



# Maghemite/nitrogen-doped graphene hybrid material as a reusable bifunctional catalyst for glycolysis of polyethylene terephthalate



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## ABSTRACT

In this paper, we present superparamagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/nitrogen-doped graphene hybrid material as an efficient and environment-friendly bifunctional catalyst for a sustainable polyethylene terephthalate chemical recycling. The presented catalyst exhibit superparamagnetic behavior because of the infinitely small coercivity arising from the negligible energy barrier in the hysteresis of the magnetization loop. By magnetic recovering of the catalyst, the danger of releasing harmful catalyst components to the environment is reduced and the process becomes more cost-effective and sustainable. To the best of our knowledge, bifunctional catalyst including acidic and basic sites have never been used in any glycolysis reactions, particularly for polyethylene terephthalate. The catalytic activity of nitrogen-doped graphene and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are also investigated which show the synergetic catalytic activity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/nitrogen-doped graphene nanocomposite.

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## 1. Introduction

The effective recycling of polyethylene terephthalate (PET) has attracted considerable attention in the field of sustainable technology and resource conservation [1]. PET, one of the most important industrial polymers produced today, is a semi-crystalline, thermoplastic polyester with thermal stability, clarity, transparency, light, and processability. Because of these excellent properties, PET is produced in considerable amount and is used in the manufacture of high strength fibers, X-ray films, soft drink bottles and in textile industry [2]. Increased world consumption of PET which has grown by 4.5% per year from 2010 to 2015 results in serious environmental problems [3]. Among the primary (re-extrusion), secondary (mechanical), tertiary (chemical) and quaternary (energy recovery) methods for recycling waste PET [4], chemical route is preponderant because it can reproduce virgin monomer products [5]. Several chemical recycling methods such as alcoholysis, aminolysis, ammonolysis, hydrolysis, and glycolysis have been reported [6–8]. Glycolysis offers some important advantages including milder reaction conditions, less volatility of the solvent, and giving bis(hydroxyethyl) terephthalate (BHET) which can be employed to produce dimethyl terephthalate-based or

terephthalic acid-based PET production lines, textile softener, and unsaturated polyester resins [9,10]. The glycolysis reaction is very slow in the absence of catalyst. So, various catalysts such as titanium-phosphate, carbonate, sulfate, and metal acetates are used for glycolysis reaction [11–13]. Some of the drawbacks of these catalyst includes impurity of products, existence of side reactions, and difficulty in separating product from catalyst.

Ionic liquids and metal oxides are the two recent catalysts [14,15] which using metal oxides could be better option because of the ease of synthesis. Moreover high monomer yield, ease of recovery, reusability, high mechanical strength, and long shelf life make metal oxides unique among the catalysts [16]. Recently, various metal oxides-based heterogeneous catalysts have been tested in the glycolysis of PET [17–19], which  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> could be an ideal option due to the cheapness, nontoxicity, abundance, and magnetic recyclability. Imran et al. reported that the mixed-oxide spinels showed high catalytic activity for PET glycolysis at 260 °C under 5.0 atm [17]. In another report, more than 90% yield of BHET was obtained after glycolysis at 300 °C using  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles [20]. However, the pristine metal oxides nanoparticles suffer from irreversible aggregation reducing their dispersion. Among the various methods to overcome these problems, we chose graphene as an attractive support because of the high specific surface area, unique planar structure, low density, flexibility, and thermal and chemical stability [21–23].

The metal oxide/graphene composite has been prepared

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through various methods. The hydrothermal reduction of metal salts and graphene oxide (GO) is widely used, owing to the simple operation and the low cost. The heteroatom doping does not only contribute to additional catalytic activity of graphene but also enhances the interaction between metal oxide or metal nanoparticles and graphene to improve the chemical stability of the composites [24]. Nitrogen doping provides additional electrons for the graphitic lattice and results in metallic or semi-conductive character [25]. N-doped graphene has been reported to be metal free catalyst for selective oxidation of benzylic alcohols and ethylbenzene [26], Knoevenagel and transesterification reactions [27] as well as the esterification of fatty acids [28].

The difficult synthesis of the catalysts, low activity as well as the need for high temperatures and high pressures limits the use of most of the previously reported catalysts in the glycolysis of PET. Therefore, development of green, efficient, easily recyclable and low-cost catalysts as well as the milder conditions and higher rates are high desirable. In this work, for the first time a bifunctional catalyst has been introduced for glycolysis of PET.

Investigation of interaction between reactants and the catalyst is necessary to provide useful information for designing efficient catalysts. It has been found that catalysts bearing functional groups with ability to form H-bonds with EG and subsequently activation of the oxygen of the hydroxyl in EG represents high activity for glycolysis of PET. The chloride and bromine ions, carbonyls, and amines are such a groups. On the other hand, a catalyst with groups interacting with the oxygen of PET carbonyls results in more partial positive charge on the carbon of PET carbonyls and then promotes the disruption of the PET chain. So, Our approach was guided by four imperatives: (i) the catalyst should have the groups with ability to form H-bonds with EG or acting as a base (ii) the catalyst should have the groups interacting with the oxygen of PET or acting as an acid, (iii) the catalyst should be magnetic which can be easily recycled and (iv) the development of an efficient process for PET recycling under the mild conditions.

## 2. Experimental

### 2.1. Materials

Graphite powder (325 mesh), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), potassium peroxodisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), di-phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ), potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), and ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) were purchased from Merck Chem. All other chemicals were purchased from Aldrich or Merck companies and used as received without any further purification.

### 2.2. Instruments and characterization

Transmission electron microscopy (TEM) was performed by LEO 912AB electron microscope. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of  $10^\circ\text{C min}^{-1}$  in air. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using  $\text{Cu K}\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultrahigh vacuum. Scanning electron microscope (SEM) was performed on a Zeiss Supra 55 VP SEM instrument. AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (AAS) with a deuterium background corrector was used for determination of the metal. The magnetization of the samples in a variable magnetic field was measured using a vibrating sample magnetometer (VSM) with a sensitivity of  $10^{-3}$  EMU and a magnetic field of up to 8 kOe. The magnetic field was changed uniformly at a rate of  $66 \text{ Oe s}^{-1}$ .  $^1\text{H}$

NMR spectra were recorded with a BRUKER DRX-300 AVANCE spectrometer, and  $\text{DMSO-}d_6$  was used as solvent.

### 2.3. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was prepared through a modified Hummers method [29,30]. Graphite powders were first oxidized by sulfuric acid. Then 2.5 g of the graphite powder was treated with a solution by mixing 12.5 ml of concentrated  $\text{H}_2\text{SO}_4$  with 2.5 g  $\text{K}_2\text{S}_2\text{O}_8$  and 2.5 g  $\text{P}_2\text{O}_5$ . The mixture was kept at  $80^\circ\text{C}$  for 6 h using a hot-plate. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL de-ionized (DI) water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pretreated graphite powder was put into cold ( $0^\circ\text{C}$ ) concentrated  $\text{H}_2\text{SO}_4$  (125 ml). Then  $\text{KMnO}_4$  (15 g) was added gradually under stirring, and the temperature of the mixture was kept below  $20^\circ\text{C}$  by cooling. The mixture was then stirred at  $35^\circ\text{C}$  for 4 h and then diluted with DI water (250 ml). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below  $50^\circ\text{C}$ . After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30%  $\text{H}_2\text{O}_2$  was added to the mixture and the color of the mixture changed into brilliant yellow and began bubbling. The mixture was filtered and washed with 0.1 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid. The resulting GO solid was dried in air.

### 2.4. Synthesis of $\gamma\text{-Fe}_2\text{O}_3$ /nitrogen-doped graphene hybrid material

$\text{Fe}_2\text{O}_3$ /nitrogen-doped graphene hybrid material was prepared by the following process. 125 mg of graphite oxide was dispersed in 54 mL of  $\text{H}_2\text{O}$  and sonicated for 10 min. Then, 200 mg of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added into GO suspension followed by intense agitation for 10 min. Then, 6 mL of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (30%) was added dropwise for 30 min, and then, the as-obtained brown viscous suspension was transferred into a stainless steel vessel and subjected to the hydrothermal reduction at  $180^\circ\text{C}$  for 12 h. The mixture was filtered and washed with DI water and  $\alpha\text{-Fe}_2\text{O}_3$ /nitrogen-doped graphene hybrid material was dried in oven. The as-prepared material was further mixed with ethylene glycol (EG) as an oxidant and refluxed at  $200^\circ\text{C}$  for 5 h to obtain  $\gamma\text{-Fe}_2\text{O}_3$ /nitrogen-doped graphene hybrid material [31]. For comparison purposes, pure  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles and nitrogen-doped graphene were fabricated. The  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles were produced by calcining  $\text{Fe}_3\text{O}_4$  nanoparticles prepared through the traditional coprecipitation method [32,33]. Nitrogen-doped graphene was synthesized with a combined hydrothermal and freeze-drying process [34].

### 2.5. General procedure for the glycolysis of PET

A round-bottom flask equipped with a reflux condenser was loaded with 0.3 g of PET, 4 g of EG, and a certain amount of catalyst. The glycolysis reaction was carried out under atmospheric pressure at  $195^\circ\text{C}$ . The flask was immersed in an oil bath at a specific temperature for the required time. After the reaction, the glycolysis product was dissolved in water at  $90^\circ\text{C}$ , in which BHET, its dimers, and EG are soluble. From this solution, the catalyst was recovered via simple magnetic decantation. The recovered catalyst was washed with deoxygenated DI water three times, dried, and reused. BHET from the glycolysis product was also recovered for further characterization. After the catalyst was recovered, the solution was kept at  $90^\circ\text{C}$  for 45 min under vigorous stirring. The PET residual

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