] and arc discharge methods [18]. Normally, the nitrogen insertion is in the form either direct substitution or in pyridinic, pyrrolic structures [19]. N-graphenes mostly found its applications in oxygen reduction reaction (ORR) associated with fuel cells [20-22]. Dai and co-workwers [23] demonstared that the N-graphene act as excellent metal free catalyst for (ORR) associated with alkaline fuel cells. The N-graphene exhibited a very high ORR activity through due to four electron transfer process which is observed to be comparable or even better than commercial Pt/C. N-graphene was also reported to exhibit high activity and selectivity for the oxidation of arylalkanes in aqueous phase, affording high value-added products for biomedical applications [24]. Other catalytic applications of N-graphene involve reductions of nitro compounds [25,26], peroxides [27] and oxidation of glucose [28] and benzyl alcohols [29].

Similar to N-Graphene, sulfur doped graphene was also used as a metal free catalyst with high stability and selectivity in ORR. Other catalytic applications of sulfated graphene involve esterification of acetic acid [30], dehydration of xylose [31] etc. S-graphene proved to be a good water tolerant catalyst with high activity for the hydrolysis reactions. In addition, doping of graphene by phosphorus [32], boron [33], silicone [34] iodine [35] or dual elements (Figure 4) [36] is also reported and demonstrated in various catalytic applications.

Graphene in Photocatalysis

Another important application of graphene based materials that are in photocatalysis. Various reactions, including degradation of pollutants, selective organic transformations and water splitting to clean hydrogen energy were accomplished using graphene as a photocatalyst Figure 4a [37]. Hence, it is clear that graphene can serve as a new family of promising photocatalysts. The hybridization of graphene with various metal photocatalysts can improve the photocatalytic performance owing to the extended light absorption range, high adsorption capacity, specific surface area and superior electron conductivity of graphene. Similarly, GO can be hybridized with organic dyes or organocatalysts to facilitate the photosensitization through charge transfer across the graphene interface to produce synergistic effects that enhance catalytic conversion.

Kamat and coworkers [38] revealed the viability of using a graphene as an electron-transfer medium. It was demonstrated that the graphene can store and transport the electrons through a stepwise electron transfer process. The electrons were photogenerated in TiO_2 and then transferred to GO; then, part of these electrons were involved in the reduction of GO, whereas the remaining were stored in the rGO sheets; finally, upon introduction of silver nitrate, the stored electrons were used to reduce Ag^+ to Ag^0. Hence, graphene could be regarded

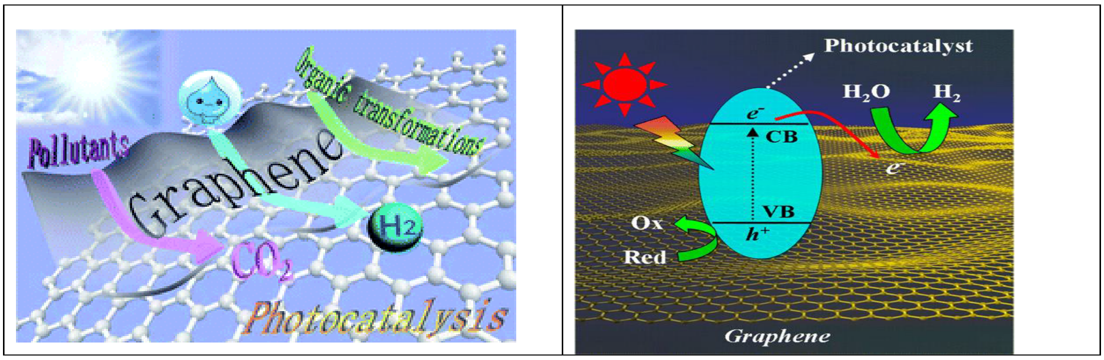

Figure 5: The use of Graphene in a. photocatalysis Reprinted with permission from ref. [37]. Copyright 2012, Royal Society of Chemistry. and b. hydrogen generation. Reprinted with permission from ref. [40]. Copyright 2013, American Chemical Society.

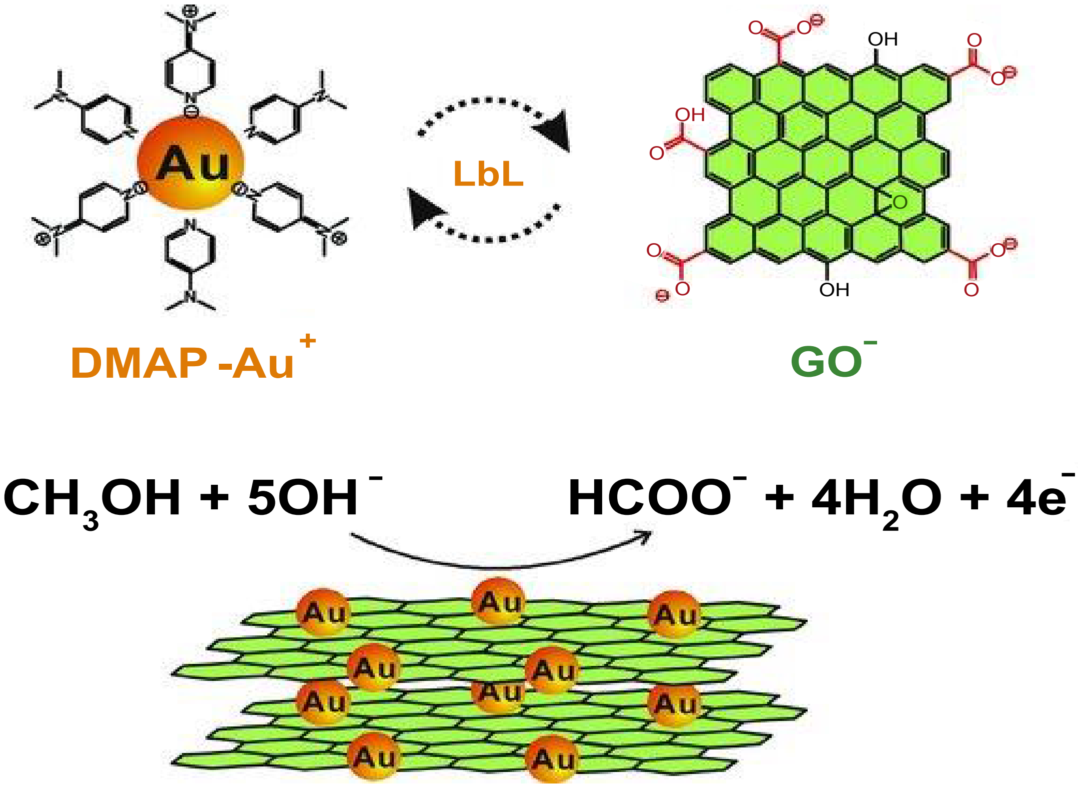

Figure 6: Schematic of methanol oxidation by gold nanoparticle supported GO. Reprinted with permission from ref. [42]. Copyright 2012, WILEY-VCH Verlag.

as an effective tool to be used in the prevention of electron–hole recombination by accepting and transporting photoelectrons. Other possible applications of graphene-based materials in photocatalysis involve mainly the degradation of pollutants [39], and water splitting for hydrogen generation as shown in figure 5 [40].

Graphene as a Catalyst Support

In addition to their activity as a carbocatalyst, graphene based materials are widely used as supports for catalytically active transition metals. Plethora of reactions is being catalyzed using different metal nanoparticles [41]. However, some obstacles are still remaining such as irreversible aggregation during electrocatalytic cycles, leading to a significant loss of nanoscale catalytic effect. Hence, proper catalyst support needed to preserve the intrinsic surface properties. Owing to their extremely high specific surface area which improves the dispersion of the catalytic metals, improved chemical and electrochemical stability at operation temperatures, enhanced electronic conductivity, graphene based materials are appealing choice as catalyst support. Hence, graphene offers a perfect platform for catalytic molecular engineering. In one such example, Kim and co-workers [42] demonstrated that gold nanoparticles (Au NPs) dispersed on graphite oxide were able to catalyze methanol oxidation (Figure 6). It is demonstrated that the GO nanosheets not only serve as structural components of the multilayer thin film, but also potentially improve the utilization and dispersion of Au NPs by taking advantages of the high catalytic surface area and the electronic conduction of graphene nanosheets. Similarly, graphene has been used as a support for various metal oxides (ZnO, TiO_2, MnO_2, Fe_2O_3, Co_2O_4 etc) [43] and nanoparticles (Pt, Pd, Ag, Au or alloys) [44-49] to fabricate hierarchical catalyst systems.

Future Perspectives

Although in its nascent stage, graphene based materials hold great promise for facilitating a wide range of transformations and may offer extraordinary potential in the design of novel catalytic systems. Considering the added value that these materials could have as catalysts, their affordability, and the sustainability of their use compared to metal-based catalysts, it can be easily anticipated that this area will grow considerably in years to come. However, associated challenges implicates severe aggregation and restacking of graphene nanosheets dominated by π–π stacking interactions, and the low stability of supported nanocatalysts due to compatibility issues between graphene and nanocatalyst. Moreover, higher surface energies of such metallic catalysts may deprive the synergistic effect with graphene in effective catalysis. Further research is also needed to identify an optimized catalyst structure/morphology, newer, cost-effective and environmentally friendly method for the synthesis of graphene.

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