



Graphene based nanomaterials as chemical sensors for hydrogen peroxide – A comparison study of their intrinsic peroxidase catalytic behavior



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ARTICLE INFO

Article history:

Received 1 December 2014

Received in revised form 3 February 2015

Accepted 28 February 2015

Available online 6 March 2015

Keywords:

N-doped graphene

Metallic nanoparticles decorated graphene

Peroxidase-like activity

Nanocomposites

ABSTRACT

In this paper we present for the first time the catalytic activity of N-doped graphene toward a peroxidase substrate oxidation in the presence of hydrogen peroxide. In addition, the activity was compared with that of metallic nanoparticles decorated-graphene, achieved either by catalytic chemical vapor deposition with induction heating (CCVD-IH) or by chemical reduction of graphene oxide (GO). From all investigated graphene-based nanomaterials, the highest activity was exhibited by N-doped graphene and gold nanoparticles supported on chemically-reduced graphene oxide. The steady-state kinetic of the two nanocomposites was carried-out in order to evaluate their peroxidase-mimetic activity. Doping the graphene surface with nitrogen atoms led to a nanomaterial with a better affinity toward hydrogen peroxide compared to the natural enzyme (horseradish peroxidase). Additionally, the systematic study of the catalytic activity for a variety of graphene-based nanomaterials offered important findings for designing new nanomaterials with peroxidase-like activity.

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1. Introduction

In recent years, the research in the field of nanomaterials with intrinsic enzyme-like activity is rapidly growing due to their better stability, low-cost production and simple storage conditions [1]. Among the nanomaterials tested for their enzyme-mimic catalytic activity are included magnetite nanoparticles [2,3], cerium oxide nanoparticles [4], gold nanoparticles [5], and carbon-based nanomaterials [6,7]. They are now generally called nanozymes [8] and are representing the intersection of nanotechnology with biology by simulating a catalytic function similar to that of the natural enzymes. Among nanomaterials, graphene has received increasing attention from the scientific community, since the 2010 Nobel Prize for Physics awarded “for groundbreaking experiments regarding the two-dimensional material graphene”. Their applications in material science and biotechnology range from electronics, photovoltaics, storing electricity, advanced composites, inks to tissue engineering, drug delivery or bio-imaging. It was therefore

just a matter of time till their potential in enzyme-like catalysis was investigated, including their evaluation as peroxidase mimetic. The synthesis of graphene based nanomaterials can be accomplished by two main approaches, the bottom-up and the top-down, respectively. The methods corresponding to the first approach (e.g. catalytic chemical vapor deposition [9–11]) are generally providing high-quality graphene with quite low productivity. Similar quality of graphene nanosheets but limited quantities can be obtained by mechanical exfoliation of graphite as a top-down approach. Instead, large quantities of graphene sheets can be synthesized by the reduction of graphene oxide (GO), but residual oxygen functional groups and the formation of defective sheets were observed [12].

Previous studies reported on the enzyme mimetic properties of metallic nanoparticles dispersed on graphene nanosheets (Gr), by chemical methods. The peroxidase-like catalytic ability of PtPd nanodendrites-graphene nanocomposites proved to be higher than in the case of Pt nanoflowers-, Pd nanoparticles-, bimetallic PtPd nanoalloys- or core-shell Pd@Pt nanoflowers-graphene hybrids [13]. Au@Pd bimetallic nanoparticles dispersed on graphene also demonstrated their ability as catalysts [14]. Gold nanoparticles on citrate functionalized graphene nanosheets [15], porous platinum nanoparticles growth in situ on graphene oxide [16] and magnetite

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nanospheres on reduced graphene oxide nanocomposites [17] were also synthesized and evaluated for their peroxidase mimic. Some graphene based nanomaterials without metallic nanoparticles were also investigated, among them being carboxyl modified graphene oxide [18] and few-layer graphene exfoliated by chitosan [19].

Although much attention has been offered to the investigation of graphene-based nanocomposites as peroxidase mimetic (or colorimetric sensor), a report that correlates their catalytic activity to the synthetic method - implicitly to the chemical composition of the carbon support is missing. Horseradish peroxidase experimental data are sometimes considered as reference for comparing the results in this area, but not always being measured under the same experimental conditions.

So far, it has been shown that besides the importance of the size and structure of the metallic nanoparticles, the scaffold for their deposition also plays a vital role [20,21]. A more systematic study on a larger number of graphene based nanomaterials will be offering a clearer perspective on the future directions in developing superior enzyme mimetic. Besides these, we found for the first time that N-doped graphene are a good candidate for peroxidase mimetic, even though the N-doped carbon materials were known for their catalytic activity toward the oxygen reduction reaction, at the cathode in fuel cells. Their high catalytic activity even encouraged further studies on their application in the reduction reaction of hydrogen peroxide in comparison to a gold catalyst [22].

We have therefore investigated the ability of N-doped graphene to act as a metal-free chemical sensor for hydrogen peroxide as a consequence of its outstanding peroxidase-like activity. On the other hand, we considered of interest to compare the catalytic activity of composites obtained by the reduction of graphene oxide (M-rGO) with that of graphene-metallic nanoparticles composites (Gr-M) synthesized by catalytic Chemical Vapor Deposition with Induction Heating (cCVD-IH).

2. Experimental

2.1. Materials

All the reagents were of analytical grade and used without further purification. All solutions were prepared using double-distilled water. 3,3'-dimethylbenzidine (ortho-tolidine) and horseradish peroxidase (HRP, Peroxidase, Type II, 167 U mg⁻¹.) were purchased from Sigma-Aldrich. H₂PtCl₆·6H₂O, H₂AuCl₄, AgNO₃, H₂O₂, sodium ascorbate, sodium acetate, sulfuric acid, KMnO₄ were purchased from Merck chemicals.

2.2. Instrumentations

The morphology of graphene nanocomposites were observed by transmission electron microscopy (TEM) (H-7650 120 kV Automatic TEM, Hitachi, Japan). All TEM samples were prepared by depositing a drop of diluted suspension in ethanol, on a copper grid. X-ray Photoelectron Spectroscopy (XPS) technique has been used for the characterization of chemical composition and state of elements present in the investigated graphenes. XPS spectra were recorded using a SPECS spectrometer, equipped with a dual-anode X-ray source Al/Mg, a PHOIBOS 150 2DCCD hemispherical energy analyzer and a multi-channeltron detector. The pressure inside the measurement chamber was maintained constant at about 1×10^{-9} torr. The sample, as a colloidal suspension in methanol, was dried in successive layers on indium foil stacked on wolfram sample holder. Irradiation was made with an Al_{Kα} X-ray source (1486.6 eV) operated at 200 W. The XPS survey spectra were recorded at 30 eV pass energy, 0.5 eV/step. The high

resolution spectra for individual elements were recorded by accumulating 10–15 scans at 30 eV pass energy and 0.1 eV/step. The surface cleaning was ensured through argon ion bombardment at 300 V for 2, 3 and 5 minutes. Data analysis and experimental curve fitting of the C1s, N1s and Au 4f spectra was performed using Casa XPS software with a Gaussian-Lorentzian product function and a non-linear Shirley background correction. The ultraviolet-visible (UV-vis) absorption spectra of enzyme mimic and the time-dependent absorbance spectra were measured with a V-570, Jasco Spectrophotometer. X-ray powder diffraction (XRD) measurements were performed at room temperature and were collected in the $5^\circ < 2\theta < 85^\circ$ angular domain with a Bruker D8 Advance diffractometer, using CuK_{α1} radiation ($\lambda = 1.5406 \text{ \AA}$). In order to increase the resolution, a Ge(1 1 1) monochromator in the incident beam was used to filter out the K_{α2} radiation.

2.3. Preparation of graphene oxide

Graphene oxide was prepared from carbon graphite powder (0.125 μm obtained from a rod - Pierce eurochemie bv) using a modified Hummers method [23,24]. In a typical oxidation procedure, graphite powder (4.6 g) was added to a warm solution (80 °C) of concentrated sulfuric acid (8 mL), potassium persulfate (2.5 g) and phosphorus pentoxide (2.5 g). The resultant mixture was heated to 100 °C and left to cool slowly and thermally isolated. After 5 h, the mixture was carefully diluted with water, filtrated and washed until the pH water was neutral. The solid was dried at ambient temperature overnight.

A suspension of the pre-oxidized graphite powder (3.5 g) and sodium nitrite (1.6 g) in sulfuric acid (60 mL) was cooled in an ice-water bath and potassium permanganate (8 g) was slowly added to the mixture, so the temperature would not reach 20 °C. The mixture was allowed to stand till next day, when it was slowly warmed to 35–37 °C and kept for 2 h at this temperature. The suspension was diluted with 150 mL water and the temperature increased up to 100 °C and after 2 h were added further 100 mL of water. Then the reaction was stopped by adding hydrogen peroxide (3%) till no more gas development was observed. The mixture was filtered and washed with a diluted HCl solution (5%). The GO product was then suspended in distilled water and dialyzed for 5 days. Exfoliation was achieved by dilution of GO and sonication for 1 h. The solid GO was obtained by liophilization.

2.4. Chemical preparation of metallic nanoparticles-graphene nanocomposites

In a typical procedure, GO powder (150 mg) was dispersed in water (50 mL) and sonicated for 15–20 min, resulting in a homogeneous GO dispersion. A solution of H₂AuCl₄, H₂PtCl₆ or AgNO₃ (1% in water, 1.5 mL) was added and the mixture stirred at room temperature for 2 h and further added a solution of sodium ascorbate (400 mg in 5 mL water). The mixture was heated at 90 °C and kept at this temperature for 3 h. Finally, the resulting homogeneous black suspension was filtered and washed with water several times. The composite materials were following denoted **Au-rGO** [25], **Ag-rGO** and **Pt-rGO**, corresponding to each metal used in the reaction.

2.5. Preparation of N-doped graphene

In a typical procedure, GO powder (350 mg) was dispersed in water (60 mL) and sonicated for 15 min, then urea (2.4 g) was added and the resulted homogeneous solution was stirred at 160 °C for 8 h. The resulting black suspension was filtered and washed with water. The dried solid was then thermally treated at 600 °C for 1 h in a stream of argon. The sample was denoted as **N-Gr**.

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