

02

## Simulation of the interaction of NiO with a graphene layer in a NiO<sub>x</sub>/CNT composite based on XANES Spectroscopy

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The interaction of NiO clusters with a graphene layer of a nanotube in NiO<sub>x</sub>/CNT composites is simulated based on a theoretical analysis of Ni K-edge XANES spectra. Various cases of orientation of crystallographic planes relative to the nanotube wall are considered. It was determined that Ni in the composite is predominantly in the 2+ state, NiO particles are oriented towards the tube wall by the (200) plane. Accounting for carbon atoms even in the first sphere of the nickel environment makes it possible to achieve good agreement between the theoretical spectrum and experiment.

**Keywords:** XANES spectroscopy, composites, carbon nanotubes.

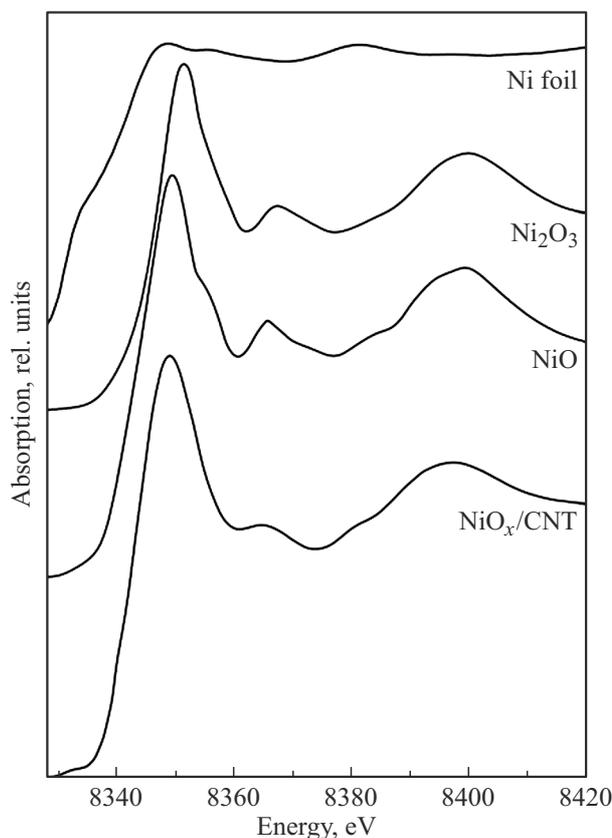
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Composites based on carbon nanomaterials and oxides/hydroxides of transition metals, in particular nickel, have unique physical and chemical properties, which makes them suitable for use as catalysts, sensors, supercapacitors and other applications [1–3]. The surface properties of the composite material interfaces, including local atomic and electronic structures, molecular orientation, and surface morphology, play a critical role in determining the performance and efficiency of such devices [4]. XANES X-ray absorption spectroscopy (X-ray absorption near edge structure) in combination with theoretical modeling allows to obtain valuable information on the local atomic structure of the absorbing atom at the interfaces, thereby determining the mechanisms of interaction between the components of the composite [5].

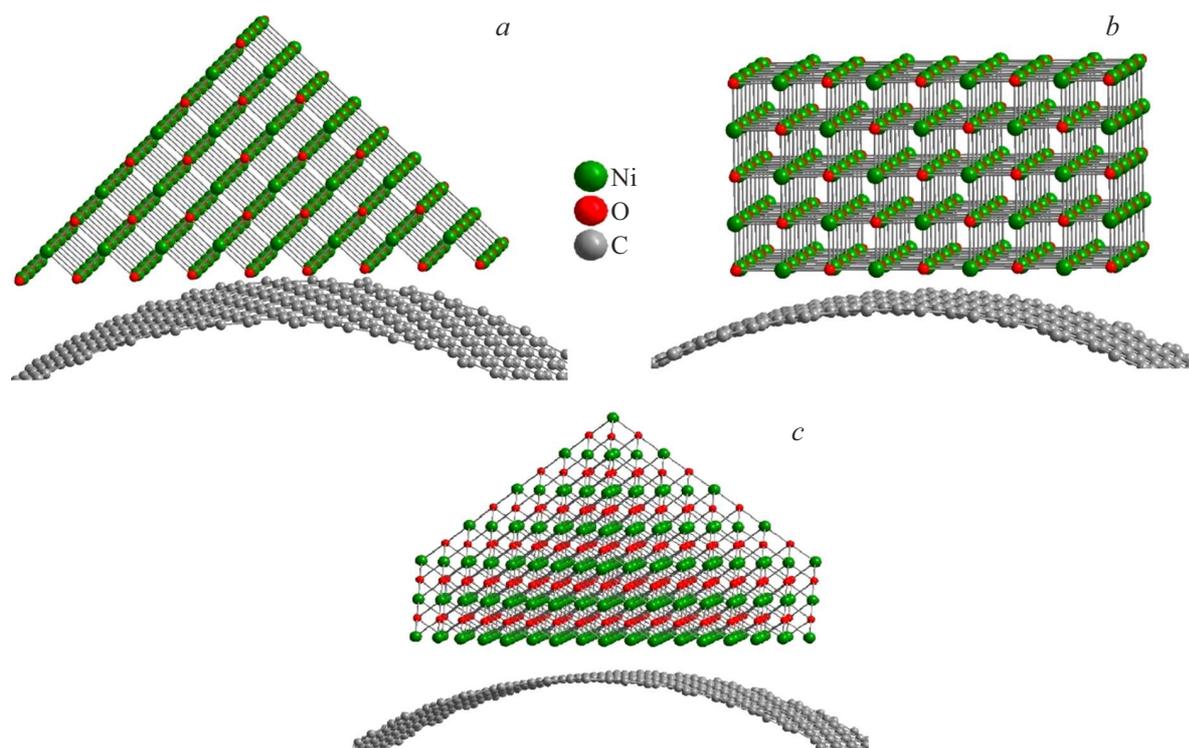
The main goal of this work — is to study the local atomic structure of Ni atoms located at the nickel oxide/graphene nanotube layer interfaces. This work presents the results of a study of the local atomic structure and oxidation state of nickel in the NiO<sub>x</sub>/CNT composite based on theoretical modeling of X-ray absorption near edge structure (XANES) spectra.

Ni K-edge XANES spectra of NiO<sub>x</sub>/CNT composites were measured in the fluorescence detection mode at the KMC-2 station of the BESSYII synchrotron center (HZB, Germany, Berlin). More detailed information on the study samples and experimental details is presented in the work [6]. Simulating of the interaction of NiO with the graphene layer of the nanotube wall was carried out on the basis of self-consistent calculations for optimizing the geometry and finding the equilibrium state at the interface of the nanotube and NiO using the Density functional based tight binding method DFTB [7]. Noncovalent interactions between the nanotube and the oxide surface were taken into

account using the Tkachenko-Scheffler correction TS [8], which describes van der Waals interactions through London atomic pair potentials  $C_6R^{-6}$ . *Ab initio* calculation of XANES spectra was carried out using the full potential



**Figure 1.** Comparison of Ni K-edge XANES spectra of NiO<sub>x</sub>/CNT and standard compounds — metallic Ni, NiO, Ni<sub>2</sub>O<sub>3</sub>.



**Figure 2.** Structural models for calculating theoretical Ni *K*-edge XANES spectra: *a* — orientation of NiO to the tube wall by plane (220), *b* — orientation of NiO to the tube wall by plane (200), *c* — orientation of NiO to the tube wall by the (111) plane.

finite difference method implemented in FDMNES [9]. For the obtained spectra, a Lorentz convolution procedure was carried out to take into account the broadening effects. The calculated cluster size was 7 Å around the absorbing one, and the theoretical spectrum included a contribution from the scattering of 142–150 atoms, depending on the model.

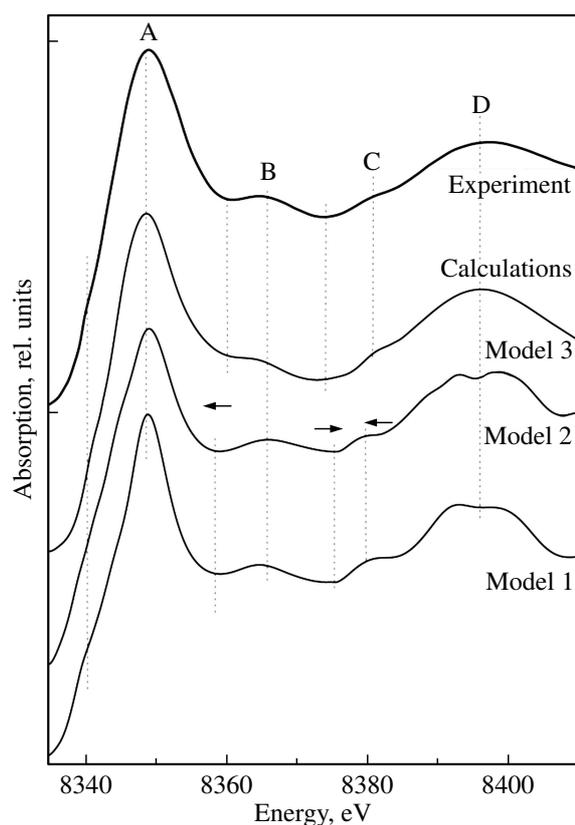
One of the methods for analyzing X-ray absorption spectra is the fingerprint analysis. The principle of the method — is a comparison of the spectra of the sample under study with an unknown local structure and the spectra of standard compounds with a known structure. It is based on the similarity of the absorption spectra of compounds with a similar local structure. In addition to fingerprint analysis of experimental spectra (in the lack of the required reference spectrum), a comparison is made of the experimental spectrum of the sample under study with the theoretically calculated spectra of several structural models with a specific local geometry.

A comparison of the experimental Ni *K*-edge XANES spectrum of the NiO<sub>x</sub>/CNT composite and the spectra of standard compounds (NiO, Ni<sub>2</sub>O<sub>3</sub>, metallic nickel) [10] shows the greatest similarity with the spectrum of NiO (Fig. 1) [6], although the spectral features are noticeably blurred. This suggests that the predominant valence state of nickel in composites is 2+ and doubly charged nickel cations have an octahedral environment (similar to nickel cations in NiO oxide). The predominant content of nickel in

the form of NiO is confirmed by diffraction data [6]. NiO in the diffraction pattern of the composite appears in the form of reflection peaks of the (200), (220), (111) planes. The diffraction pattern also contains peaks corresponding to CNT. Diffraction studies did not show the formation of joint nickel-carbon phases. However, blurring of the spectral features and some difference in the spectra of the composite and NiO oxide indicate disorder and changes in the local structure of nickel in the composite [5]. Changes in the spectrum may be the result of the fact that some of the nickel atoms may have in their immediate environment not only oxygen, but also carbon atoms of the graphene layer of the nanotube. Indeed, heterophase and composite materials often exhibit unique structural motifs that have no analogues among bulk materials.

Structural models for calculating XANES spectra were a fragment of a chiral nanotube with a diameter of about 5 nm and a fragment of a NiO crystal with a surface corresponding to the lattice planes (111), (200) and (220), oriented towards the graphene layer of the nanotube wall (Fig. 2). Lattice planes were selected according to X-ray diffraction data.

Simulating of the adsorption of NiO clusters onto the graphene plane of a nanotube shows that the most probable model for the orientation of NiO relative to the graphene plane is the orientation of the oxide cluster towards the tube wall with the (200) plane. This is also confirmed by theoretical calculations of XANES spectra.



**Figure 3.** Comparison of experimental and theoretical Ni *K*-edge XANES spectra of NiO<sub>x</sub>/CNT. Model 1 — orientation of NiO to the tube wall by plane (220), model 2 — orientation of NiO to the tube wall by plane (111), model 3 — orientation of NiO to the tube wall by plane (200).

Figure 3 shows a comparison of the calculated spectra of the constructed structural models. It can be seen that all spectra have a similar shape and the same set of most intense spectral features (peaks A-D). However, the spectrum of the model 3 (orientation of the NiO cluster to the graphene layer of the tube wall by the (200) plane) has better agreement with the experimental spectrum in terms of the shape of the white line, the energy position of the spectral features A-D, and the position of the minima. For models 1 and 2 (with the orientation of the NiO cluster to the graphene layer of the tube wall by the (220) and (111) planes, respectively), there is a shift of the minimum between the peaks A and B to the low-energy region, and there is minimum between the peaks B and C towards high energies. The energy position of the white line (peak A) and peak B coincides with the experiment, while peak C shifts towards lower energies, peak D is split, which is not in the experimental spectrum. The figure shows spectra in which, when calculating, nickel atoms on the surface of the NiO cluster closest to the graphene layer of the tube wall were chosen as absorbing atoms. It can be seen that taking into account the presence of carbon atoms in the immediate environment of nickel

allows to achieve reproduction of all spectral features and good agreement between the theoretical spectrum and the experimental one. Probably, due to the small size of the NiO particles in the composite, the contribution of distortion of the octahedral oxygen environment of the surface nickel atoms becomes significant due to the appearance of a graphene layer of carbon nanotube walls surrounding the NiO<sub>x</sub> particles in their immediate environment of carbon atoms.

Differences in the work function of the NiO (200) surface and the carbon nanotube lead to electron transfer at the interface. As shown by measurements of the NiO<sub>x</sub>/CNT composite using scanning electron spectroscopy (SEM), carbon nanotubes in it are intertwined with each other and with NiO<sub>x</sub> [6] particles, and the NiO<sub>x</sub>-CNT heterointerface can act as a conductive path, accelerating electron transport between NiO<sub>x</sub> particles and nanotubes. This result illustrates the promise of using NiO/CNT composites as electrode material in supercapacitors.

Based on fingerprint analysis of the experimental spectra of the composite and spectra of nickel oxides, as well as calculations of X-ray absorption spectra XANES, it was determined that the predominant oxide state of nickel in the NiO<sub>x</sub>/CNT 2+ composite, and the local structure of nickel cations in the composite is noticeably disordered in comparison with NiO. Surface nickel atoms have carbon atoms in their immediate environment, which leads to distortion of the oxygen octahedron characteristic of crystalline NiO. NiO particles are predominantly oriented toward the tube wall with the (200) plane.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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