

Research Article

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Low pressure RF plasma modification of the surface of three different nano-carbon materials

Abstract: Well-ordered nano-carbon materials, like multi-wall carbon nanotubes, graphene oxide, graphene due to their unique physical and chemical properties, are candidates for promising applications.

In this work thin multilayered graphene, single layer graphene oxide layers and highly oriented pyrolytic graphite (HOPG) surface were treated by RF activated N₂ gas plasma at nominally room temperature. Negative bias in the 0–200 V range and treatment time of 10 min was applied. Surface chemical alterations were followed by X-ray photoelectron spectroscopy (XPS). The applied treatments resulted in a significant build-up of nitrogen in the surface of these nano-carbon materials. The amount of nitrogen varied between 4 and 10 atomic %, depending on type of carbon and on biasing conditions. Evaluating the high-resolution N1s XP spectral region, typically three different chemical bonding states of the nitrogen were delineated. Peak component at 398.3 eV is assigned to C=N–C type, at 399.7 eV to sp² N in melamine-type ring structure and at 400.9 eV to N substituting carbon in a graphite-like environment. Identical chemical bonding of the nitrogen was detected on the surface of HOPG treated in the same way for comparison.

Keywords: RF plasma, surface modification, nano-carbon materials, XPS

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1 Introduction

Well-ordered nano-carbon materials, among others, multi-wall carbon nanotubes, graphene oxide, graphene due to their unique physical and chemical properties, are candidates for promising application in various areas ranging from novel structural materials, field emission devices to pharmaceutical drug-delivery vehicles [1-4]. Many of these applications require some kind of surface modification of these materials. Moreover, surface groups may significantly influence the wettability, acid/base properties or even the shape of the carbon nanoparticles [5-6]. Concerning drug carrier application, reactive surface groups are needed for attachment of bioactive molecules. When using them for reinforcing in polymeric matrices, not only the dispersion, but also strong covalent attachment to the matrix is required [7].

Recently, we have investigated application of low-pressure radio frequency (RF) plasma activation of N₂ and to explore this approach to the covalent attachment of the nitrogen to various carbon materials [8]. In this work thin films of graphene oxide, multilayered graphene and highly oriented pyrolytic graphite, were treated by RF activated N₂ gas plasma at nominally room temperature and the amount of built-in nitrogen and its chemical states were studied by X-ray photoelectron spectroscopy (XPS).

2 Experimental

2.1 Samples

Thin layers of powdered graphene (GR) obtained by disintegration [9] of synthetic graphite (Aldrich, USA) and commercial single layer graphene oxide (SLGO) flakes (Cheaptubes, USA), were deposited dropwise from ultrasonicated alcoholic slurry onto a stainless steel holder (Ø 9 mm), suitable also for XPS measurements. Pieces of freshly cleaved highly oriented pyrolytic graphite (HOPG) samples of similar size were used as reference materials.

2.2 Treatments

Plasma treatments were performed in the stainless steel sample preparation chamber of the XPS instrument (base pressure $<1 \cdot 10^{-4}$ Pa). N_2 flow regulated by a bleeding valve to set the pressure to 5 Pa. Constant RF power of 100 W at 13.56 MHz was applied through a matching circuit to a stainless steel coil built into the preparation chamber. The sample bias was varied between 0 and -200 V. The treatment time was always 10 min.

2.3 Characterisation

The plasma treated samples were characterised by X-ray photoelectron spectroscopy using a Kratos XSAM 800 spectrometer (Mg $K\alpha_{1,2}$ (1253.6 eV) excitation, fixed analyzer transmission mode). Low resolution survey spectra were recorded in the 150–1300 eV kinetic energy range with 0.5 eV steps. High resolution spectra of the O1s, N1s and C1s were acquired by 0.1 eV steps and 1 s dwell time. For the determination of the chemical shifts of the hetero-atoms (N and O), each set of spectra was carefully referenced to the C1s line of the sp^2 type graphitic carbon, set at 284.1 ± 0.2 eV BE (binding energy). Quantitative analysis, based on peak area intensities after removal of the Shirley-type background, was performed by the Kratos Vision 2 and the XPS MultiQuant 7 programs [10,11] (<http://aki.ttk.mta.hu/XMQpages/XMQhome.htm>). Experimentally determined photo-ionization cross-section data of Evans *et al.* [12] and asymmetry parameters of Reilman *et al.* [13] were used for the calculation. The chemical states of the implanted nitrogen were evaluated by applying the peak decomposition procedure by using the Kratos Vision 2 software.

3 Results and discussion

3.1 Chemical composition

The overall surface compositions (calculated by the generally applied “infinitely thick homogeneous sample” model) of the treated samples are summarized in Figs. 1 and 2. The data show that 4-10 atomic % nitrogen can be incorporated into the sample surface at the plasma treatment even at the applied relatively short 10 min reaction time. Somewhat higher N content (≈ 14 atomic %) was measured for the GR sample at 20 min exposure with 200 V bias. The nitrogen attachment to the samples shows

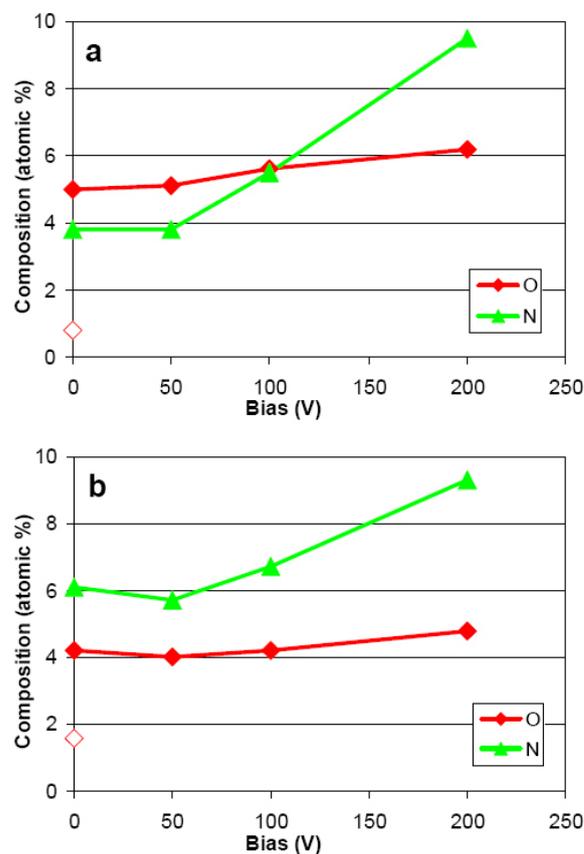


Figure 1: The surface composition of the HOPG (a) and GR (b) samples, treated for 10 min, as the function of the applied bias. Open symbols represent untreated samples.

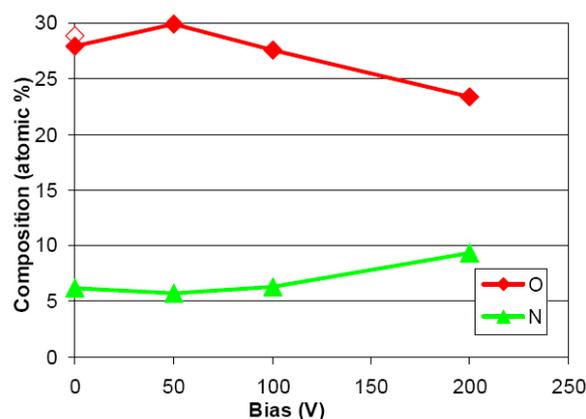


Figure 2: The surface composition of the SLGO samples, treated for 10 min, as the function of the applied bias. Open symbol represents untreated sample.

significant bias dependence. At low bias (50 V), only a small amount of N could be incorporated into HOPG while similar amount surface N content was found for all samples at 200 V bias. As concerning the bias dependence,

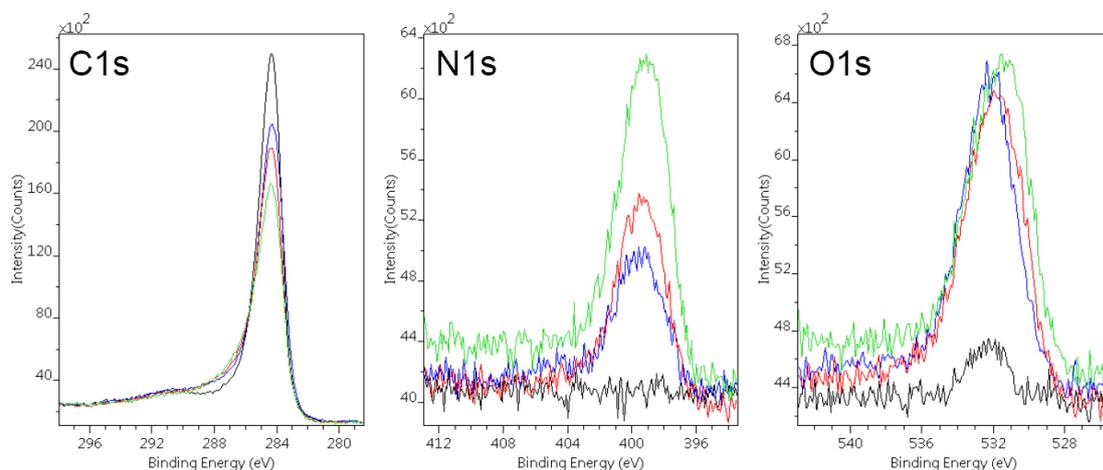


Figure 3: C1s, N1s and O1s lines of the HOPG samples treated at different bias (untreated black, 50 V blue, 100 V red, 200 V green) (colour online).

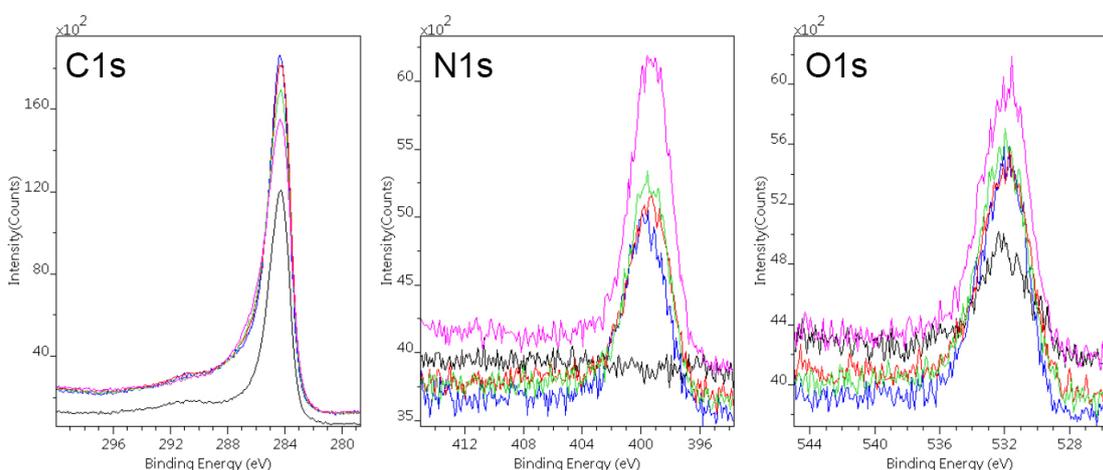


Figure 4: C1s, N1s and O1s lines of the GR samples treated at different bias (untreated black, 0 V blue, 50 V red, 100 V green, 200 V magenta) (colour online).

it is interesting to note that the 50 V negative bias does not affect increase of N content above the values obtained at zero bias for GR and SLGO. A very low (1-2 atomic %) oxygen content was measured both on untreated HOPG and on graphene. After all plasma treatments it rises up to 4-6 atomic % and it does not show significant bias dependence. The possible source of the oxygen contamination may be the O_2 and H_2O impurity of the reagent gas or desorption of these species from the chamber walls.

3.2 Chemical Structure

The incorporation of nitrogen into these nano-carbons will inevitably modify the chemical structure of the ordered graphene type carbon network.

The C1s, N1s and O1s spectra for the HOPG, GR and SLGO samples recorded at different biases (0-200 V) are depicted in Figs. 3-5. The chemical states of the measured elements in the HOPG and GR samples are similar. During the plasma treatment, only their intensities are decreasing, demonstrating that the implanted nitrogen (and oxygen) incorporated into the first 10 nm layer. The C1s spectrum of the SLGO sample is significantly different, because of the extra peaks of the carbon bonded to the large amount of oxygen. Both the elemental and oxygen bonded carbon content decreases with the increasing bias.

The chemical states of oxygen do not vary significantly for the treatments with different biases, while their content changes slightly. The O1s line of oxygen contamination, related to the presence of O_2 and H_2O , for the HOPG and GR is centred at 532.0 eV. This shift can be most probably

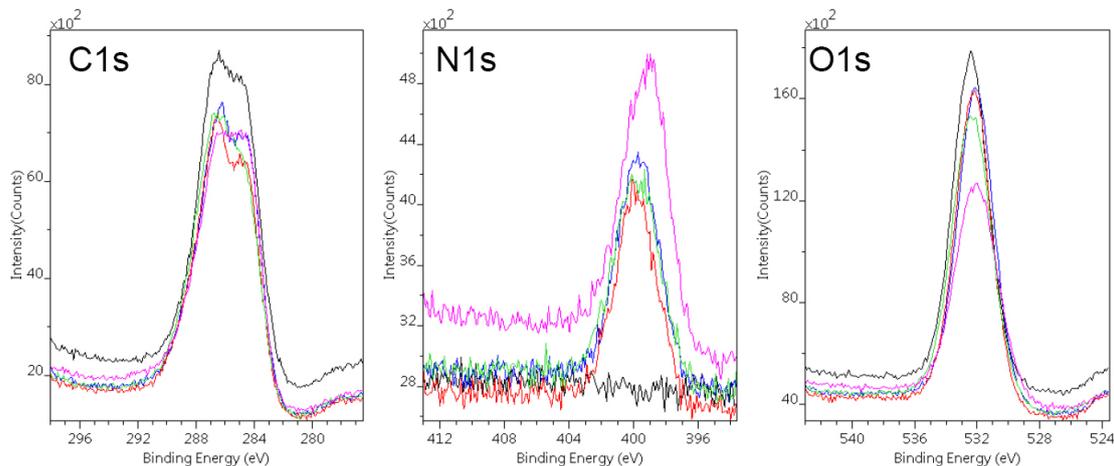


Figure 5: C1s, N1s and O1s lines of the SLGO samples treated at different bias (untreated black, 0 V blue, 50 V red, 100 V green, 200 V magenta) (colour online).

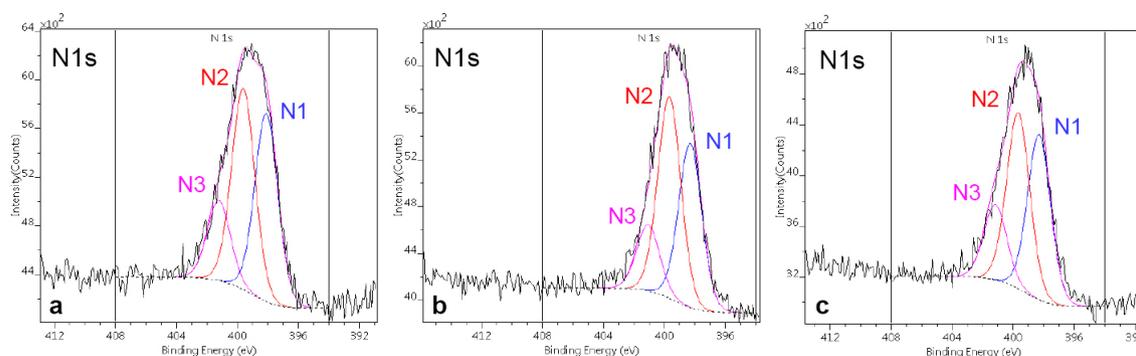


Figure 6: Decomposition of the N1s lines of the HOPG (a), GR (b) and SLGO (c) samples treated at 100 V bias.

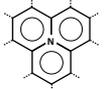
assigned to C–OH chemical states [14]. The high BE sub-peak at about 533.5 eV indicates the presence of ketone and carboxyl groups [14,15].

XP spectra of the N1s energy region for the GR and SLGO and also for HOPG samples, treated at 100 V bias, are depicted in Fig. 6. The broad peaks clearly indicate that the bonded nitrogen atoms have different chemical environments. Performing peak synthesis fitting with 1.75 eV half-widths components, corresponding to individual chemical states, three N1s components (denoted further as N1, N2 and N3) were found in all treated samples, positioned at 398.3 ± 0.3 eV, 399.7 ± 0.3 eV and 400.9 ± 0.3 eV, corresponding to minimum three different chemical environments. According to Fig. 5, the same chemical states of nitrogen were detected also on the surface of SLGO, although their relative amount was somewhat different. The assignment of this peak components to certain bonding states were discussed in a large number of publications based on experimental works

devoted to the synthesis of CN_x type materials [16-23], N doped graphene [24,25] and nitrogen-containing DLC coatings [8,26,27]. The controversy existing in rendering N-C structures to different chemical shifts was discussed in [16-19,28]. The determined chemical shifts were assigned in accordance with published data as follows: N1 peak component at 398.3 eV was assigned to C=N–C type chemical bonds, i.e. to the sp^2 nitrogen bonded to two sp^2 type carbon, like in pyridine [21,22,27]. The N2 component at 399.7 eV is attributed to sp^2 N in diazine or triazine-type structure [28]. The smallest N3 type N at 400.9 eV we assigned to N bonded to three graphitic rings, i.e., substituting a carbon atom in graphite-like environment [27]. These assignments were summarised in Table 1.

The ratio of the different chemical states of nitrogen does not seem to alter with the applied bias. As an exception, the treatment of SLGO sample where at 200 V bias the relatively higher abundance of the N1 type nitrogen is obvious.

Table 1: Assignment of N1s components of the plasma treated nano-carbon materials.

Component	Energy (eV)	Assignment
N1	398.3 ± 0.3	sp ² N in pyridine type ring 
N2	399.7 ± 0.3	sp ² N in diazine/triazine type ring structure 
N3	400.9 ± 0.3	N substituting C in graphite plane 

4 Conclusions

It was demonstrated that three different carbon materials (GR, SLGO, HOPG) could be conveniently modified using low-pressure RF plasma activated nitrogen.

4-10 atomic % of nitrogen could be incorporated into the surface at short 10 min treatment time. The amount of nitrogen can be varied by the negative sample bias of 0-200 V. The implanted nitrogen (and the oxygen impurity) is incorporated in the first few atomic layers of the samples.

Identical chemical bonds of the nitrogen were detected on the surface of all these samples. The three different chemical bonding states of the nitrogen was delineated and assigned to C=N-C (imine, pyridine) type (N1), to sp² N in melamine-type ring structure (N2) and to N substituting carbon in a graphite-like environment (N3). The relative abundance of these three types of N does not vary significantly with the applied bias.

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References

- [1] Soldano C., Mahmood A., Dujardin E., Production, properties and potential of graphene, *Carbon*, 2010, 48, 2127–2150.
- [2] Hu Y.H., Wang H., Hu B., Thinnest Two-Dimensional Nanomaterial-Graphene for Solar Energy, *ChemSusChem*, 2010, 3, 782–796.
- [3] Kuila T., Bose S., Mishra A.K., Khanra P., Kim N.H., Lee J.H., Chemical functionalization of graphene and its applications, *Progress in Materials Science*, 2012, 57, 1061–1105.
- [4] Feng L., Wu L., Qu X., New Horizons for Diagnostics and Therapeutic Applications of Graphene and Graphene Oxide, *Advanced Materials*, 2013, 25, 168–186.
- [5] Tóth A., Törőcsik A., Tombácz E., Oláh E., Heggen M., Li C., et al., Interaction of phenol and dopamine with commercial MWCNTs, *J. Coll. Interface Sci.*, 2011, 364, 469–475.
- [6] Whitby R.L.D., Gun'ko V.M., Korobeinyk A., Busquets R., Cundy A.B., László K., et al., Driving Forces of Conformational Changes in Single-Layer Graphene Oxide, *ACS Nano*, 2012, 6, 3967–3973.
- [7] Kuila T., Bhadra S., Yao D.H., Kim N.H., Bose S., Lee J.H., Recent advances in graphene based polymer composites, *Progress in Polymer Science*, 2010, 35, 1350–1375.
- [8] Bertóti I., Mohai I., Mohai M., Szépvölgyi J., Surface modification of multi-wall carbon nanotubes by nitrogen attachment, *Diamond Relat. Mater.*, 2011, 20, 965–968, DOI: 10.1016/j.diamond.2011.05.011
- [9] Kun P., Weber F., Balácsi C., Preparation and examination of multilayer graphene nanosheets by exfoliation of graphite in high efficient attritor mill, *Cent. Eur. J. Chem.*, 2011, 9, 47–51, DOI: 10.2478/s11532-010-0137-5.
- [10] Mohai M., XPS MultiQuant: Multimodel XPS Quantification Software, *Surf. Interface Anal.*, 2004, 36, 828–832, DOI: 10.1002/sia.1775.
- [11] M. Mohai M., Bertóti I., Calculation of Overlay Thickness on Curved Surfaces Based on XPS Intensities, *Surf. Interface Anal.*, 2004, 36, 805–808, DOI: 10.1002/sia.1769.
- [12] Evans S., Pritchard R.G., Thomas J.M., Relative Differential Subshell Photoionization Cross-sections (Mg K α) from Lithium to Uranium, *J. Electron Spectrosc. Relat. Phenom.*, 1978, 14, 341–358.
- [13] Reilman R.F., Msezane A., Manson S.T., Relative Intensities in Photoelectron Spectroscopy of Atoms and Molecules, *J. Electron Spectrosc. Relat. Phenom.*, 1976, 8, 389–394.
- [14] Lakshminarayanan P.V., Toghiani H., Pittman Jr. C.U., Nitric acid oxidation of vapor grown carbon nanofibers, *Carbon*, 2004, 42, 2433–2442.
- [15] Zhou J-H., Sui Z-J., Zhu J., Li P., D. Chen, Dai Y.-C., et al., Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR, *Carbon*, 2007, 45, 785–796.
- [16] Baker A., Hammer P., A Study of the Chemical Bonding and Microstructure of Ion Beam-deposited CN_x Films Including an XPS C 1s Peak Simulation, *Surf. Interface Anal.*, 1997, 25, 629–642.
- [17] Souto S., Pickholz M., dos Santos M.C., Alvarez F., Electronic structure of nitrogen-carbon alloys (a-CN_x) determined by photoelectron spectroscopy, *Phys. Rev. B*, 1998, 57, 2536–2540, DOI: 10.1103/PhysRevB.57.2536.
- [18] Ujvári T., Kolitsch A., Tóth A., Mohai M., Bertóti I., XPS characterisation of the composition and bonding states of elements in CN_x layers prepared by ion beam assisted deposition, *Diamond Relat. Mater.*, 2002, 11, 1149–1152.
- [19] Marton D., Boyd K.J., Rabalais J.W., Synthesis of carbon nitride, *Int. J. Modern Physics B*, 1995, 9, 3527–3558, DOI: 10.1142/S0217979295001385.
- [20] Bertóti I., Characterization of nitride coatings by XPS, *Surf. Coat. Technol.*, 2002, 151–152, 194–203.
- [21] Rodil S.E., Muhl S., Bonding in amorphous carbon nitride, *Diamond Relat. Mater.*, 2004, 13, 1521–1531, DOI: 10.1016/j.diamond.2003.11.008.
- [22] Ronning C., Feldermann H., Merk R., Hofsass H., H.P. Reinke, J.U. Thiele, Carbon nitride deposited using energetic species: A review on XPS studies, *Phys. Rev. B*, 1998, 58, 2207–2215, DOI: 10.1103/PhysRevB.58.2207.

- [23] Lin Y.-C., Lin Ch.-Y., Chiu P.-W., Controllable graphene N-doping with ammonia plasma, *Appl. Phys. Lett.*, 2010, 96, 133110–133110-3, DOI: 10.1063/1.3368697.
- [24] Koch R.J., Weser M., Zhao W., Viñes F., Gotterbarm, K., Kozlov S.M., et al., Growth and electronic structure of nitrogen-doped graphene on Ni(111), *Phys. Rev. B*, 2012, 86, 075401, DOI: 10.1103/PhysRevB.86.075401.
- [25] Zhao W., Höfert O., Gotterbarm K., Zhu J.F., Papp C., Steinrück H.-P., *J. Phys. Chem. C*, 2012, 116, 5062–5066, DOI: 10.1021/jp209927m.
- [26] Bertóti I., Tóth A., Mohai M., Ujvári T., Comparison of Composition and Bonding States of Constituents in CN_x Layers Prepared by DC Plasma and Magnetron Sputtering, *Surf. Interface Anal.*, 2000, 30, 538–543.
- [27] Zheng W.T., Xing K.Z., Hellgren N., Lögdlund M., Johansson Å., Gelivs U., et al., Nitrogen 1s electron binding energy assignment in carbon nitride thin films with different structures, *J. Electron Spectrosc. Relat. Phenom.*, 1997, 87, 45–49, DOI: 10.1016/S0368-2048(97)00083-2.
- [28] Dementjev A.P., de Graaf A., van de Sanden M.C.M., Maslakov K.I., Naumkin A.V., Serov A.A., X-ray photoelectron spectroscopy reference data for identification of the C₃N₄ phase in carbon-nitrogen films, *Diamond Relat. Mater.*, 2000, 9, 1904–1907, DOI: 10.1016/S0925-9635(00)00345-9.