



Controlled density of defects assisted perforated structure in reduced graphene oxide nanosheets-palladium hybrids for enhanced ethanol electro-oxidation



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ARTICLE INFO

Article history:

Received 8 December 2016

Received in revised form

21 February 2017

Accepted 22 February 2017

Available online 23 February 2017

Keywords:

Reduced graphene oxide
Pd nanoparticles
Microwave irradiation
Perforated structure
Defect-engineered graphene
Ethanol electro-oxidation

ABSTRACT

Controlled creation of defects in graphene based materials is a promising strategy to tailor the electrical, electrochemical, mechanical and other properties aiming at novel applications. In this work, we report a simple and reliable strategy for producing large-scale perforated graphene oxide nanosheets-Pd hybrids as promising catalytic material through in situ formation and insertion of palladium nanoparticles (Pd-NPs) employing continuous microwave irradiation technique. A tentative mechanism for obtained microstructures with controlled density of defects is proposed based on structural and morphological characterization of the synthesized material. During the treatment, high enough temperatures are achieved to allow melting of PD-NPs. Further, the particles migrate randomly over the graphene surface gradually dissolving carbon atoms at the defective sites, and eventually leading to the formation of holes of different sizes and shapes by perforation. These processes (particles formation and migration, perforation, etc.) can easily be controlled by tuning the parameters of the irradiation process. The synthesized hybrid material was used as catalysts with improved sensitivity for ethanol electro-oxidation with current density of 10 mA/cm².

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1. Introduction

Graphene is a two-dimensional (2D) monolayer structure of carbon atoms arranged in a honeycomb-like lattice, which was successfully isolated from bulk graphite about a decade ago [1]. In these days, graphene has an important role in nanoscience/nanotechnology because of its exceptional electrical, mechanical and optical properties. There is a vast amount of research going on for the development of graphene applications, especially in electronics and optics. Introducing nanoscale level defects into graphene has

shown to be promising for band gap modulation that could be extremely useful and exploited to generate novel, innovative and useful materials and devices [2–4]. Several approaches have been adopted for the creation of vacancies [5–8], point defects [9], so called 5–7 defects [10–12], pentagon-octagon-pentagon (5-8-5) defects [13,14], Stone–Thrower–Wales (STW, 5-7-7-5) defects [15–18] and others [19,20]. In the context of electronics, the presence of defects can disrupt charge transport by acting as scattering centres, lowering the electron mobility of graphene and can be used in some device applications [21–23]. The opening of band gap and reactivity modification through functionalization with foreign atoms/molecules or structural defects are excellent examples of the utilization of defects in graphene materials [24,25]. Also, the defective surface of graphene shows great promise in various novel

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applications, such as sensors, fuel cells and energy storage/conversion devices [26–30].

Surface structural defects can be deliberately introduced into graphene using various techniques, for example, by irradiation with electron beams, chemical reactions with strong acids or exposure to high temperatures in presence of reactive gases. Also in some cases, high energy ion bombardment has been used to create defects in graphene [31–35]. Very recently two research groups have fabricated structural defects in graphene on Cu substrates by employing chemical vapour deposition (CVD) method [36,37]. Zhang et al. [36] created the micro-structural defects in graphene by hydrogen etching while Roy et al. [37] induced pinhole defects in a monolayer graphene during its growth by CVD method. Among other techniques used for the synthesis of controllably defective graphene, solvothermal method [28] and CVD grown graphene modified by scanning probe lithography [38] have been cited.

In this article, we report the engineering of defects in reduced-graphene oxide nanosheets (rGONSs) through perforation by in-situ grown metal nanoparticles using continuous microwave irradiation. The decoration and perforation of rGONSs has been performed by small-sized Pd nanoparticles (Pd-NPs) and larger Pd nanoparticles (L-Pd-NPs), respectively. Several techniques for morphological and structural characterization were employed for observing the phenomena responsible for graphene decoration and perforation. The sequence of events leading to the observed porous structure involves the formation of metallic particles, their melting and reaction with carbon at defective surface sites. Through this mechanism, different defects can be controllably produced by varying the duration of the microwave irradiation. As a proof-of-concept, the synthesized material was successfully applied for ethanol electro-oxidation with enhanced efficiency.

2. Experimental section

2.1. Synthesis of graphite oxide and rGONSs

Graphite oxide (GO) was synthesized by chemical oxidation of graphite powder, using the modified Staudenmaier's method [39]. Graphite powder (5 g) (Aldrich, particle size <45 μm) was continuously stirred with a mixture of sulphuric acid (H_2SO_4) (90 ml) (Aldrich, 99.99%) and nitric acid (HNO_3) (45 ml) (Aldrich, 99.99%) solution at room temperature. Subsequently, the solution container was placed into an ice-water bath to ensure a constant temperature and fine powder (solid) of potassium chlorate (KClO_3) (55 g) (Aldrich, $\geq 99\%$) was slowly poured into solution to avoid explosion due to the exothermic reaction. This solution was kept at room temperature for five days under continuous magnetic stirring for better oxidation of the graphite powder. The as synthesized GO product was washed with DI water and 10% hydrochloric (HCl) solution was added to remove sulphate and other ion impurities. It was then washed with DI water several times until a pH of 7 was reached. Afterward the GO powder was dried at 70 $^\circ\text{C}$ under vacuum. The dried GO powder was reduced with microwave for the formation of pristine rGONSs.

2.2. Synthesis of palladium-rGONSs hybrids

Different types of palladium-rGONSs (Pd-rGONSs) hybrids were synthesized through continuous microwave irradiation of the mixture of GO powder and palladium (II) acetate ($\text{Pd}(\text{OAc})_2$) (Aldrich, 99.98%) for different times using a microwave power of 810 W. About 2.63 g of GO and 0.164 g of $\text{Pd}(\text{OAc})_2$ were dissolved in 150 ml $\text{C}_2\text{H}_5\text{OH}$ (Sigma-Aldrich, $\geq 99.5\%$) under magnetic stirring for 30 min to form homogeneous suspensions. A small amount (5 ml) of diluted ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) (0.2 M) solution was added

and stirred for another 20 min and then ultrasonicated for 10 min. The solution was kept in air for complete evaporation of $\text{C}_2\text{H}_5\text{OH}$ and afterwards, the clay-like materials were dried at 40 $^\circ\text{C}$ for 1 h. This chemically modified powder was collected in an amorphous silica cup and treated using a microwave oven (Consul-CMW30AB, 1 kW total power). Different microwave exposure reaction times (t_{mw}) (55, 90 and 125 s) were used for the formation of Pd-rGONSs hybrids having different morphologies.

2.3. Materials characterization

The crystal phases of the as-prepared samples were determined using an X-ray diffractometer (XRD - D/MAX-2500/PC; Rigaku Co., Tokyo, Japan) over the 2θ range of 10–75 $^\circ$. The surface morphology and elemental analysis were investigated using scanning electron microscope (SEM - Dual Beam FIB/ FEG model FEI Nova 200) equipped with energy dispersive X-ray spectroscopy (EDS). Raman measurements were carried out using a spectrometer with a 473 nm laser (NT-MDT NTEGRA Spectra). The X-ray photoelectron spectroscopy (XPS) spectrum was recorded on a MultiLab 2000 photoelectron spectrometer (Thermo-VG Scientific, USA) with Al $K\alpha$ (1486.6 eV) as the X-ray source. All XPS spectra were corrected using the C1s line at 284.6 eV.

2.4. Electrochemical measurements

The electrochemical measurements were performed in an AUTOLAB PGSTAT 12, interfaced with NOVA software, using a three-electrode cell. Ag/AgCl (3 M KCl) and Pt foil (1 cm^2) were used as reference (RE) and counter electrodes (CE), respectively. The working electrode (WE), a glassy carbon (GC) electrode (3 mm diameter), was polished with alumina and rinsed thoroughly with doubly distilled water. Subsequently, 5 μL of dispersion (2 mg of the synthesized materials in 45 μL Nafion[®] 5%wt and 955 μL ethanol) was dropped on the surface of the GC electrode and dried to obtain an rGONSs/GC, Pd-D-rGONSs/GC and Pd-FP-rGONSs/GC modified electrodes. The electrolyte was bubbled with nitrogen during 30 min to remove oxygen interference.

3. Results and discussion

3.1. Structural analysis

The as synthesized hybrids formed using continuous microwave irradiation with varying reaction times were characterized by scanning electron microscopy. Fig. 1 shows different magnifications of the surface morphology of Pd-decorated rGONSs (Pd-D-rGONSs) at $t_{\text{mw}} = 55\text{s}$. The pristine rGONSs (after microwave reduction and exfoliation of GO powder) contains wrinkles on its surfaces as shown in Fig. S1. Fig. 1a reveals that the surface of Pd-NPs attached rGONSs which are also contains wrinkles and homogeneously covered by Pd-NPs that have a narrow size distribution. Fig. 1b shows that the Pd particles have diameters near 50 nm and there is no indication of agglomeration. These Pd-NPs are attached to the surfaces and edges with help of various kinds of functional groups, such as epoxy and hydroxyl onto surfaces and carboxyl and carbonyl at edges. Fig. 1b also shows the formation of a few short carbon nanotubes (CNTs) or nano fibers grown on Pd-NPs. Further growth of these CNTs may not have taken place due to the short time of microwave treatment. It can be expected that high thermal energy delivered to tiny Pd-NPs in a very short time is not favorable for the growth of longer carbon nanotubes. However, as the nucleation of nanotubes requires elevated temperatures (700–900 $^\circ\text{C}$), the nanotubes formation give the evidence of very strong surface heating achieved during the short exposure to microwave.

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