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Regular Article

Three-dimensional nitrogen-doped graphene foam as metal-free catalyst for the hydrogenation reduction of *p*-nitrophenol

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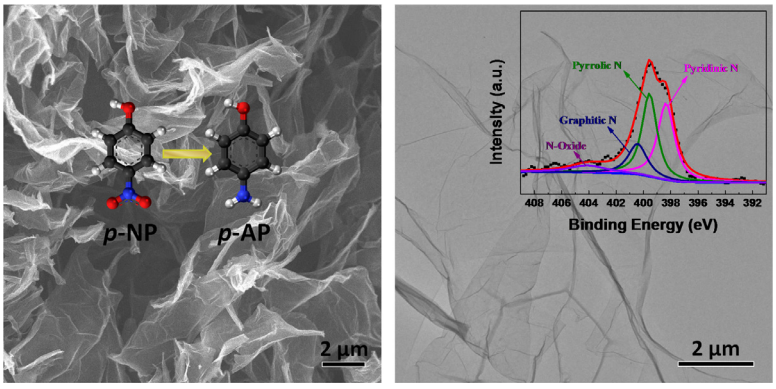
GRAPHICAL ABSTRACT



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ABSTRACT

Developing metal-free catalysts for various applications has been the focus of high interest over the past decade, especially aiming to replace the expensive noble metal-based catalysts. Herein, a well-defined three-dimensional nitrogen-doped graphene foam (3D-NGF) is synthesized and employed as a metal-free catalyst for the hydrogenation reduction of *p*-Nitrophenol to *p*-Aminophenol. The apparent activation energy is calculated, and the reaction mechanism with 3D-NGF as the catalyst for the hydrogenation reduction of *p*-Nitrophenol is proposed. Importantly, the 3D-NGF demonstrates high catalytic activity and robust stability. The high activity can be ascribed to the synergistic effect between the nitrogen-doping induced change in electronic property and the 3D foam-like structure.

1. Introduction

p-Nitrophenol (*p*-NP) is a common organic pollutant in the industrial wastewater, but it can be the raw material for the synthesis of *p*-Aminophenol (*p*-AP). The latter is a very important intermediate in the pharmaceutical industry and can be applied for the production of medicines, such as paracetamol, phenacetin and acetanilide [1,2]. Therefore, converting the harmful side product *p*-NP into *p*-AP is of high interest to reduce the pollutant and simultaneously generate value-added product. Recently, great attention has been paid to the catalytic reduction of *p*-NP to *p*-AP owing to its effectiveness [3,4]. The commonly used catalysts usually contain metals, especially precious metals such as Au, Pt, Pd

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and Ag [5–10]. However, the noble metals are rare and expensive, hampering their practical applications on a large scale. Therefore, it is highly desirable to develop cost-effective metal-free catalysts for the hydrogenation reduction of *p*-NP.

In fact, metal-free catalysis currently has been proposed and developed rapidly in various research areas including electrocatalytic water splitting into hydrogen and oxygen, and oxygen reduction reaction in order to avoid the use of expensive metal-based materials [11–13]. Among them, carbonaceous materials have attracted much attention owing to their earth abundance, high stability and good conductivity. Specially, graphene, a two-dimensional sp^2 carbon network with unique electrical, thermal, optical and mechanical properties, has been intensively studied for these purposes [14–16]. Pristine graphene generally exhibits low catalytic activity, while structure engineering via so-called heteroatom doping with nitrogen, sulfur and/or boron will endow graphene with extraordinarily high activity. It is believed that introduction of heteroatom into the framework of graphene can effectively modulate the charge distribution of graphene and dramatically increase active sites [12,17,18]. For the hydrogenation reduction of *p*-NP with metal-free catalysts, conventional nitrogen-doped graphene sheets have been verified to be promising candidate catalysts [19–21]. However, just as demonstrated in our previous studies [22,23], materials with the same chemical compositions but different morphologies and microstructures can result in substantial difference in catalytic performance. Hence, morphology control opens another avenue to the design of materials with desirable properties. In this study, we report on the synthesis of a well-defined three-dimensional nitrogen-doped graphene foam (3D-NGF) which can function as a very efficient and stable metal-free catalyst in the hydrogenation reduction of *p*-NP. To the best of our knowledge, this is the first report regarding nitrogen doped graphene with 3D structure for the application in hydrogenation reduction of *p*-NP. The 3D structure can effectively prevent the graphene from aggregating together, and thus offers a high effective interface for the reduction reaction to occur. The 3D-NGF thus presented a high activity comparable to the metal catalysts and better than the conventional nitrogen-doped graphene sheets. In addition, the apparent activation energy was calculated, and the reaction mechanism was proposed.

2. Experimental

The chemically exfoliated graphene oxide used in this work was prepared according to the modified Hummers' method [24]. All the reagents were used as received without further purification. In a typical experiment, 2.0 g natural graphite powder was added to 70 mL sulfuric acid in a flask under vigorous agitation, followed by the addition of 2.0 g sodium nitrate at room temperature. The mixture solution was then cooled down to 0 °C in an ice bath. Thereafter, 8.0 g potassium permanganate was slowly added into the mixture. The rate of addition was carefully controlled to keep the reaction temperature lower than 20 °C. The mixture was kept stirring for 2 h at 35 °C. After that, 100 mL of deionized (DI) water

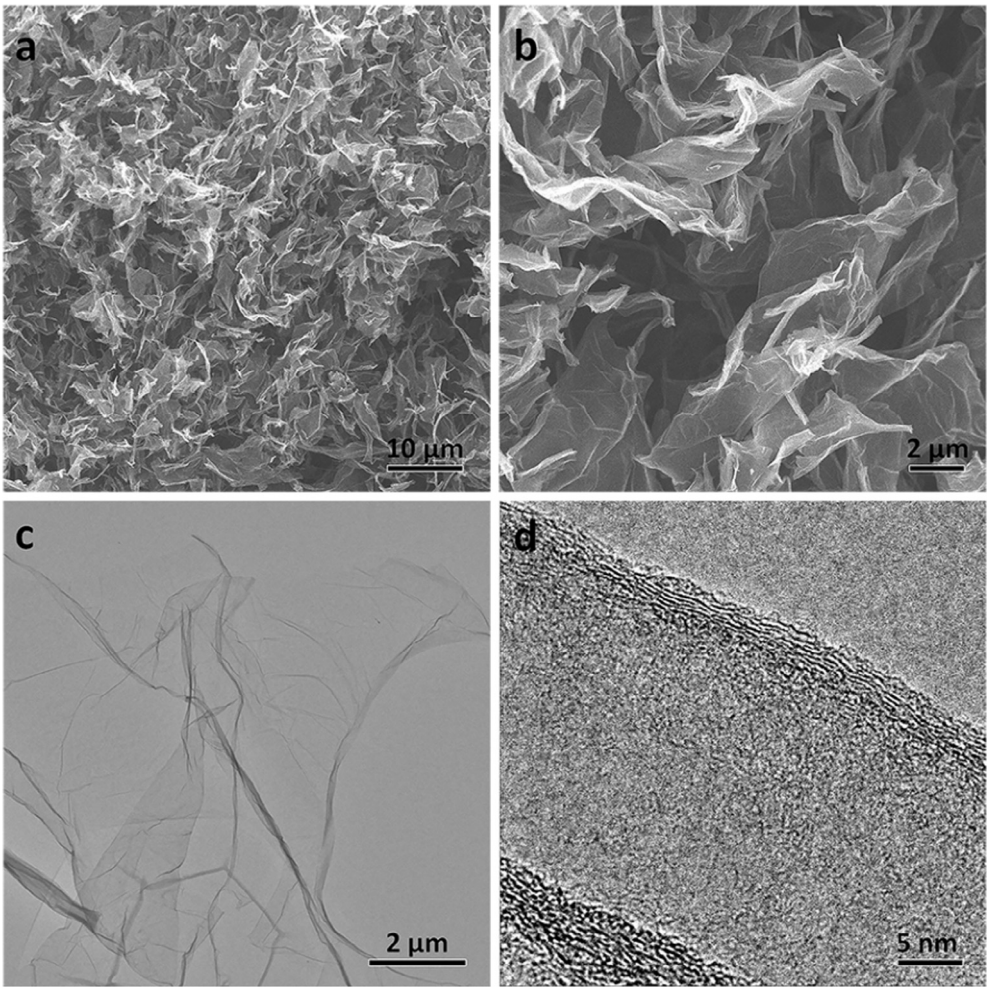

Fig. 1. Representative SEM (a and b) and TEM (c and d) images of the prepared 3D-NGF.