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Review

Metal-free graphene-based catalyst—Insight into the catalytic activity: A short review

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ABSTRACT

For responding to the rapidly increasing trend of research on carbocatalyst, an emerging metal-free all carbon-based catalyst, we present here a timely short review article to summarize some relevant state-of-the-art contributions, to find the bottleneck of the research in the current stage, and to offer a guideline for rational exploration and design of a high-performance graphene-based carbocatalyst for a specific catalytic reaction. Special emphasis is brought to the aspects of what make graphene-based carbocatalysts active for many kinds of synthetic transformations, such as reduction and oxidation reactions. Due to the importance of active species identification for graphene materials in the field of carbocatalysis, the possible active sites on the surfaces of graphene and its related materials are summarized and presented schematically as a general model, which can shed light on the mechanistic study on the catalytic performance of graphene-based carbocatalysts. Moreover, the difference between oxygenated graphene and reduced graphene oxide are specially reviewed and analyzed in terms of the relationship between their respective unique structures and catalytic performances. Finally, a conclusive model map is provided for combining the respective catalytic reaction models with the corresponding probable active sites on the surfaces of graphene-based carbocatalysts. The article presented here is expected to advance research on the biocompatible, sustainable, low-cost, scalable and green graphene-based carbocatalysts as promising alternatives to the metal-based catalysts that are being under excessive exploitation despite their scarcity, high cost and relative environmental unfriendliness, especially the noble metallic materials.

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1. Introduction

Up to 90% of all commercially available chemical products involve using catalysts at certain production stage [1], reflecting the pivotal role that the catalytic materials are playing in various industries. The catalytic materials have already made significant contributions to the human development, and will continue to bring increasing scientific, economic, environmental and even social benefits with the advance of science and technology. To date, the most widely explored catalytic materials have been concentrated on the transition metals and metal oxides, hybrid materials or composite structures with the active metallic centers,

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and organometallic compounds [2–13]. It is worth pointing out that active metallic particles, especially the nano-structured ones, are ready to aggregate due to their high surface energy, which leads to the decrease of the accessible active surfaces and hence degradation of the catalytic activity. Besides, particle leaching is another serious problem for the hybrid structures containing the active transition metal and metal oxide particles [14]. Such leaching not only decays the catalytic properties of the catalytic materials but also causes secondary environmental pollution. Moreover, it should be recognized that many metallic resources on earth are becoming scarce, especially the noble metallic materials, as caused by the excessive exploitation from the rapidly developing modern industries. It is therefore highly desirable to explore promising catalytic alternatives being metal-free, low-cost, scalable and sustainable in order to alleviate the heavy dependence on the metallic resources for many catalytic reactions, which can thus help to balance the exploitation, to stabilize the metallic resources on earth, to reduce the environmental pollution caused by heavy metals, and to maintain ecological balance. As a result, increasing attention has turned to metal-free catalysts, particularly the carbon materials because they are biocompatible, inexpensive, stable, environmentally friendly and readily available [1,15,16].

Since the ground-breaking work by Novoselov and Geim who provided a simple yet effective micromechanical exfoliation method for peeling off graphene from graphite and explored its unique electrical properties, graphene and other two-dimensional sp^2-hybridized carbon nanomaterials have become tremendously popular in the areas of modern physics, chemistry, and materials science and engineering [17,18]. The significant impact of these materials on different scientific disciplines is attributed to their extraordinary physical and chemical properties such as the huge specific surface area (up to $\sim$2600 $m^2\,g^{-1}$), and remarkable electrical, thermal and mechanical properties of graphene materials [19–22].

Accompanied by the exploration of graphene properties, many feasible routes have been developed to prepare various kinds of graphene materials, which can be classified roughly into top-down and bottom up methods [23]. Among them, the top-down graphite oxide exfoliation method is regarded as the most feasible one for industrial scale production of graphene material because it uses naturally abundant, low-cost graphite as the raw material, and has much higher production yield as compared to other top-down methods such as micromechanical cleavage [17] and liquid-phase exfoliation [24]. Additionally, the fascinating oxygenated graphene or graphene oxide (GO) before converted to reduced graphene oxide (r-GO) is an equally important product to r-GO, rather than simply regarded as a precursor to r-GO and its derivatives [25], due to the abundant active sties on GO surfaces that can be harnessed in a versatile manner for various kinds of modification, functionalization and applications. Even though some fascinating properties of GO are severely impaired such as the electrical conductivity, thermal stability and chemical resistance, the abundant oxygen-containing functional groups on the GO surfaces provide rich chemical properties; *e.g.*, affording an attractive platform to tether other catalytically active species such as amine and sulfonic groups [26]. These indicate a great adaptability of GO to many promising applications such as high-performance composites [27], drug-release control materials [28,29], adsorbents [30], catalyst supports [31,32], and intrinsic catalysts on its own [33–36].

On another hand, the graphene material converted from GO has been demonstrated to possess much more structural defects and remaining oxygen functionalities [37,38] as compared to those prepared by bottom-up methods such as chemical vapor deposition (CVD) and epitaxial growth [39], and by some other top-down methods such as micromechanical delamination [17] and liquid-phase exfoliation of graphite [24]. Owing to such unique structures with many beneficial active sites, the graphene derived from GO is much more suited as the carbocatalysts for many kinds of synthetic transformations relative to other kinds of high-quality graphenes such as CVD-graphene and mechanically cleaved graphene [16,40]. More importantly, considering the superiority of low-cost and large-scale production, the GO- and r-GO-based carbocatalysts hold great potential for real-world applications in many industries involving catalytic reactions.

Although GO and its related materials such as r-GO and functionalized graphene have been explored extensively as the supports for various semiconductor and metal nanoparticles, and this is still a hot topic [41–55], especially for applications in catalysis [44–47,49–53,55], the graphene moiety in these hybrid or composite materials is not considered as the catalytically active component in the presence of the catalytically active nano-crystals intimately covered on graphene surfaces. It is also worth pointing out that employing graphene materials as the metal-free carbocatalyst to accelerate synthetic transformations is a relatively new area with enormous potential [18]. In particular, exploration of the catalytic mechanism for a variety of transformation reactions with metal-free graphene-based catalysts is still in its infancy and much work remains to clarify the active sites for specific catalytic reactions. Moreover, the non-stoichiometric and inhomogeneous nature of GO poses a substantial challenge to unravel the underlying mechanism of the catalytic activity of GO. This also indicates the sensitivity and uncertainty of the counterpart r-GO, making it difficult to establish the relationship between the structure and catalytic properties since they are varied with reduction conditions. Specifically, the final structure, morphology and properties of r-GO can be affected by the reduction method adopted, the type of reducing agent, addition ratio and concentration of reactants, reaction temperature and pressure, pH condition, sonication condition, reaction time, *etc.* As another variable affecting the structure and properties of r-GO, the parameter of the precursor GO should also not be ignored, such as oxidation extent, surface area and density of specific oxygen groups [25]. In these regards, big challenges but also opportunities are presented for research communities to explore and deeply understand the mechanism of carbocatalysis that is an intriguing and promising research direction in the area of graphene-based catalysis. The deep mechanistic understanding can subsequently facilitate further work on controllable and effective isolation of the active sites on the graphene surfaces, selective removal of the undesired active sites from the surfaces of graphene in a controlled manner, and flexible creation of desired active sites on the graphene surfaces using chemical, physical, thermal, electrical, electrochemical, optical, acoustic method, or the combined two or more thereof. High-performance graphene-based carbocatalysts can thereby be designed for specific catalytic reactions with high efficiency and selectivity. It is worth mentioning that the importance of active site isolation on the heterogeneous catalyst surfaces has also been emphasized by Védrine in his latest review article, with the detailed case studies of metal oxide catalysts to exemplify the concepts [3]. All in all, more effort needs to be invested in the research and development of the sustainable, eco-friendly, cost-effective and scalable graphene-based carbocatalysts for various synthetic reactions in order to realize the real-world applications of the carbocatalysts. If so, at least part of precious metallic catalysts will be saved from the excessive exploitation, and environmental pollution caused by heavy metals will be reduced.

2. Graphene and its related materials as metal-free catalyst

Here, we highlight some important work dedicated to exploring graphene-based materials as carbocatalysts, including GO, r-GO, and functionalized graphene, as well as graphene allotropes