Electron energy loss spectroscopy of Pd and Pd–Au catalysts supported on multiwall carbon nanotubes

B. Lesiak [a,*], L. Stobinski [a], L. Kövér [b], J. Tóth [b]

[a] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
[b] Institute of Nuclear Research, Hungarian Academy of Sciences (ATOMKI), P.O. Box 51, H-4001 Debrecen, Hungary

ABSTRACT

The X-ray PhotoElectron Energy Loss Spectroscopy (XP-EELS) and Reflection Electron Energy Loss Spectroscopy (REELS) were used for analysing surface layers of "as-received" and functionalised multiwall carbon nanotubes (MWCNT), and MWCNT decorated with Pd and Pd–Au particles after calcination/reduction. The decorated MWCNT were previously applied as catalysts in a reaction of formic acid electrooxidation. These spectroscopies, used as complementary methods of structural surface analysis, provide information on the energy position, intensity and full width at half maximum of the quasi-elastic peak and inelastic π and $\pi + \sigma$ energy loss peaks. Analysing the $\pi + \sigma$ energy loss peak, the bulk and surface C sp^2/sp^3 components can be separated. Functionalisation of MWCNT, catalyst reduction and Ar$^+$ ion sputtering increase the C sp^3 content in comparison to the "as-received" MWCNT and calcined catalysts. The intensity ratios of surface and bulk C sp^3 and sp^2 components evaluated from the REELS $\pi + \sigma$ energy loss peak indicate: (i) functionalisation leads to attachment of functional groups to the MWCNT surface, (ii) calcined catalysts show an amorphous carbon overlayer at the surface and (iii) reduction of calcined catalysts leads to increasing C sp^3 hybridisations.

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1. Introduction

The Pd and Pd–Au catalysts supported on the MWCNT have recently been by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron spectroscopic methods, i.e. X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) [1–6]. Such Pd/MWCNT and Pd–Au/MWCNT samples were previously tested for their catalytic activity in the reaction of formic acid electrooxidation [4,5]. The reduced catalysts were active, the Pd–Au/MWCNT catalyst showed higher activity than Pd/MWCNT, whereas the calcined catalysts were inactive. This catalytic activity was attributed to a larger metallic surface area, a thinner palladium oxide and amorphous carbon layers on Pd metallic crystallites due to reduction causing increase of metallic palladium surface area [5–8].

The X-ray PhotoElectron Energy Loss Spectroscopy (XP-EELS) and the Reflection Electron Energy Loss Spectroscopy (REELS) spectra are also of importance in characterisation of surfaces and thin films [9]. The electron passing through a surface layer of a solid interacts with the free (quasi-free) and weakly bound electrons.

Quanta of collective excitations running as longitudinal charge density oscillations through a solid volume are referred to as volume plasmons, whereas along the surface region as surface plasmons. The expression "bulk excitation" denotes any energy loss phenomenon occurring in an infinite medium without any boundary, whereas "surface excitation" denotes excitation due to the presence of a solid–vacuum boundary. The surface modes of the inelastic excitation have a lowered resonance frequency and are orthogonal to the volume modes. The energy loss process involves the energy quanta of the oscillations (plasmons) and their excitation probability. The plasmon energy, $Ep = \hbar\omega$, is related to the frequency, ω, of the oscillations, which depends on the density of weakly bound electrons for which the plasmon energy is large in comparison to their binding energy. The electron energy loss spectrum is characterised by the energy loss peaks, i.e. the π loss involving only π type valence electrons known as free-like electrons and $\pi + \sigma$ loss involving all the valence electrons. The energies and intensities (the latter ones measured by the peak areas) of the electron loss peaks (XP-EELS and REELS) characterise the near-surface valence electron density and the structural organisation of C sp^2/C sp^3 bonds, which can be also quantified from the equation [10]:

$$sp^2 = \frac{\text{Area}_\pi/\text{Area}_{\pi+\sigma}}{(\text{Area}_\pi/\text{Area}_{\pi+\sigma})_{\text{standard}}} \quad (1)$$

with a normalisation to a standard, e.g. graphite. Therefore, fitting of the REELS spectra into the π and $\pi + \sigma$ (surface and volume)

* Corresponding author. Tel.: +48 22 343 3432; fax: +48 22 632 5276.
E-mail address: blesiak-orlowska@ichf.edu.pl (B. Lesiak).

loss peaks may be applied for characterisation of the surface and volume contributions [9]. Otherwise, the C sp^2/C sp^3 content may be evaluated from the C 1s XPS spectra by fitting to C sp^2 and C sp^3 components and from the energy width of the first derivative of the C KLL XAES spectra (parameter D), using a linear interpolation of the parameter D for graphite (100% of C sp^2) and diamond (100% of C sp^3) [11]. The accuracy of this estimation depends on the accuracy of the assumed values of parameter D for diamond and graphite, which vary from 13.0 eV to 14.5 eV (diamond) and from 21.1 eV to 22.8 eV (graphite) [12 and references within].

The research using the REELS spectroscopy may have a broader impact for catalysis due to the possibility of distinguishing the electron signal from boundary from the respective signal from the outer layers since the catalytic reactions proceed at the surface. Such research can be especially useful for characterisation of catalyst performance and catalyst designing. Application of commonly used techniques of surface analysis such as XPS, XP-EELS and XAES provides the surface sensitivity from outer layers and is described by a few parameters, *i.e.* the inelastic mean free path (IMFP), the mean escape depth (MED), the information depth (ID), *etc.* where the IMFP is a material parameter dependent on electron kinetic energy (KE) and the other parameters depend on the IMFP and experimental conditions [13]. The above parameters are calculated from the emission depth distribution function (DDF), defining the probability that a photoelectron and/or Auger electron leaving a surface in a given direction originates from a specified depth measured inward along the surface normal. The MED is defined as an average depth normal to the surface from which the electron escapes. The ID is a maximum depth normal to the surface from which useful signal information is obtained, *i.e.* a thickness from which a specified percentage P (95%, 99%) of the detected signal originates. Neglecting elastic scattering, the following analytical expressions are valid: MED = $\lambda \cos \alpha_{out}$ and ID = $\lambda \cos \alpha_{out} \ln(1/((1-P)/100))$, where λ is the IMFP and α_{out} is the emission angle of the electron with respect to the surface normal. By analogy, in REELS the depths in the solid for a particular electron trajectory contribution are distributed according to probability density function referred to as a penetration depth distribution function (PDDF). This parameter is defined as a probability that an electron incident on the surface at an angle α_{in} be elastically backscattered from a maximum depth, z, and emitted in the direction of the analyser at an angle α_{out} and not inelastically backscattered, where α_{in} and α_{out} are measured with respect to the surface normal. Neglecting elastic scattering the mean penetration depth (MPD) and ID are expressed as: MPD = $\lambda(\cos \alpha_{in} \cos \alpha_{out}/(\cos \alpha_{in} + \cos \alpha_{out}))$ and ID = $\lambda(\cos \alpha_{in} \cos \alpha_{out}/(\cos \alpha_{in} + \cos \alpha_{out})) \ln(1/((1-P)/100))$. Assuming an electron IMFP in graphite for respective electron KE of 272 eV, 1202 eV and 4000 eV as: 0.72 nm (C KLL), 2.10 nm (C 1s) and 5.60 nm (REELS) [14] the above parameters are: MED = 0.72 nm (C KLL), MED = 2.1 nm (C 1s) and MPD = 2.2 nm (REELS), with the ID values for P of 99%: 3.3 nm (C KLL), 9.7 nm (C 1s) and 10.1 nm (REELS). Therefore, the MED given by Auger electrons refers to about 2 carbon walls, whereas the MED and MPD from the C 1s XP-EELS and REELS spectra to about 6 carbon walls. For an overlayer/substrate system the ID may differ depending on the material atomic number, Z, of the overlayer and substrate and their electron elastic differential scattering cross-sections [15] and morphology [16]. The importance of characterisation using the REELS $\pi + \sigma$ energy loss spectra is based on the possibility of distinguishing the surface boundary and bulk components between the respective C sp^2/C sp^3 contributions.

The XP-EELS and REELS spectroscopies are applied for investigating the surface of "as-received" MWCNT, functionalised by oxidation MWCNT (ox-MWCNT), and MWCNT decorated with Pd and Pd–Au particles after different chemical and physical treatments, *i.e.* reduction, calcination, and Ar$^+$ ion surface cleaning of Pd–Au/MWCNT calcined sample. Structural changes in the XP-EELS and REELS spectra are discussed accounting for the energy positions and the intensity of the quasi-elastic peak, the inelastic π and $\pi + \sigma$ loss peaks, and the $\pi + \sigma$ loss peak surface and bulk contributions.

2. Experimental

2.1. Samples and preparations

Commercial MWCNT (Echo-nanobio. Tech. Co. Ltd., Japan) with an average diameter of 50 nm and length of 5–15 mm, were purified and functionalised (65% aq. HNO$_3$, 6 h, 118oC) [2,17]. Precursors of 17.8 wt% Pd/MWCNT and 8.8 wt% Pd–10.0 wt% Au/MWCNT catalysts were prepared by a polyol method described in details elsewhere [2].

2.2. Apparatus

The XPS and REELS spectra were measured in the ultra-high-vacuum ESA-31 spectrometer [18] equipped with a high energy resolution electron analyser, an electron gun, an X-ray excitation source and Ar$^+$ ion source. The C 1s XPS, C KLL XAES and XP-EELS spectra were measured using Al K$_a$ X-rays ($h\nu$ = 1486.67 eV), in a fixed retarding ratio (FRR) working mode, at photon incidence and electron emission angles of 70° and 0°, respectively, with respect to the surface normal. The REELS spectra were measured using the FRR working mode, a primary electron beam with a spot diameter of 1.5–2.0 mm, an electron current of about 5 nA and primary electron beam of 4000 eV KE, the incidence and emission angles of 50° and 0°, respectively, with respect to the surface normal. The applied measurement geometries resulted from optimisation of experimental signal intensity and apparatus set up. The ion sputtering was carried out using an Ar$^+$ ion beam of 3 keV energy with a current of 30 µA for 1 min.

3. Results

3.1. Samples – surface compositions and notations

The investigated samples exhibit the following bulk compositions resulting from the chemical synthesis, *i.e.* 17.8 wt% Pd/MWCNT and 8.8 wt% Pd–10.0 wt% Au/MWCNT, *i.e.* below 1 at.% of metallic content. The XPS analysis indicated the presence of Au, Pd, C and O at the surface [4,5]. The surface content of Au and Pd resulting from XPS quantitative analysis [4,5], chemical treatments and assumed notations denoting the samples after chemical treatments are the following:

 (i) 10.6 wt% Pd/MWCNT calcined at 250 °C in Ar: Pd-C250;
(ii) 4.3 wt% Pd–4.6 wt%Au/MWCNT calcined at 250 °C in Ar: Pd–Au-C250;
(iii) 9.1 wt% Pd/MWCNT reduced at 200 °C in Ar and 5% H$_2$: Pd-R200;
(iv) 4.4 wt% Pd–5.0 wt% Au/MWCNT reduced at 200 °C in Ar and 5% H$_2$: Pd–Au-R200;
(v) 5.5 wt% Pd–3.8 wt% Au/MWCNT calcined at 250 °C in Ar and Ar$^+$ ion sputtered in UHV: Pd–Au-C250–Ar$^+$.

The O content for the Pd decorated samples after calcinations and reduction was 11.7 wt% and 7.7 wt%, respectively, whereas for the Pd–Au decorated samples – 6.5 wt% and 7.0 wt%, respectively [4,5].