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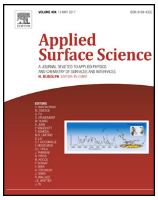

Full Length Article

Chemical and structural properties of Pd nanoparticle-decorated graphene—Electron spectroscopic methods and QUASES

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ABSTRACT

Graphite (Gr) and carbon nanomaterials such as graphene oxide (GO) and reduced graphene oxide (RGO) and those decorated with Pd nanoparticles were investigated by photoelectron spectroscopy (XPS) aided with Quantitative Analysis of Surfaces by Electron Spectroscopy (QUASES) and reflected electron energy loss spectroscopy (REELS).

Oxidation of Gr decreased the C/O ratio from 10 (Gr) to 2.2 (GO), whereas reduction of GO by N_2H_4 increased this ratio to 6.6 (RGO) due to decreasing number of oxygen groups (hydroxyl, epoxy, carbonyl and hydroxyl). Graphene materials and those after Pd decoration had 6–11 average number of layers in stacked nanostructures. Pd decoration using $NaBH_4$-reducing agents formed nanoparticles of size 6.9 nm (Pd/Gr) > 5.3 nm (Pd/RGO) > 4.25 nm (Pd/GO), with PdO_x overlayer thickness of 2.20 nm (Pd/GO) > 1.42 nm (Pd/Gr) > 1.20 nm (Pd/RGO), decreased number of oxygen groups and average number of layers. Smaller Pd nanoparticles of larger PdO_x overlayer thickness were observed on highly hydrophilic substrates (functional oxygen groups content). Decoration accompanied by reduction using $NaBH_4$ led to the removal of water attached by hydrogen bonding to graphene interplanes and the formation of PdO_x overlayer from oxygen functional groups. Nanoparticle size obtained from QUASES was confirmed by Pd $3d_{5/2}$ spectra binding energy and full-width at half maximum. Various chemistry and mechanisms of graphene reduction using N_2H_4 and $NaBH_4$ were observed, where $NaBH_4$ was more efficient to remove water bonded by hydrogen bonding to oxygen groups and thus further graphene exfoliation. A substantial influence of substrate, functional group content on nanoparticle coverage, size and Pd oxide overlayer thickness was observed.

1. Introduction

Graphene materials such as graphene oxide (GO) and reduced graphene oxide (RGO) and those decorated with metal and metal oxide nanoparticles have recently gained an interest because of their wide range of applications in catalysis, medicine, energy storage, *etc.* The performance of devices based on such materials largely depends on their chemical and structural properties, which can be substantially modified by variation in synthesis conditions. Physicochemical properties of GO and RGO depend on the substrate properties (height and diameter of stacked nanostructures, number of average layers in stacked nanostructures), substrate surface functionalisation (number of functional groups), type, size and amount of nanoparticles and chemical state of nanoparticles (amount of metallic and oxide forms). Several reports have been recently published on the preparation and characterisation of Pd nanoparticles on graphite [1] and graphene materials such as GO [2–6] and RGO [5,7–10]. Preparation procedures applying different substrates, GO syntheses, surface functionalisations, Pd precursors, stabilizers, reducing agents, solution concentrations, pH and temperature resulted in a wide range of Pd nanoparticle size evaluated in the majority of cases by transmission electron microscopy (TEM) and/or scanning electron microscopy (SEM) [1–12]. Graphite decorated with Pd showed nanoparticle size of 5–10 nm, agglomerating to 20 and 50 nm due to hydrogen and high-temperature treatment [1]. Additionally functionalised surface of Pd-decorated GO resulted in Pd nanoparticle size of 3–7 nm [2]. The smallest Pd nanoparticle size was obtained on GO surface using sodium borohydride ($NaBH_4$) during decoration, i.e. 1–4 nm [3] and 3–5 nm [4], whereas a polyol method using polyethylene glycol resulted in Pd nanoparticle size of 15 nm [5] and 5–10 nm [6]. Decoration of RGO surface after preliminary reduction using hydrazine (N_2H_4) or $NaBH_4$ resulted in

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much wider distribution of Pd nanoparticle size than that on the surface of GO. Additionally functionalised surface of RGO resulted in Pd nanoparticle size distribution of 15–22 nm [7] and 5–25 nm [8] in contrary to the smallest size of 8 ± 2 nm obtained on "as-received" GO surface [9]. The largest Pd nanoparticles (50 nm) were reported for Pd-decorated RGO surface using a polyol method applying polyethylene glycol as a reducing agent [5]. Pd nanoparticles of various sizes on the multiwall carbon nanotubes reported elsewhere [10] showed dependence on the preparation conditions, i.e. reducing agent and temperature, where increased sintering temperature led to the enlargement of their size. In addition, the diameter of Pd nanoparticles decorating GO substrate showed a remarkable increase with temperature, precursor solution concentration, and deposition time [11]. The XRD, XPS, and zeta potential measurements of Pd nanoparticles of 5, 10 and 20 wt.%, respectively, on RGO obtained by spontaneous deposition without any reducing agents for pH from 1 to 12 provided the mean size of Pd nanoparticle of 3.8 nm (pH = 1), 33–53 nm (pH = 2–11) and 27 nm (pH = 12), accompanied by decreasing Pd content below pH = 2 and above pH = 11 [12]. It was shown that the zeta potential was affected by a gain or loss of protons (H^+) by RGO oxygen-containing functional groups such as C—O—C or C—OH, which in H_2O were ionized or hydrolysed:

$$C - OH \leftrightarrow C - O^- + H^+ \tag{1}$$

$$C - O - C + H_2O \leftrightarrow C - OH^+ - C + OH^-. \tag{2}$$

In this redox reaction, the oxidation of RGO releases electrons and protons (H^+), where protons decrease pH. From the equilibrium constants, it was found that Pd species present in an aqueous solution of $PdCl_2$ precursor of pH between 2 and 11 existed as Pd^{2+}, $Pd(OH)^+$ and neutral soluble $Pd(OH)_2{}^0$, whereas $Pd(OH)_3{}^-$ ion dominated above pH = 11. At pH = 2–11, Pd ions were deposited on oppositely charged RGO oxygen-containing groups and were reduced. For pH above 11, electrostatic repulsion of similarly charged Pd ions and RGO oxygen groups led to a decreasing amount of Pd.

Characterisation methods with X-ray diffraction (XRD), SEM and TEM may not precisely determine the structural parameters of Pd nanoparticles, i.e. metallic Pd nanoparticle size and Pd oxides overlayer thickness, because of nanoparticle agglomeration [10]. Additionally, for the purpose of studying surface phenomena important in different heterogeneous reactions, the investigations of strictly surface properties are important because these properties may remarkably differ from those in a bulk. Therefore, the surface analyses using X-ray photoelectron spectroscopy (XPS) aided with Quantitative Analysis of Surfaces by Electron Spectroscopy (QUASES) and reflected electron energy loss spectroscopy (REELS) were used to determine: (i) the chemical and structural properties of graphite, graphene oxide, reduced graphene oxide and those decorated with Pd nanoparticles using the same Pd decoration procedure and (ii) influence of substrate and number of oxygen functional groups at these substrates on the chemical and structural parameters of Pd nanoparticles.

2. Experimental

2.1. Sample preparation

The graphite flakes (Asbury Carbons, USA) were washed by an H_2SO_4:HNO_3 (3:1) solution and then rinsed with deionised water to obtain a stable pH of the filtrate (pH ~ 7). Graphite flakes (sample denoted as Gr) were then dispersed in water by using high-power ultrasonic and mechanical homogenizers and dried.

Preparation of GO proceeded using commercially available graphite Across (Acros Organics, USA, 325 mesh). GO sample was prepared using a modified Hummers method [13]. Water suspension of GO was washed with deionised water until the suspension reached pH ≈ 6 and then dried.

Reduction procedure of the prepared GO proceeded by mixing 50 ml of 50 wt% water solution of hydrazine (N_2H_4) at room temperature (RT) (sample denoted as RGO).

Decoration with Pd nanoparticles of graphite, GO and RGO proceeded in a water solution of Pd precursor [$PdCl_2$ in 10% HCl (Sigma)] and 1 M NaOH (pH = 11), with slow addition of 1 M solution of sodium borohydride ($NaBH_4$) (90 min) at RT, followed by rinsing with water and acetone, and then drying. These samples were denoted as Pd/Gr, Pd/GO and Pd/RGO, respectively. All chemicals used were of analytical purity.

Similar functionalisation procedures of graphite flakes; synthesis of GO and RGO; and characterisation of GO and RGO using the TEM, XRD and electron spectroscopy methods have previously been performed and published [14].

2.2. XPS and REELS spectrometers

Measurements of survey, detailed XPS spectra and REELS spectra were performed by ultra-high-vacuum (UHV) AXIS-SUPRA (Kratos, UK) and ADES-400 (VG Scientific, UK) spectrometers.

The AXIS-SUPRA high-performance automated photoelectron spectrometer was equipped with a hemispherical analyser (WX-600) and X-ray excitation source. The XPS measurements were carried out using Al $K\alpha$ monochromatic radiation ($h\nu = 1486.69$ eV). The XPS C 1s, O 1s and Pd 3d spectra were recorded with the pass energy $E_p = 20$ eV, whereas the wide scans and spectra of contaminations were recorded with $E_p = 80$ eV. The X-ray incidence angle was 54.4°, and the photoelectrons emission angle was of $\alpha_{out} = 0°$, with respect to the surface normal. Overall, energy resolution was 0.48 eV (measured at Ag 3d photoelectron line). No surface cleaning was applied. The REELS spectra were recorded in ADES-400 spectrometer, equipped with a hemispherical analyser, a scanning electron gun (Kimball Physics, model EGG-3101) and an X-ray excitation source. The REELS spectra were measured using an electron beam of kinetic energy (KE) of 2000 eV, beam current of 5×10^{-6} A, a spot of $2r = 1$ mm, $Ep = 20$ eV, within a conical analyser acceptance angle of ±4.1°. Electron-beam incidence angle was of $\alpha_{in} = 0°$ and the emission angle of $\alpha_{out} = 35°$, with respect to surface normal.

3. Results and discussion

3.1. Elemental surface content by XPS

The XPS survey spectra recorded from carbon nanomaterials (Gr, GO and RGO) indicated carbon, oxygen and traces of S and Na (GO), N (RGO) resulting from preparation conditions using sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), sodium hydroxide (NaOH) and hydrazine (N_2H_4). Pd-decorated carbon nanomaterials showed Pd and traces of Na (Pd/GO, Pd/RGO), N and B (Pd/RGO) resulting from preparation conditions using $NaNO_3$, NaOH, N_2H_4 and $NaBH_4$. Quantification of surface atomic content was performed from C 1s, O 1s, Pd $3d_{5/2\text{-}3/2}$, Na 1s, N 1s, S 2p and B 1s spectra peak areas after Tougaard's inelastic background subtraction [15] using the MultiQuant software [16], described in detail elsewhere [17], assuming a homogeneous distribution of atoms at the surface, Scofield's subshell photoionisation cross sections [18], corrections for analyser transmission, asymmetry parameters of angular distribution of photoelectrons and elastic scattering. The content of oxygen was evaluated after subtracting the intensity of Pd $3p_{3/2}$ spectra overlapping with O 1s spectra, accounting for the intensity ratio of Pd $3d_{5/2\text{-}3/2}$ to Pd $3p_{3/2\text{-}1/2}$ for a clean Pd surface. Results of atomic content showed differences for all the investigated samples indicating various chemical processes during N_2H_4 reduction