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## Progress on the graphene-involved catalytic hydrogenation reactions

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## ABSTRACT

Graphene is a hot topic in many research fields due to its outstanding physicochemical properties. It is also a new carbon catalyst support after activated carbon, carbon nanotube, fullerene and mesoporous carbon. In the present article, we focused on the application of graphene in the field of catalytic hydrogenation, summarized the preparation and characterization of graphene, and discussed the advantages and disadvantages of graphene as a catalyst support and metal-free catalyst. Some factors that may affect the catalytic hydrogenation activity have also been discussed in detail.

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## 1. Introduction

The application of graphene in materials science, condensed-matter physics [1], and catalysis science [2] has been rapidly developed since its first synthesis in laboratory by Novoselov et al. [3] in 2004. It is considered as a new-generation carbon support material for heterogeneous catalysts compared with activated carbon, carbon nanotubes, fullerene and mesoporous carbon because of its excellent physical and chemical properties, such as large specific surface area, conjugated  $\pi$ -bond system, strong hydrophobicity, thermal stability, acid and alkali resistance, and easy chemical functionalization [4–6].

The main purpose of this paper is to review the current progress on the graphene-involved catalytic hydrogenation, including (1) the fabrication and characterization of graphene, (2) the inherent, functionalized and doped graphene-involved catalytic hydrogenation reactions, and (3) discussions on some key topics such as stability of graphene, interaction between metal and graphene, stability of supported metal, specific surface area of graphene and metal size control, which may be helpful to the development of graphene in the hydrogenation field.

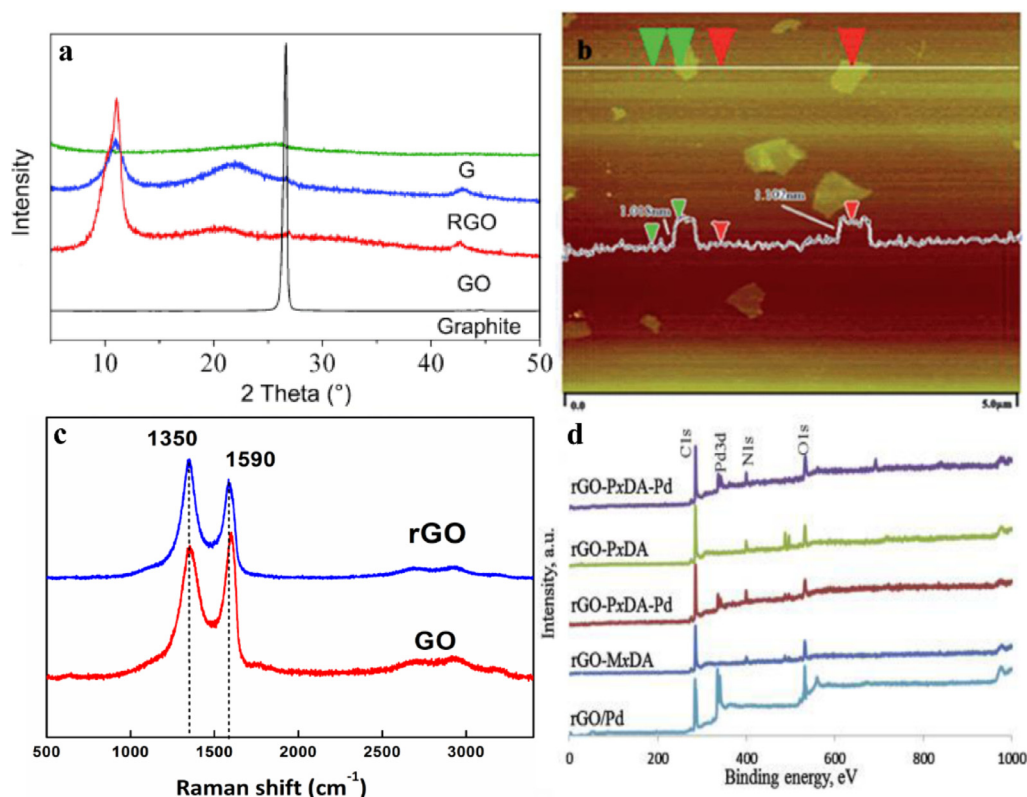
## 2. Preparation and characterization of graphene

## 2.1. Preparation of graphene

Generally, there are several methods to obtain graphene nanosheets, (1) mechanical exfoliation method is to strip highly oriented pyrolytic graphite to get graphene sheets, which can be achieved through various strategies such as scotch tape stripping, laser pulses method, mechanical cutting, and high efficiency grinding, and mechanical ablation of pencil lead [6–13]. (2) Liquid-phase exfoliation of graphite to graphene is conducted in certain solvents, such as water, ammonia, THF, tetrabutylammonium hydroxide, *N,N*-dimethylformamide, and *N*-methyl-2-pyrrolidone [14–18]. The penetration of the solvents into the graphite layers will decrease the interaction between them. Therefore, graphene sheets could be obtained by some highly intensive ultrasonic technique or microwave irradiation [14,17]. (3) Chemical vapor deposition (CVD) is to grow graphene on substrates such as Ni [19,20], Ir [21,22], Cu [23,24], Ru [25,26] and alloy [27]. Specifically, the substrate is exposed to volatile carbon precursors (gaseous CH<sub>4</sub> [19,28,29], propene [30], solid polymethyl methacrylate [31], polystyrene [32], polyacrylonitrile [33], and so on), which will decompose because of the high temperature and/or metal catalysis. And then the desired graphene with large area and high quality is produced on the substrate's surface [34]. (4) Chemical reduction method comprises three steps: the oxidation of graphite to graphite oxide, the subsequent exfoliation to separated graphene oxide (GO), and the reduction to reduced graphene oxide (rGO) eventually. (5)

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**Fig. 1.** (a) XRD patterns of GO, rGO and graphite [59]; (b) AFM images of GO [63]; (c) RAMAN spectra of rGO and GO; (d) XPS spectra of rGO [155]. Reprinted with permission from ref. [59] © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, [63] Copyright © 2013, Royal Society of Chemistry, and [155] Copyright © 2015 Elsevier.

Epitaxial growth method is also used to synthesize high-quality and large-area graphene sheets via ultrahigh vacuum annealing of single-crystal silicon carbide [35–37]. Under the harsh conditions, Si on the surface will firstly sublime, leaving excess carbon to form graphene nanosheets self-assembly. (6) Many other methods, such as longitudinal unzipping of carbon nanotubes [38–40], arc-discharge method [41–43], electrochemical synthesis [44,45], etc., have also been developed to fabricate graphene. But in general, chemical reduction method has been the most widely used to prepare-involved catalysts for the catalytic hydrogenation due to its simple and convenient processes [46].

There are three typical chemical methods nominated by different oxidants used to prepare graphene oxide from graphite as follows: Brodie method [47–49], Staudenmaier method [50] and Hummers method [51–53]. Brodie method utilizes KClO<sub>3</sub> and HNO<sub>3</sub> to oxidize graphite; Staudenmaier method uses HNO<sub>3</sub>, KClO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> as oxidants; while Hummers method chooses KMnO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> as oxidants. With the in-depth study on the preparation of graphene oxide, scientists turned to use facile KMnO<sub>4</sub> instead of the dangerous explosive KClO<sub>3</sub>. Therefore, Hummers method has been the most widely used because it was a safer and more efficient method to produce graphene oxide. After reduction of graphene oxide by some reducing agents such as NaBH<sub>4</sub> [54], ethylene glycol [55,56], and hydrazine [57,58], or by microwave radiation [59] or thermal deoxygenation [60], the formed graphene can be applied as an ideal metal catalyst support for hydrogenation reactions.

## 2.2. Characterization of graphene

The characterization of a catalyst using modern analysis techniques is a common strategy to explore the relationship between the structure and activity of the catalyst. By this means, the unique

physico-chemical characteristics of a graphene material can be identified clearly to determine the formed structure and its effects on the catalytic performance.

In a typical XRD (X-Ray Diffraction) pattern of graphene oxide (Fig. 1a), a strong diffraction peak at 10–13° represents the oxidation degree of the graphene nanosheets: generally, the lower the diffraction angle, the higher the oxidation degree [55,61]. After reduction of GO to rGO, the diffraction peak at 10–13° disappears while a new peak forms at 25–27°, which stands for two important parameters for rGO layers: the layer-to-layer distance (also known as *d*-spacing, about 0.335–0.384 nm [61,62]) and the average number of layers. They can be roughly estimated by the Bragg equation ( $d = \lambda / 2 \sin \theta$ ) and Scherrer equation ( $\tau = K \lambda / \beta \cos \theta$ ), respectively, where  $\lambda$  is the X-ray wavelength,  $\theta$  is the Bragg angle,  $\tau$  is the mean size of the crystalline domains,  $K$  is the shape factor, and  $\beta$  is full width at half maximum intensity (FWHM) in radians [61]. Furthermore, the *d*-spacing of rGO can also be obtained from TEM (transmission electron microscope) observation and simulation calculation [61,62]. AFM (atomic force microscopy) is another powerful tool for layer measurement, by which the area, thickness, surface topography and atomic component can all be measured (Fig. 1b) [63].

Raman spectroscopy is a powerful characterization technique to detect the structural deformation of graphene [64], which can be generally featured as D band and G band in a Raman spectrum. The D band at 1300–1400 cm<sup>-1</sup> is attributed to structural defects and other disordered structures such as the functional groups on the graphitic plane. While the G band at 1560–1620 cm<sup>-1</sup> arises from the E<sub>2g</sub> vibrational mode at the Brillouin zone center existing in the sp<sup>2</sup> bonded graphitic carbons (Fig. 1c). The intensity ratio I<sub>D</sub>/I<sub>G</sub> thus provides a gauge for the comparison of structural defect degree and the quantitative measure of edge plane exposure. Graphene materials with higher I<sub>D</sub>/I<sub>G</sub> are more beneficial

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