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Charge transfer-resistance in nitrogen-doped/undoped graphene: Its influence on the electro-catalytic reduction of H_2O_2

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ABSTRACT

Nitrogen doped (N-Gr) and undoped (TRGO) graphene were chemically synthesized and characterized by TEM, STEM-EDX and XPS. The electrochemical reduction of H_2O_2 was investigated with bare glassy carbon (GC) electrode and with GC modified with each graphene sample. The active area of TRGO/GC and N-Gr/GC modified electrodes were found to be 0.75 and 0.295 cm^2, respectively. Both were considerably larger than that of bare GC (0.07 cm^2). We carefully looked at the kinetic of interfacial electron transfer process and found that the charge-transfer resistance (R_{ct}) of TRGO/GC electrode (7.83×10^6 Ω) was significantly lower than that of N-Gr/GC electrode (4.81×10^7 Ω) or bare GC (1.74×10^9 Ω). Interestingly, although TRGO/GC electrode had the largest active area and the smallest charge transfer resistance, it did not promote the H_2O_2 electrochemical reduction. In contrast, N-Gr/GC modified electrode exhibited an enhanced electro-catalytic activity towards H_2O_2 reduction, which was related to the presence of heterogeneous atoms into the sp^2 carbon network.

1. Introduction

Hydrogen peroxide (H_2O_2) is known for its important role in various physiologic processes. Several studies have reported that H_2O_2 is an important regulator of eukaryotic signal transduction and of other biological processes like the immune cell activation or vascular remodeling in mammals [1]. It is also an important contaminant of different industrial products and wastes [2] so, finding a reliable and economical method for H_2O_2 determination is of great significance.

Many enzyme-based sensors for H_2O_2 detection were reported to have high sensitivity and good selectivity, but they also had several drawbacks like instability and poor reproducibility. For these reasons, the fabrication of non-enzymatic H_2O_2 sensor using metal nanoparticles was intensively explored [3–5] with the purpose of improving not only the electro-catalytic activity towards the H_2O_2 detection, but also its selectivity.

Another approach recently used was based on the replacement of the enzymes with the so-called “enzyme mimics” [6] which are alternative materials (e.g. supramolecular catalysts) that mimic the functions of natural enzymes. Over the last decade, the research interest in enzyme mimics has greatly expanded, resulting in the synthesis of multifunctional materials with outstanding properties. Hence, Qu and co-workers [7] have reported that single-layer graphene oxide (GO) without metallic impurities, exhibits peroxidase-like activity. Similar to horseradish peroxidase (HRP), its activity was strongly dependent on pH, temperature, and H_2O_2 concentration. As diagnostic tool for peroxidase-like catalytic activity was the reaction between 3,3′,5,5′-tetramethylbenzidine (TMB) and H_2O_2 in the presence of GO, which produced a blue color solution. More recently, Gao et al. have shown that nanocarbon oxide also exhibits peroxidase-like activity, which has been attributed to the presence of carboxyl groups in the aromatic domains, rather than any metal impurity [8].

Our group has recently reported the peroxidase-like activity of N-doped graphene towards 3,3′-dimethylbenzidine (ortho-tolidine), in the presence of hydrogen peroxide. Its activity was compared with that of metallic nanoparticles decorated-graphene, synthesized either by catalytic chemical vapor deposition with induction heating (CCVD-IH) or by chemical reduction of GO. The highest activity was exhibited by N-doped graphene and gold nanoparticles supported on chemically-reduced graphene oxide.

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The doping of graphene network with nitrogen atoms has increased its affinity towards hydrogen peroxide, compared to the natural enzyme (horseradish peroxidase) [9].

Several techniques used for H_2O_2 detection, such as fluorimetry [10], chemiluminescence [11] or liquid chromatography [12] generally require sophisticated equipments and laborious sample pre-treatments. For these reasons, the electrochemical techniques are gaining more attention; in particular, amperometric sensors are preferred due to their high sensitivity and selectivity, being also suitable for on-site detection.

The purpose of the paper was to get a better understanding of the charge-transfer resistance, R_{ct}, in nitrogen-doped graphene (N-Gr) and to compare with that of undoped graphene (or thermally reduced graphene oxide –TRGO). For the first time, the influence of this parameter on the electrochemical reduction of H_2O_2 was reported. In order to accomplish this, nitrogen-doped/undoped graphene were chemically synthesized and characterized by Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM) with Energy-Dispersive X-ray (EDX) spectroscopy technique for the elemental mapping of atom (C, N, O) distribution and X-ray Photoelectron Spectroscopy (XPS). Following, the same volume (8 μL) of N-Gr or TRGO suspension in DMF (1 $mg \cdot mL^{-1}$) was used to modify glassy carbon (GC) electrode. Finally, the electrochemical signal was collected in a hydroquinone (HQ)/H_2O_2 system by Cyclic Voltammetry and Amperometry. The optimization of the experimental conditions and the performances of the modified electrodes were studied in details.

2. Experimental

2.1. Chemicals

All the reagents were of analytical grade and used without further purification. Urea was purchased from Merck (Germany) and N,N-Dimethylformamide (DMF) from J.T. Baker (Holland). Methanol HPLC grade, KCl, $K_4[Fe(CN)_6]$ and H_2O_2 were obtained from Alfa-Aesar (Germany). All the solutions were prepared in purified water (Milli-Q system – Millipore, USA).

2.2. Apparatus

Transmission Electron Microscopy (TEM) images were obtained with an H-7650 120 kV automatic TEM instrument, Hitachi, Japan. STEM-EDX images were obtained with an SU-8230 STEM system, Hitachi, Japan. Before measurements, the nitrogen doped/undoped graphene samples were diluted in ethanol then dropped on copper grid (200 mesh) and dried at room temperature for several minutes.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out with an XPS SPECS spectrometer equipped with a dual-anode X-ray source Al/Mg, a PHOIBOS 150 2D CCD hemispherical energy analyzer and a multichanneltron detector. The AlK_α radiation (1486.6 eV, non-monochromatic) operated at 200 W was used for data collection. The survey scans were recorded at fixed pass energy of 30 eV, 0.5 eV/step; the high resolution spectra for individual elements were recorded by accumulating 30–50 scans at 30 eV pass energy and 0.1 eV/step. During data acquisition, the background pressure inside the analysis chamber was kept below 1×10^{-9} Torr. Nitrogen doped/undoped graphene sample prepared as colloidal suspension in methanol (HPLC grade) was drop-casted on pure indium foil, dried at room temperature and then attached to the metallic holder (wolfram) with carbon tape. The cleaning of the sample (nitrogen-doped graphene) surface was performed by argon ion bombardment at 500 V, for 5 minutes. XPS fittings and data analysis were performed with Casa XPS software. The raw data were used with no preliminary smoothing. The binding energies were determined with respect to the Au ($4f_{7/2}$) peak of pure metallic gold, used as an inner calibration standard, which was set at 84.0 eV. A Gaussian-Lorentzian product function was used to approximate the line shapes of the fitting components and a non-linear Shirley background subtraction was performed.

The electrochemical measurements (*Cyclic Voltammetry- CV; Amperometry*) were recorded with an AUTOLAB 302N electrochemical work-station (The Netherlands). A three-electrode system was employed, with the modified glassy carbon (GC- 3 mm diameter) as the working electrode, Ag/AgCl with saturated KCl solution as the reference electrode, and platinum foil as the counter electrode. The calibration curves (*I vs H_2O_2 concentration*) obtained from the amperometric measurements, were background subtracted. In all cases, Ar-saturated 0.2 M PBS pH 7 was used as supporting electrolyte.

2.3. Synthesis of nitrogen-doped/undoped graphene

Nitrogen-doped graphene (N-Gr) was synthesized by using a solvothermal method. In a typical procedure, graphene oxide (350 mg) was dispersed in water (60 ml) under sonication (1000 Watt) for 25 minutes. Then, urea (1.9 g) was added and the reaction with graphene oxide (GO) was carried out at 160 °C for 8 hours, in 100 mL autoclave. The synthesis product was washed several times with water, and finally dried by lyophilization. After drying, the black powder was thermally treated for 1 hour at 600 °C, under argon flow.

The synthesis of undoped graphene (or thermally reduced graphene oxide-TRGO) was described with details in [13]. Briefly, the freeze-dried GO (150 mg) was transferred to a quartz boat which was put inside a temperature-programmed furnace. The temperature was gradually increased from 25 to 300 °C with a ramping rate of 10 °C min^{-1} in the presence of argon gas. The exfoliation and graphene oxide reduction took place around 190 °C, resulting 82 mg of thermally reduced graphene oxide (TRGO). The morphological and structural characterization of nitrogen-doped/undoped graphene was performed by TEM, STEM-EDX and XPS techniques.

2.4. Preparation of N-Gr and TRGO modified GC electrodes (N-Gr/GC and TRGO/GC)

The glassy carbon (GC) electrodes were initially cleaned by polishing on a felt cloth then rinsed with double-distilled water. The electrodes were dried at room temperature for several hours then covered with TRGO or N-Gr suspension (8 μL) in DMF (1 $mg \cdot mL^{-1}$). The GC modified electrodes were subsequently denoted N-Gr/GC and TRGO/GC and were further used for electrochemical investigation of H_2O_2, 24 hours after modification.

3. Results and Discussions

3.1. Morphological and structural characterization

Fig. 1a,b shows the TEM images of TRGO and N-GR graphene samples, respectively. As can be seen in these images, the samples consist of thin and crumple sheets, with scrolled edges. The two-dimensional structure is well preserved, indicating a high surface/volume ratio, which is beneficial to the investigation of various electrochemical processes.

Scanning transmission electron microscopy (STEM) with Energy Dispersive X-ray spectroscopy (EDX) mapping analysis was employed in order to determine the element distribution in TRGO (Fig. 1c) and N-Gr (Fig. 1d) samples. The element mapping evidences uniform nitrogen doping in the N-Gr product, thus