



# One-step amine modification of graphene oxide to get a green trifunctional metal-free catalyst



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## ABSTRACT

Graphene oxide is modified by diethylenetriamine through a one-step route to prepare GO-NH(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> (GO-DETA), which has primary and secondary amino groups and carboxyl groups. GO-DETA is characterized by Fourier transform-infrared spectrum (FT-IR), X-ray diffraction spectroscopy (XRD), thermo-gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The catalytic performance of obtained GO-DETA is investigated in Knoevenagel condensation and Michael addition in water; the results show it can be used as an efficient and stable catalyst. In addition, it has other features, such as simple preparation, good recyclability and environmental friendliness.

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## 1. Introduction

Transition metals, particularly noble metals, have played a major role as catalysts for C–C bond formation in synthetic organic chemistry over the past two decades. However, these catalysts have some disadvantages, including energy-consuming, resource-wasting, sometimes lowly selective, high cost and detrimental effects on the environment [1,2]. Therefore, it is highly desirable to develop metal-free catalysts with high performance. Over the years, a lot of different types of metal-free catalysts have been exploited, ranging from zeolites [3], ion-exchange resins [4], ionic liquids [5] to silica gel [6].

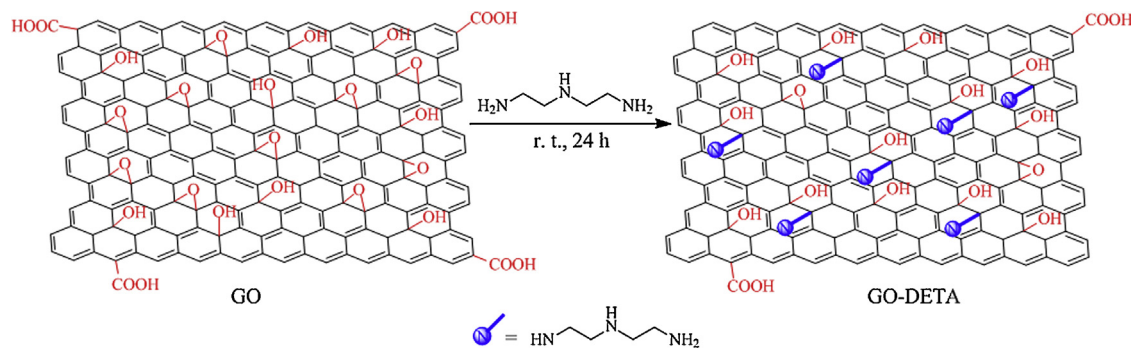
Carbon nanomaterials have been ideal candidates for metal-free catalysts due to their inexpensiveness, easy availability, environmental friendliness and unique surface properties. As carbocatalysts, fullerenes [7], carbon nanotubes [8] and graphite [9] have been reported over the past few years. Recently, graphene oxide (GO), the precursor of graphene, has attracted enormous attention due to its huge surface area, unique two-dimensional structure and outstanding mechanical properties. GO has a wide range of oxygen functional groups on its surface, which allows

GO to function as a green oxidant [10–12] or a metal-free catalyst [13–20]. Moreover, the aromatic scaffold and high surface area of GO provide a template to anchor active species for catalysts [21–23]. The most fascinating property of GO is its modifiable surface properties derived from the active oxygen-containing functional groups on its surface. Therefore, chemically functionalized GOs have been studied widely in recent years and some of them could be applied to various organic transformations as effective catalysts. For example, sulfated GO was used as an efficient solid acid catalyst [24–26], amine-modified GO was employed as a base catalyst [27–30] and bifunctional GO could serve as an acid–base catalyst [31–33]. However, the previously reported preparation methods of catalysts often have complex modification processes or harsh conditions, which may destroy the integrity of GO. For instance, Fan et al. obtained sulfonated graphene through radical addition [24]; Zhang et al. got amino-grafted graphene oxide subjected to hydrothermal treatment at 333–453 K for 3 days [29].

In this study, we demonstrate a moderate and economical route to functionalize GO by diethylenetriamine (DETA) through ring-opening reactions of epoxy groups on the surface of GO at room temperature (Scheme 1). This provides a new method to get a metal-free catalyst and the as-obtained GO-NH(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> (GO-DETA) shows high catalytic activity for Knoevenagel condensation and Michael addition in water (Scheme 2).

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**Scheme 1.** Schematic description for the preparation of GO-DETA.

## 2. Experimental

### 2.1. Materials

Natural graphite powder (325 meshes) was bought from Alfa Aesar.  $\text{H}_2\text{SO}_4$  (98%), potassium permanganate, sodium nitrate, hydrogen peroxide (30 wt%), HCl (38%), benzaldehyde, acetophenone, and malononitrile were obtained from commercial sources and used without further purification.

### 2.2. Apparatus and characterization

FT-IR spectra (KBr) were recorded on a Bruker ALPHA spectrophotometer in the range of  $400\text{--}4000\text{ cm}^{-1}$ . X-ray diffraction (XRD) measurements were performed using a D/MAX-2500 X-ray diffractometer with  $\text{Cu K}\alpha$  radiation. TEM images were carried out on a JEOL 2100F microscope. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI5000VersaProbe with  $\text{Al K}\alpha$  X-ray source. Thermogravimetric analysis (TGA) was recorded by a NETZSCH STA 409 PC/PG under a heating rate of  $10^\circ\text{C}/\text{min}$  and a nitrogen flow rate of  $2\text{ cm}^3/\text{min}$ . Transmission electron microscopy (TEM) analyses were conducted using a JEM-2100F electron microscope at 200 kV and the samples for the TEM measurements were prepared by one drop casting on a lacey copper grid followed by evaporation of the solvent in the air at room temperature.

### 2.3. Preparation of GO

GO was prepared from natural graphite by modified Hummers method according to previous report [34]. In a typical procedure, natural graphite (3.0 g) and  $\text{NaNO}_3$  (1.5 g) were added to a three-neck flask which contained  $\text{H}_2\text{SO}_4$  (69 mL) and kept the temperature below  $5^\circ\text{C}$  in the process. Next,  $\text{KMnO}_4$  (9.0 g) was added

to the flask and the temperature was maintained below  $20^\circ\text{C}$ . Subsequently, the reaction system was reacted for 7 h at  $35^\circ\text{C}$ . After that, another batch of  $\text{KMnO}_4$  (9.0 g) was slowly added to the flask. Then the reaction system continued to react for 12 h at this temperature. Finally, the mixture was cooled to room temperature and then diluted by 400 mL of ice water, followed by the slow addition of 3 mL of 30% aq.  $\text{H}_2\text{O}_2$ . A golden yellow dispersion was obtained and washed repeatedly with  $\text{H}_2\text{O}$  (200 mL) and 40% aq. HCl (400 mL) to remove the remaining salt. Lastly, the solid was vacuum-dried for 24 h.

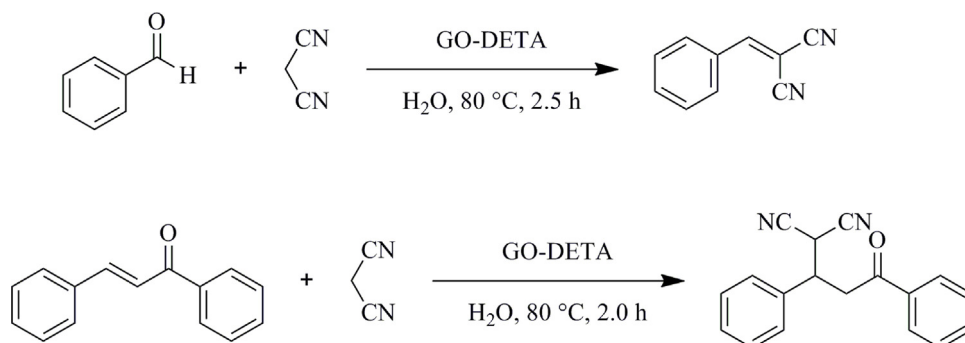
### 2.4. Preparation of GO-DETA

GO (100 mg) and diethylenetriamine (1.0 g) were dispersed in 100 mL 95% ethanol. Next the mixture was sonicated for 40 min at power level of 100 W using KQ3200DE ultrasonic apparatus. Then the mixture was under stirring for 24 h at room temperature. Subsequently, the suspension was filtrated, washed several times with ethanol, methanol and acetone and then dried in the vacuum overnight to get  $\text{GO-NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$  (GO-DETA).

### 2.5. Catalytic reactions of GO-DETA

GO-DETA is first tested as a catalyst for the Knoevenagel condensation. In brief, into a round-bottomed flask were placed 0.21 mmol of total amines, benzaldehyde (1.0 mmol), malononitrile (1.1 mmol) and water (3 mL). The mixture was stirred at  $80^\circ\text{C}$  for 2.5 h.

GO-DETA is further tested in Michael addition. In brief, a round-bottomed flask equipped with a magnetic stirring bar was charged with 0.48 mmol of total amines, 1 mmol of (*E*)-chalcone and 1.5 mmol of malononitrile and water (3 mL). The mixture was stirred at  $80^\circ\text{C}$  for 2 h.



**Scheme 2.** Knoevenagel condensation and Michael addition catalyzed by GO-DETA.

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