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Activation of few layer graphene by μW-assisted oxidation in water via formation of nanoballs – Support for platinum nanoparticles

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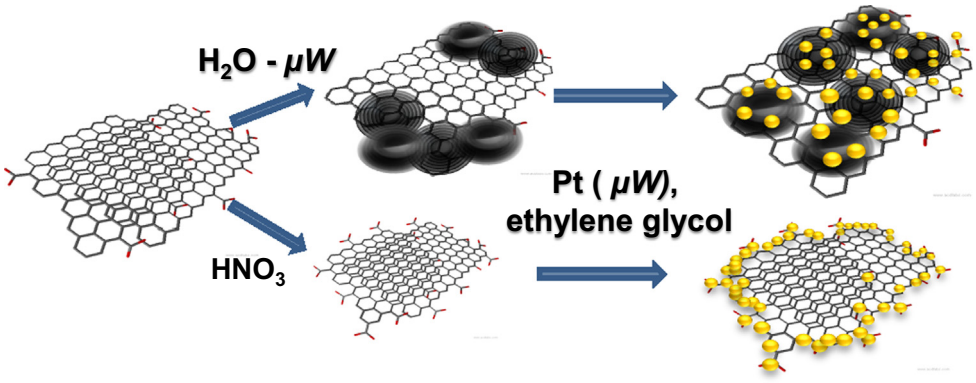
GRAPHICAL ABSTRACT



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ABSTRACT

The functionalization of carbon nanomaterials in controlled and selective manner and in order to stabilize small metal nanoparticles is of high interest particularly in the catalysis field. We present the μ-waves assisted few layer graphene (FLG) oxidation in water, which results in a partial sheets exfoliation and formation of oxygen functionalized carbon nanoballs, supported on highly graphitized graphene sheets. This double morphology material allows homogenous anchoring of Pt nanoparticles, while the advantages of planar and highly crystallized FLG are preserved. For comparison, acid treated FLG (conventional heating) exhibits highly hydrophobic and inert surface with carboxylic groups as anchoring sides localized at the FLG edges. Despite similar oxygen content, the performed physicochemical analyses depict different nature and localization of the oxygen/defects functionalities introduced in water (in μ-waves) and acid treated FLGs. Finally, the addition of FLG during the preparation of Pt particles-carried out by μ-wave assisted polyol method yields small nanoparticles with average size of 1 nm.

1. Introduction

Graphene and/or few-layer graphene (FLG) have received an ever increasing scientific interest in different areas of applications since the isolation of graphene. Low oxygen/defect content within

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the sp^2 carbon network is necessary to get conductive materials, but related hydrophobic character renders a dispersion of graphene difficult in most of solvents [1]. In view of potential applications in the field of heterogeneous catalysis, the high surface area, high thermal and electrical conductivity as well as mechanical resistance are highly desired properties, however for a dispersion of an metal active phase, defects/oxygen sites on graphene surface are in general necessary [2,3]. Surface oxidation in graphitic materials (nanotubes or nanofibers) is often performed in nitric acid or nitric-sulfuric acids' mixture [4–7]. Much stronger, harsh and long duration conditions (days) are commonly applied for intercalation of oxygen functional groups into graphite to subsequently produce graphene oxide (GO) (Hummer method). High oxygen content in GO allows its use as catalytic support and its dispersion in polar solvents (water) for nanocomposites, polymers applications [8–10]. A breaking of sp^2 carbon lattice, however, makes GO an insulator material [11]. Notwithstanding, GO is commonly produced as "graphene precursor" that is subsequently reduced in order to restore a sp^2 carbon network. Similarly to its preparation, the reduction of GO requires harsh chemical and thermal conditions as well. In general, hydrazine treatment and temperatures above 1000 °C are applied to reach mechanical and conductive performance being adequate to graphene, whereas a total restoration of the conjugated carbon lattice is still a challenge [12]. The recently achieved effective reduction of GO paper was performed by two step reduction and minimum temperature treatment of 1500 °C [13].

While the oxidation of graphene surfaces by acids is a common method, the use of water as an oxidant is unusual [14–16]. In the case of Highly Oriented Pyrolytic Graphite (HOPG), a reported low temperature oxidation by water vapor initiates at point defects in basal plane (mostly steps) and formation of circular and hexagonal pits with monolayer depth. At high temperature, water vapor reacts also with carbon atoms in basal plane, creating new defects sites which nucleate monolayer pits [15]. Reported H_2O radio frequency plasma treatment results in the introduction of defects (and —OH) in HOPG allowing a decrease of subsequently deposited Pt nanoparticles size (from 6 to 3.5–4 nm) [16]. The introduced O-containing species enhance an adhesion of the metal by providing hydrogen bonding to interact with surface oxidized Pt nanoparticles (Pt-OH). On the other hand, Pt particles deposition over GO by polyol method is accompanied by long GO reduction and final particles size of 2.75 nm [17]. Extensively studied, supported platinum is an important catalyst for fuel cell oxidation reactions, where Pt-support interactions and Pt size determine their catalytic performance. High activity and stability of catalyst was established for Pt-graphene system, due to the conductive properties of the support [18]. Theoretical data affirm that a strength of interaction between Pt and oxygen decorated graphene surfaces is seven times higher compared to unsubstituted graphenes and higher compared to nitrogen or beryllium doped graphene [2,19]. The adhesion of Pt to oxygen rich sites of graphenes is due to hydrogen bonds formation (PtOH-oxidized HOPG) [16], or can be defined as coordination chemistry, where Pt is coordinated by one or two oxygen from graphene [20]. According to other report, a charge transfer between C=O group of PVP (N-vinyl-2-pyrrolidone) and small Pt particles (2–7 nm) as electron acceptor can occurs while, the large size particles behave as electron donor to PVP [21]. The size dependent property and related catalytic performance of metal particles is well established. The phenomenon is more pronounced for very small, subnanometer particles, which exhibit particular catalytic properties [22]. Both, the synthesis of very small nanoparticles as well as their stabilization is therefore of high importance. In this context the graphene support needs to be activated by introduction of oxygen in controlled qualitative and quantitative manner, while a prevention of exceptional properties linked to planar sp^2C lattice of graphene (conductivity or mechanical resistance) would be benefic. Additional challenge in design of 2D graphene-based catalysts is linked to protection of surface accessibility, which is often reduced by inter π–π stacking.

At present we report on surface activation of few-layer graphene (FLG) induced by μ-waves assisted water vapor treatment. To better understand the oxidation effect induced by water-μ-waves treatment, the FLG is in parallel submitted to oxidative treatment with nitric acid under traditional heating mode. The FLG was previously obtained by high yield, scalable and low-cost method that consists of mechanical ablation of pencil lead [23,24]. The nature and localization of the introduced functionalities in both, via μ-waves-water and acid oxidized FLGs, are characterized by various physicochemical techniques. Finally, the impact of FLG addition into a reductive medium during preparation of Pt particles by μ-wave assisted polyol method is discussed.

2. Experimental

2.1. Preparation of FLG materials

2.1.1. FLG

Few layer graphene (*FLG*) was prepared by mechanical ablation and acid/base purification [23,24]. Prior to subsequent oxidative treatment, the FLG was annealed in Ar at 900 °C for 2 h.

2.1.2. FLG-HNO_3

300 mg of *FLG* were heated under stirring with 110 mL of HNO_3 (aqueous) 15% at 100 °C for 3 h, then filtered, washed with distillated water to reach neutral pH and dried at room temperature (r.t.) for 24 h and subsequently at 110 °C for 2 h.

2.1.3. FLG-H_2O

30 mL of distillated water was added to 300 mg of *FLG* and the suspension was stirred and heated at 160 °C for 1 h with the μ-waves irradiation of 400 W. The powder was next filtered and dried at r.t. for 24 h and at 110 °C for 2 h.

2.1.4. Pt suspension

30 mg of H_2PtCl_6 was solubilized in 20 mL of ethylene glycol; then 1 M NaOH solution in ethylene glycol was added to the solution of Pt to reach pH = 10. The resulting solution was next mixed during 1.5 h and heated by μ-waves (800 W) for 1 min at 160 °C and 5 min ramp (in the presence or not of *FLG*). This prepared suspension of Pt nanoparticles was then used for deposition on the FLG supports.

2.1.5. Pt/FLG-HNO_3; Pt/FLG-H_2O

20 mg of *FLG-HNO_3* or *FLG-H_2O* was sonicated in 5 mL of ethylene glycol for 10 min. Then 6 mL of Pt suspension was added to the solution which was next sonicated for 40 min followed by evaporation under stirring and heating at 120 °C till a muck was formed. A final drying at 110 °C under vacuum for 24 h was applied.

2.2. Experimental setup/tools

Microwaves irradiation experiments were performed using a multi-mode Mars System from CEM Corporation using a standard Teflon vessel. The temperature profiles for microwaves experiments were recorded using a fiber-optic probe protected by a sapphire immersion well inserted directly into the reaction mixture.

The TEM analysis of FLGs and Pt/FLGs were performed on Topcon 002B-UHR microscopes working with an accelerated