



Graphene-based materials for the catalytic wet peroxide oxidation of highly concentrated 4-nitrophenol solutions



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ABSTRACT

Reduced graphene oxide (rGO) samples were prepared from graphene oxide (GO) using different reducing agents (*i.e.*, glucose, hydrazine and vitamin C, resulting in rGOG, rGOH and rGOV, respectively). These samples were tested in the catalytic wet peroxide oxidation (CWPO) of highly concentrated 4-nitrophenol (4-NP) solutions (5 g L⁻¹) at mild operating conditions (*i.e.*, atmospheric pressure, $T=323$ K, pH=3, [catalyst]=2.5 g L⁻¹ and [H₂O₂]₀=17.8 g L⁻¹). The highest catalytic activity was found for the rGOV sample, reaching a 4-NP removal of 1294 mg g⁻¹ and a TOC removal of 241 mg g⁻¹ after 24 h runs (corresponding to 4-NP and TOC removals of 65% and 23%, respectively).

The TOC removal per unit of H₂O₂ decomposed decreases with the increase of the surface oxygen content of the samples, as well as with the increase of their amounts of structural defects. This was ascribed, respectively, to the electron withdrawal capacity of oxygen-containing functionalities and to reduced adsorption of 4-NP in the samples with higher amounts of defects, which diminish the efficiency of the reaction between hydroxyl radicals resulting from the decomposition of H₂O₂ and the organic compounds.

In a series of three consecutive CWPO runs, rGOH was the most stable material (4-NP removal slightly decreasing from 980 mg g⁻¹, in the first and second runs, to 841 mg g⁻¹ in the third run, corresponding to 4-NP removals of 49% and 42%, respectively). The development of oxygen functionalities at the surface of the rGO samples during the CWPO runs was found to be the major cause of catalyst deactivation.

4-Nitrocatechol was the main aromatic intermediate detected in the CWPO of 4-NP. Hydroquinone, benzoquinone, catechol and several low molecular weight carboxylic acids (*e.g.*, malonic, malic, maleic and acetic acids) were also identified as reaction intermediates.

To the best of our knowledge, graphene-based materials are reported for the first time as active and stable catalysts in the CWPO process, even when applied to highly polluted waters at mild conditions.

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1. Introduction

Graphene and its derivatives possess unique electronic, optical, thermal and mechanical properties, in addition to large theoretical specific surface areas and high adsorption capacities [1–3]. Graphene properties fascinated the scientific community, as recognized by a Nobel Prize in 2010. This two-dimensional honeycomb lattice, formed by hexagonally arrayed sp²-bonded carbon atoms, can be considered as the basic building block for all other

dimensionalities: 0D buckyballs, 1D nanotubes or 3D graphite [1,4]. Specifically, it is known that the strong σ bonds work as the rigid backbone of the 2D honeycomb graphene structure, whereas the out-of plane π bonds control the interaction between the graphene sheets, allowing delocalized π electrons to be easily conducted through the basal plane [1].

Graphene is a very promising nanostructure in several technological applications. Nevertheless, it still suffers from a typical problem of many novel materials: the lack of well established synthesis processes for large scale production [1]. One of the most popular and developed ways to produce graphene-based materials consists of the initial strong chemical oxidation of natural graphite to graphite oxide, followed by mechanical, chemical or thermal

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exfoliation of graphite oxide to graphene oxide (GO) sheets, which are finally chemically reduced, resulting in reduced graphene oxide (rGO) materials. Although incomplete exfoliation of graphite to the level of individual graphene sheets might occur, this method allows the synthesis of rGO in high yields, since large-scale production of its precursor (GO) is reliable, resulting in low production costs [1,2].

At the same time, different carbon materials (e.g., activated carbons, activated carbon xerogels, carbon nanotubes, graphite and carbon blacks) have been reported as metal-free catalysts for the catalytic wet peroxide oxidation (CWPO) of toxic and bio-recalcitrant organic pollutants in aqueous phase [5–10] – commonly associated with negative impacts on conventional biological wastewater treatment processes. Specifically, CWPO is an advanced oxidation process (AOP) involving the transference of electrons from the active sites of a suitable catalyst to hydrogen peroxide (H_2O_2) molecules, in order to decompose them through reduction of H_2O_2 to hydroxyl radicals (HO^\bullet) and hydroxide ions (OH^-), the former exhibiting high oxidizing potential and serving as effective species for the degradation of several organic pollutants in liquid phase [11–13]. Thus, materials containing electron donating active sites available for H_2O_2 decomposition should be more efficient in CWPO [13,14].

In the present work, aiming to explore the presence of electron donating active sites at the surface of graphene-based materials, and their unique structural and electronic transfer properties, rGO samples were prepared from GO using different reducing agents (i.e., glucose, hydrazine and vitamin C) and subsequently tested in the CWPO process performed under mild conditions.

Furthermore, although most applications for the CWPO process typically deal with pollutants present in water at low concentrations (up to 0.1 g L^{-1}), recent works show that the efficiency of this treatment option may be increased when operating at high pollutant loads (in the range $0.5\text{--}5 \text{ g L}^{-1}$) [6,15,16]. Therefore, in order to explore this possibility, the CWPO experiments were performed using a high pollutant load of 5 g L^{-1} . 4-Nitrophenol (4-NP) was used as non-biodegradable model pollutant.

2. Materials and methods

2.1. Chemicals

4-Nitrophenol, 4-NP ($\text{O}_2\text{NC}_6\text{H}_4\text{OH}$, Mr 139.11, 98 wt.%) [CAS number: 100-02-7], was purchased from Acros Organics. Hydrogen peroxide (H_2O_2 , 30%, w/v) was obtained from Fluka. Sodium hydroxide (NaOH, 98 wt.%) was obtained from Panreac and potassium permanganate (KMnO_4 , 99 wt.%) from Merck. Sulphuric acid (H_2SO_4 , 96–98 wt.%) was obtained from Riedel-de-Haën. Hydrazine hydrate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, 50–60 wt.%), D-(+)-glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, 99.5 wt.%), L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 99 wt.%), titanium (IV) oxysulphate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$, 15 wt.% in dilute sulphuric acid, 99.99%), hydrochloric acid (HCl, 37 wt.%) and sodium sulphite (Na_2SO_3 , 98 wt.%) were purchased from Sigma-Aldrich. Methanol (HPLC grade), glacial acetic acid (analytical reagent grade) and acetonitrile (HPLC grade) were obtained from Fisher chemical. All chemicals were used as received without further purification. Distilled water was used throughout the work.

2.2. Synthesis of graphene oxide

GO was synthesized from natural graphite (particle size $\leq 20 \mu\text{m}$, from Sigma-Aldrich), by a modified Hummers method [17,18] described elsewhere [19]. Concentrated sulphuric acid (50 mL) was added gradually with stirring and cooling to a 500 mL flask containing 2 g of graphite. Then, 6 g of potassium

permanganate were added slowly to the mixture. The suspension was continuously stirred for 2 h at 308 K. After that, it was cooled in an ice bath and subsequently diluted with 350 mL of distilled water. Afterwards, H_2O_2 (30%, w/v) was added in order to reduce residual permanganate to soluble manganese ions, a bright yellow colour appearing in the suspension. The oxidized material was purified with an hydrochloric acid solution (10 wt.%) and the suspension was then filtered, washed several times with distilled water until the neutrality of the rinsing waters was reached, and dried at 333 K for 24 h to obtain graphite oxide. The resulting material was dispersed in a given volume of water and sonicated in an ultrasound bath (ultrasonic processor UP400S, 24 kHz) for 1 h. The sonicated dispersion was centrifuged for 20 min at 3000 rpm to remove unexfoliated graphite oxide particles from the supernatant, GO being obtained in this way (ash content of ca. 0.06 wt.%, as determined by thermogravimetric analysis).

2.3. Chemical reduction of graphene oxide

rGO samples were obtained by chemical reduction of GO using vitamin C (rGOV) [20], glucose (rGOG) [21] and hydrazine (rGOH) [22] as reducing agents and employing the aqueous dispersion of GO, as described elsewhere [23]. Namely, the GO suspension (0.1 g L^{-1}) containing the reducing agent (2 mmol L^{-1}) was heated at 368 K for 3 h under vigorous stirring. Before reduction, the pH of the GO dispersion was adjusted to 9–10 with a 25% ammonia solution to promote the colloidal stability of the GO sheets through electrostatic repulsion.

2.4. Characterization techniques

The textural properties of the graphene-based materials were determined from N_2 adsorption–desorption isotherms at 77 K, obtained in a Quantachrome NOVA 4200e adsorption analyser. Before the analysis, all samples were outgassed for 8 h at 393 K. The apparent surface area (S_{BET}) was determined by applying the Brunauer–Emmett–Teller (BET) equation [24]. The micropore volume (V_{micro}) and the non-microporous surface area (S_{meso}) was determined by the *t*-method using an appropriate standard isotherm [25].

Thermogravimetric analysis was performed using a STA 490 PC/4/H Luxx Netzsch thermal analyser, by heating the sample in an air flow from 323 K to 1273 K at 20 K min^{-1} .

The point of zero charge (pH_{PZC}) of the graphene-based materials was determined following the methodology described elsewhere [26]. Briefly, solutions with varying initial pH (2–12) were prepared using HCl (0.1 mol L^{-1}) or NaOH (0.1 mol L^{-1}) and 50 mL of NaCl (0.01 mol L^{-1}) as electrolyte. Each solution was contacted with 0.15 g of the carbon material and the final pH was measured after 24 h of continuous stirring at room temperature. The pH_{PZC} value of the material was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH [27,28].

Temperature programmed desorption (TPD) was performed in a fully automated AMI-300 Catalyst Characterization Instrument (Altamira Instruments), equipped with a quadrupole mass spectrometer (Dymaxion, Ametek). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 K min^{-1} up to 1073 K using a constant flow rate of helium ($25 \text{ cm}^3 \text{ min}^{-1}$). The mass signals $m/z=28$ and 44 were monitored during the thermal analysis, the corresponding TPD spectra being obtained. CO and CO_2 were calibrated at the end of each analysis with the respective gases [29].

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