Eur. Phys. J. D **34**, 271–274 (2005)
DOI: 10.1140/epjd/e2005-00156-y

The European Physical Journal D

Electronic state of nitrogen incorporated into CN_x nanotubes

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Received 6 September 2004

Abstract. CN_x nanotubes have been prepared by acetonitrile decomposition over Ni, Co and Ni/Co catalysts. X-ray photoelectron spectroscopy study on the samples revealed a change of nitrogen concentration and shape of N 1s line with variation of the catalyst used. Quantum-chemical calculations on tube fragments showed the energy of N 1s level depends on the atomic structure of carbon tube and kind of incorporated nitrogen. The largest binding energies were found to be characteristic of three-coordinated nitrogen atoms doping the zigzag and chiral carbon nanotubes.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 71.23.An Theories and models; localized states – 79.60.-i Photoemission and photoelectron spectra

1 Introduction

Electronic properties of carbon nanotubes are strongly sensitive to the atomic arrangement of tube, namely, diameter, chirality, defects and impurities [1]. Nitrogen atom, having a size close to that of carbon atom, is an ideal substitution impurity, which can be easy incorporated into the tube walls through various synthetic techniques [2]. Nitrogen doping was demonstrated to improve electric conductivity, field electron emission properties of carbon nanotubes and their chemical activity towards the gaseous molecules [3]. Electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) have revealed two types of bonding of the nitrogen and carbon within the hexagonal network [4]. The higher binding energy in the N 1s spectra corresponds to three-coordinated nitrogen atoms replacing carbon ones, the lower binding energy is attributed to pyridinic nitrogen incorporated into tube walls with a vacancy defect formation. The holes in the CN_x nanotube network have been observed using scanning tunneling microscopy (STM) [4]. Density functional theory (DFT) calculations on metallic armchair carbon nanotubes doped with different kinds of nitrogen showed that three-coordinated atom produces a donor energy level, while pyridinic atom acts as an acceptor impurity [5]. This suggests a way to tune the electronic property of carbon nanotubes by adjusting methods for incorporation of certain form of nitrogen. Moreover, the electronic state of three-coordinated substitutional nitrogen was found using DFT computations to depend on the atomic structure of pristine tube [6]. The impurity state is totally delocalized in the case of the armchair tube and spatially localized in the semiconducting zigzag tube. Electron localization makes the impurity site chemically and electronically active.

Recently we have demonstrated that composition of the catalyst, used in chemical vapor deposition (CVD) process, can influence on the proportion of different kinds of nitrogen in multiwall CN_x nanotubes [7]. The greatest proportion of the pyridine-like nitrogen was found for the sample obtained with the Ni/Co 1:1 catalyst. The equal quantity of Ni and Co in the catalyst is likely to provide the higher solubility of nitrogen in metal particle and more high kinetics of growth of the CN_x nanotube that result in formation of many vacancies with nitrogen atoms on the boundaries. The purpose of the present work is to study a change of binding energy of N 1s electrons for doped tubes differed by the atomic structure. We invoke ab initio calculations on armchair, zigzag, and chiral carbon tubes doped with three-coordinated and pyridinic nitrogen for interpretation of XPS measured for CN_x nanotubes synthesized using different catalysts.

2 Experimental

CN_x nanotubes were obtained using a CVD method described in details elsewhere [8]. The catalysts were synthesized by the thermal decomposition of bimaleates of Ni and Co and their mutual solid solutions with the ratios of Ni/Co equal to 1:1. CN_x nanotubes grew via pyrolysis of acetonitrile in an argon flow (3 l/min) at 850 °C and

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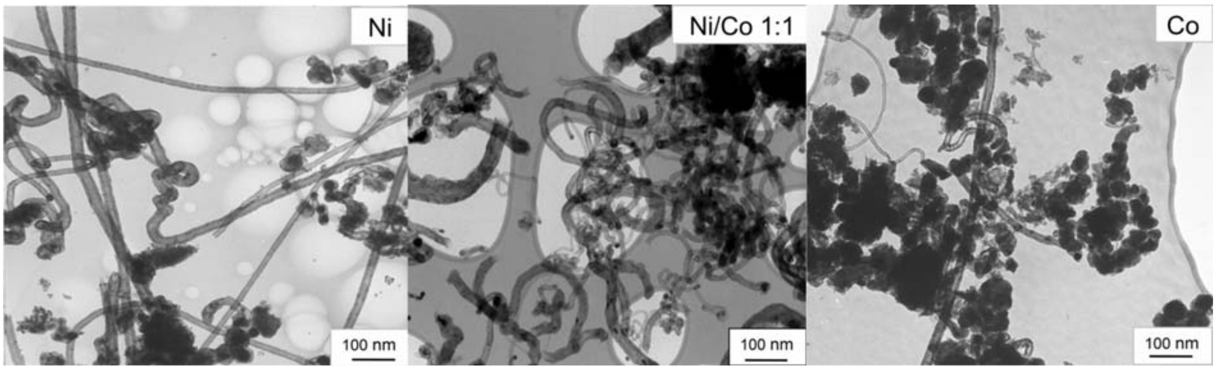

Fig. 1. Transmission electron micrographs of the samples produced by acetonitrile pyrolysis over Ni, Ni/Co, and Co catalyst.

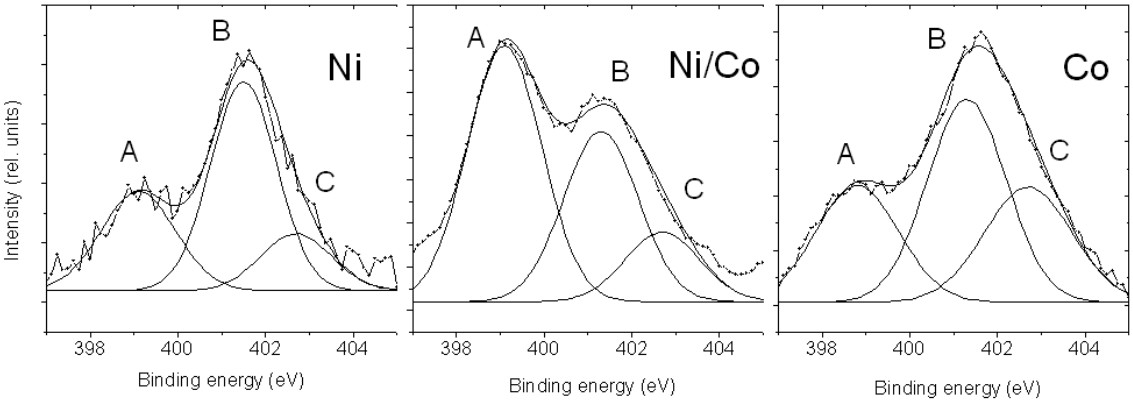

Fig. 2. N 1*s* spectra measured for the samples produced using Ni, Ni/Co, and Co catalyst. The spectra were fitted by three Gaussian components.

atmospheric pressure. The synthesized samples were studied with a transmission electron microscope JEOL-100C and an XPS spectrometer Quantum 2000 Scanning ESCA Microprobe. The concentration of nitrogen in the samples was estimated from the ratio of the areas of the N 1*s* and C 1*s* lines with taking into account the photoionization cross-sections. The samples obtained over Ni and Ni/Co catalysts involve ~1.2% of nitrogen, using of the Co catalyst reduces the nitrogen concentration up to ~0.7%.

3 Calculations

Geometry of fragments of nitrogen-doped carbon tubes was relaxed in Hartree-Fock self-consistent field using 3-21G basis set within the quantum chemical package Jaguar [9]. This approach calculates ground state of a system while the XPS lines arise in the result of sample ionization. Thus, for the XPS spectra interpretation, the calculated N 1*s* level energy (E) should be corrected to take into account the relaxation for the ionized state. The correction factor was determined from the correlation dependence between the experimental and theoretical values for ten nitrogen-containing molecules [7]. The theoretical binding energies E^{BE} were computed using the derived linear dependence $E^{BE} = 75.69 + 0.78271E$.

4 Results and discussion

Transmission electron microscopy (TEM) images of the samples obtained are presented in Figure 1. The synthesized materials contain multiwall carbon nanotubes, catalyst particles capsulated into graphite shells, and amorphous carbon. The maximal amount of nanotubes was found in the sample obtained over Ni/Co catalyst. Using of Ni and Co catalysts yields carbon nanotubes with diameter varying within 20–40 nm. The sample obtained over Ni/Co catalyst contains tubular structures of diameter 60–90 nm and thinner nanotubes 15–30 nm in diameter.

The XPS of N 1*s* line measured for the samples produced are compared in Figure 2. The spectra exhibit two peaks located around 399.0 and 401.4 eV. The relative intensity of the peaks is changed with catalyst variation. The spectra were fitted by three Gaussian components of the width 2.1 eV. The binding energy corresponding to the components and their energy separation are collected in Table 1.

To interpret the experimental data we calculated three tubes, which are close in diameter and drastically differed in the atomic arrangement (Fig. 3). Two bonds of carbon hexagons are oriented perpendicularly and along a tube axis in armchair (7,7) and zigzag (12,0) carbon tube respectively. The (10,4) carbon tube has chiral structure. Two different nitrogen impurities were introduced in a carbon tube: (1) a three-coordinated atom and (2) three

Table 1. Parameters of the N 1s spectra of samples synthesized using different catalysts.

Catalyst composition	Binding energy for feature (eV)			Separation of features (eV)	
	A	B	C	A and B	B and C
Ni	399.1	401.5	402.7	2.4	3.6
Ni/Co	399.1	401.3	402.7	2.2	3.6
Co	398.8	401.3	402.7	2.5	3.9

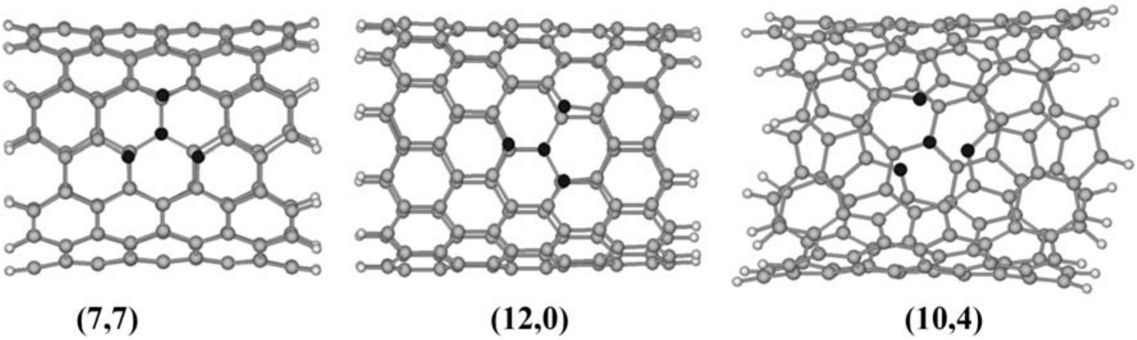

Fig. 3. Optimized geometry of fragments of nitrogen-doped carbon nanotubes. Nitrogen atoms are indicated by dark circles, hydrogen atoms (white circles) saturate dangling bonds at the fragment boundaries.

Table 2. Energy of N 1s level, calculated for pyridinic (E_{pyr}) and three-coordinated (E_{th}) nitrogen incorporated into fragments of carbon tubes and graphite, and difference between these values (ΔE).

Fragment	E_{pyr}(eV)	E_{th}(eV)	ΔE (eV)
graphite	399.1	401.7	2.6
(7,7) tube	399.2	401.9	2.7
(12,0) tube	399.5	403.2	3.7
(10,4) tube	398.9	403.3	4.4

pyridinic atoms located at the edges of one-atomic vacancy. The boundary dangling bonds of fragments were saturated by hydrogen atoms and the nitrogen impurities were maximally spaced from fragment boundary and from each other. The energy of N 1s levels was corrected in accordance with the correlation dependence, described in the Calculations part, and the work function of the spectrometer (6 eV). The values obtained for the pyridinic and three-coordinated nitrogen incorporated into the carbon tubes are listed in Table 2 together with those for nitrogen atoms embedded into the graphite fragments [7]. The 1s electron energies for the pyridinic nitrogen atoms have the similar values for all considered carbon structures, while those for the three-coordinated nitrogen atoms are strongly dependent of a tube arrangement. The obtained variation in the 1s energies for the latter kind of nitrogen could be due to a difference in local distribution of density associated with the unpaired electron. The difference has been found to be caused by breaking of the left-right mirror symmetry in zigzag carbon nanotube with the nitrogen impurity inserting [6].

Comparison between the experimental data and calculation results (Tabs. 1 and 2) shows the feature A of the N 1s spectra of CN_x nanotubes corresponds to the pyridinic nitrogen. The features B and C can be attributed to the three-coordinated nitrogen atoms incorporated respectively into armchair tubes and zigzag or chiral tubes. The N 1s spectrum of the CN_x nanotubes synthesized over Co catalyst exhibits the greatest relative intensity of the feature C and the lowest energy of the feature A. Both these facts suggest that Co particles promote growth of chiral nanotubes. The Ni and Ni/Co catalysts produce the carbon nanotubes with similar arrangement, being armchair or zigzag type mainly. However, the Ni/Co solid solution provides large inserting of pyridinic nitrogen into tube walls. The N 1s spectrum of CN_x nanotubes synthesized using Ni/Co catalyst shows the smallest separation of the features A and B. The calculation of N 1s electron energies for doped graphite fragments [7] has shown the decrease of A and B features distance can be expected when nitrogen atoms occupy one or two sites at the boundaries of one-atomic vacancy.

In summary, the N 1s spectra of CN_x nanotubes were shown to be decomposed on three components which relative intensity and separation depend on the catalyst, used in the CVD process. The ab initio Hartree-Fock calculations on the fragments of nitrogen-doped carbon nanotubes indicated the low-energy spectral component corresponds to the pyridinic nitrogen. The electronic state of three-coordinated nitrogen atoms was found to be largely sensitive to the atomic arrangement of carbon nanotube that leads to appearance of two high-energy components in N 1s spectrum of CN_x nanotubes. The relative intensity of these components varies with change of a catalyst and could be a mark for indication of chiral tubes formation.

The work was financially supported by the Russian Basic Research Foundation (grants 03-03-32286, 03-03-32336) and European Office of Aerospace Research and Development (grant CRDF RUP1-1501-NO-04).

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