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Oxygen atom loss coefficient of carbon nanowalls

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ABSTRACT

Extremely high values of atomic oxygen loss coefficient on carbon nanowall (CNW) surface are reported. CNW layers consisting of interconnected individual nanostructures with average length of 1.1 μm, average thickness of 66 nm and surface density of 3 CNW/μm^2 were prepared by plasma jet enhanced chemical-vapor deposition using $C_2H_2/H_2/Ar$ gas mixtures. The samples were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectrometry (RS) as well as X-ray photoelectron spectroscopy (XPS). The surface loss coefficient was measured at room temperature in a flowing afterglow at different densities of oxygen atoms supplied from inductively coupled radiofrequency O_2 plasma. The RF generator operated at 13.56 MHz and different nominal powers up to 900 W corresponding to different O-atom density in the afterglow up to 1.3×10^{21} m^{-3}. CNW and several different samples of known coefficients for heterogeneous surface recombination of neutral oxygen atoms have been placed separately in the afterglow chamber and the O-atom density in their vicinity was measured with calibrated catalytic probes. Comparison of measured results allowed for determination of the loss coefficient for CNWs and the obtained value of 0.59 ± 0.03 makes this material an extremely effective sink for O-atoms.

1. Introduction

Carbon nanowall (CNW) materials [1] present useful properties related to the graphene based structure, the nano-micro topography of surface, the open architecture, high porosity and large specific surface area determined by the vertically oriented, interconnected walls with thickness in the nanoscale range and length/height in the micron scale.

Various deposition procedures have been reported for carbon nanowalls, to mention a few of them: Microwave Plasma Enhanced Vapor Deposition [2], Radical Injection Plasma CVD [3], PECVD in pin-plate discharge geometry [4], downstream deposition in a low pressure RF plasma jet injected with acetylene in presence of hydrogen [5], radiofrequency PECVD applied to large area substrates [6].

The remarkable properties listed above make these materials very attractive for applications. Various reports pointed out to the potential of using CNW layers as large area supports for catalytic nanoparticles [7], stable and chemical resistant electrodes in electrochemical devices and batteries [8], in supercapacitors [9], almost total light trapping layers in energy devices [10], as tentative materials for heat management [11] or electric field electron emitters in electrical devices [12].

Special attention was paid recently to the use of CNW layers as platforms of interaction with biological entities, in view of developing biosensors [13] or scaffolds for tissue engineering [14]. While the properties of as-grown CNWs could be adequate for other applications, the lack of adequate surface chemistry prohibits application in cases where good adhesion intermediated by polar compounds is required. In such cases the CNWs should be functionalized with polar functional groups. A widely used method for surface activation is treatment with non-equilibrium oxygen plasma [15,16]. Since many nanostructured carbon materials just burn upon exposure to aggressive oxygen plasma the plasma parameters should be selected carefully to retain the original properties. A suitable method for functionalization of delicate materials with polar functional groups is application of extremely weakly ionized oxygen plasma or its flowing afterglow [15,16]. The latter does not contain measurable concentration of charged particles so the main reactants are neutral oxygen atoms in the ground state. They allow for rather rapid functionalization of carbon-containing materials but a major drawback of flowing afterglows is that the

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Table 1
Recombination coefficients of selected materials.

Material	Recombination coefficient	Reference
PTFE	6.6×10^{-4}	[23]
Stainless steel	0.07	[24]
Cu	0.225	[25]
Ni	0.27	[26]

supply of atoms may not be sufficient to cover losses by heterogeneous surface recombination. Large samples are therefore treated non-uniformly – the section close to the atom source is treated more intensively than the rest of the sample. The loss of atoms on the surface of treated materials therefore represents a major concern and should be known. Several groups addressed the oxygen atom loss on surfaces of various materials and several techniques have been invented to determine the loss coefficient, which is often called "recombination coefficient" [17–22]. The coefficients for poly tetrafluor ethylene (PTFE) [23], stainless steel (SS) [24], copper (Cu) [25] and nickel (Ni) [26] are presented in Table 1. Although atomic oxygen loss coefficients have been reported for several carbon containing materials [27–29] little work has been done on determination of the coefficient for CNWs.

2. Experimental

2.1. Synthesis and characterization of carbon nanowalls

The deposition procedure of CNW layers has been described in detail previously [5]. Basically, an argon plasma jet is formed in a continuously pumped vacuum chamber under high gas flow by expanding a narrow gap radiofrequency discharge through a nozzle. An injection ring placed in the nozzle proximity is used to admixing acetylene and hydrogen in the argon jet. The carbon species created following the acetylene decomposition are transported at substrate where the deposition takes place. The samples used in the present experiments were deposited on polished graphite substrates heated at 700 °C at the following settings: RF power 300 W, gas flow rates $Ar/H_2/C_2H_2$: 1050/25/1 sccm, distance from nozzle to substrate 50 mm, and nozzle diameter 10 mm.

The samples were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectroscopy (RS) as well as X-ray photoelectron spectroscopy (XPS).

The SEM investigations were performed using an Inspect S FEI Company instrument operating at 20 kV, with a maximum resolution of 3 nm. The AFM investigations were done with Park Systems XE-100 instrument (maximum horizontal scan range of 50 μm × 50 μm and maximum vertical movement of 12 μm), operating in tapping mode. TEM measurements were performed using an atomic resolution analytical Jeol JEM-ARM 200F electron microscope operating at 200 kV. The Raman spectra were acquired with a Raman Horiba spectrophotometer – Jobin Yvon T64000.

XPS measurements were performed by a TFA XPS instrument from Physical Electronics. The base pressure in the XPS analysis chamber was about 6×10^{-10} mbar and the samples were excited with X-rays over a specific 400 μm area using monochromatic Al $K_{\alpha 1,2}$ radiation at 1486.6 eV. The photoelectrons were detected by a hemispherical analyser, positioned at an angle of 45° with respect to the surface normal. Energy resolution was about 0.6 eV. Survey-scan spectra were measured at a pass energy of 187.85 eV, while for C1s individual high-resolution spectra were taken at a pass energy of 23.5 eV and a 0.1-eV energy step. The measured spectra were analyzed using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer.

2.2. Determination of O-atom loss coefficient

A powerful source of oxygen atoms was used in order to determine the O-atom loss coefficient on the surface of CNWs. Details about the experimental setup have been already reported [30] so only key features are described here. The experimental setup consists of 80 cm long glass tube terminated with standard KF 40 flanges. The tube (3.6 cm of inner diameter) is made from borosilicate glass of a low coefficient for heterogeneous surface recombination of oxygen atoms in order to prevent substantial loss of atoms along the tube. The tube is pumped with a rotary pump on one side and molecular oxygen is leaked on the other side. A copper coil is mounted onto the tube as shown schematically in Fig. 1. The coil is connected to a radiofrequency (RF) generator (13.56 MHz) of nominal power up to 1000 W via a matching network. The network impedance is adjusted manually and best coupling between generator and plasma is realized in the H-mode of the discharge [30]. Dense plasma is created in the volume within the coil as shown schematically in Fig. 1 when the discharge operates in the H-mode. In the E-mode, rather weak plasma also fills the volume between the coil and the grounded flange on the side where the gas inlet is marked in Fig. 1. Such an asymmetry is realized by shifting the RF coil from the center of the tube toward the flange. The distance from the coil to this flange is 35 cm while the distance to the opposite flange (where the pump duct is mounted) is 45 cm as indicated in Fig. 1.

A glass holder is mounted 20 cm from the coil toward the pump duct. Samples of different materials are placed onto the holder as shown in Fig. 1. In this study, high purity samples obtained from Goodfellow or Sigma Aldrich with different coefficients for surface association of oxygen atoms to parent molecules were used: poly tetrafluoroethylene (PTFE), stainless steel (SS), copper (Cu) and nickel (Ni). The recombination coefficients for these materials are shown in Table 1. All samples were of disk shape with diameter of 25 mm and visually exhibited smooth surfaces. No pre-cleaning was performed but any organic impurities that might be present on the samples' surface were removed by brief treatment with oxygen plasma. The plasma treatment also allowed for surface activation assuring time-independent recombination coefficients.

A catalytic probe was mounted inside the glass tube at the position shown in Fig. 1. The probe was activated well prior to measurements. Details of the probe properties including the accuracy and repeatability of results are disclosed elsewhere [31].

3. Results and discussion

3.1. Surface characterization of CNW samples

Typical SEM and AFM images of a sample are presented in Fig. 2. They show an open network of interconnected nanowalls, with average length of 1.1 μm, average thickness of 66 nm, and surface density of 3 CNW/μm^2. More details on the deposition mechanism and the structural and compositional characteristics of the CNW can be found in reference [32].

A typical TEM image is presented in Fig. 3(a). A thin foil is observed with the edge of CNW showing the graphene based structure of the material. The structure is confirmed by Raman spectrum presented in Fig. 3(b). The laser wavelength was 514 nm. The typical peaks of carbon nanowalls are observed at 1345 (D band), 1585 (G band), 1612 (D" band), 2690 (2D band) and 2960 cm^{-1} (D + G band). The 2D and D + G bands indicate a highly ordered structure with graphene-like domains, as we reported before [33].

Both survey and high-resolution XPS characterization of the samples prior and after measuring the recombination coefficients are presented in Fig. 4. The as-synthesized sample does not contain