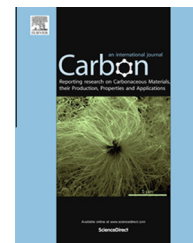


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Generation of nitrile groups on graphites in a nitrogen RF-plasma discharge

Andreas Mueller^a, Matthias Georg Schwab^a, Noemi Encinas^b, Doris Vollmer^b, Hermann Sachdev^{a,b,*}, Klaus Müllen^{a,b,*}

^a Carbon Materials Innovation Center, BASF SE, Ludwigshafen, Germany

^b Max-Planck-Institute for Polymer Research, Synthetic Chemistry, Ackermannweg 10, 55128 Mainz, Germany

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ABSTRACT

Graphite particles were treated in a nitrogen radio frequency-plasma (RF-plasma) at different excitation power. The morphological as well as chemical surface modifications were investigated by Raman spectroscopy, SEM, and XPS. Changes of the sp^2/sp^3 bonding ratio and selective surface terminations by functional groups were achieved. Especially, a direct functionalization of the graphites with nitrile groups was evidenced by a characteristic signal at 2240 cm^{-1} in the Raman spectra after a high energy RF-nitrogen plasma treatment. A total nitrogen content of up to 11 at.% was reached by the applied conditions. The increased polarity of the surfaces was confirmed by contact angle measurements. The nitrile functionalization may serve as synthetic scaffold for the development of new routes towards the chemical surface modification of carbon substrates. Furthermore, the modified graphites can be processed by common exfoliation techniques yielding nitrogen modified graphene nanoplatelets directly in polar and non-polar solvents.

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1. Introduction

Carbon materials like graphite, carbon black, graphene, carbon nanotubes or any other subcategories thereof are promising candidates for a wide variety of applications, e.g. within the fields of energy storage and energy conversion [1,2]. These carbons, and especially graphene, can act as active materials, additives or supports, e.g. like graphites in battery electrodes, or like carbon blacks and graphene in electrodes for batteries and supercapacitors or catalyst supports in fuel cells [3–5]. They also find applications in hybrid composite materials or ink formulations, e.g. for conductive bulk composites, adhesives, coatings and inks [6,7].

The introduction of chemically reactive sites either by a surface site or a lattice site modification is a general method to improve the performance of these carbon materials. The functionalization is mainly based on moieties which can be linked either directly to the carbon atom framework or e.g. through reactive oxygen- or nitrogen atoms bound to the carbon lattice. Especially the incorporation of nitrogen is important for the provision of chemical reaction centers as well as for altering the electronic and electrochemical properties [8–12].

The most common functionalities are reactive nitrogen centers revealing either nitrogen atoms with donor properties or chemically reactive functional groups which even may be

* Corresponding authors at: Max-Planck-Institute for Polymer Research, Synthetic Chemistry, Ackermannweg 10, 55128 Mainz, Germany. E-mail addresses: sachdev@mpip-mainz.mpg.de (H. Sachdev), muellen@mpip-mainz.mpg.de (K. Müllen).

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charged [e.g. amines, imines, nitriles, isonitriles, cyanates, isocyanates and cyanamides, NO_x -groups]. So far, the usually discussed species for the direct functionalization of carbon materials with nitrogen are pyridinic, pyrolic and graphitic nitrogen sites within the graphene lattice [10]. On the other hand, nitrile groups are valuable for further chemical modification as well [13–16]. For example, their chemical reduction to amine groups would allow for the application of a broad synthetic toolbox for tailor-made post-functionalization strategies. Furthermore, nitrile groups can be of great interest as non-hydrogen terminated, aprotic reaction sites, e.g. for the coordination of catalytically and electrochemically active metal centers [16].

The nitrogen functionalization and incorporation has been previously demonstrated by wet chemical methods [17,18], gas phase procedures such as chemical vapor deposition (CVD) [19] or plasma-chemical processes [20–24] or by any other means of doping [19,25]. Among these strategies, the products from “dry” plasma-chemical processes are highly desirable since there is no need regarding isolation from solvents, byproducts or reactants [20,21,23–25]. In this context the presence of nitrile groups was only observed so far within the deposition of highly amorphous sputtered carbon nitride films by a gas phase process, but was not used in a targeted fashion for the surface tuning of bulk carbon materials [26,27].

Herein, we present the powder modification of two different graphite grades by nitrogen plasma treatment at different excitation energies. The experiments were performed in a specially customized inductively coupled-radio frequency-plasma (RF-plasma) CVD reactor [28] on a pilot plant scale for powder treatment in controlled gas atmospheres. This setup allows high flexibility regarding reaction time and energy input as well as a statistical treatment of the individual powder particles within a sample. We were able to directly functionalize graphites with nitrile groups by such a gas phase process without the need of any additional wet-chemical treatment and thus can directly introduce polar nitrogen containing groups. This increases the hydrophilic character of the materials and their surface interactions with polar solvents or any composite materials, thus improving their dispersibility. The resulting materials were characterized in detail regarding their morphological and chemical changes by SEM, Raman spectroscopy, XPS and contact angle measurements.

2. Experimental

Two different graphite grades were modified by a RF-plasma treatment [spherical particle graphite, SPG, (synthetic, –20 + 84 mesh size, 99.9%, Alfa Aesar) and flake graphite, FG, (natural, –10 mesh size, 99.9%, Alfa Aesar)]. All carbon materials were dried at 120 °C *in vacuo* for at least 12 h prior to the experiments. A Huettinger PFG 500 RF generator was used for the generation of the inductively coupled RF-plasma (13.56 MHz) in a pressure range of 0.2–2.0 mbar for the particle modifications. The reactor loading depends on the density of the material and typically 40.0 g for spherical particle graphite, SPG, and 20.0 g for flake graphite, FG, were used.

A nitrogen gas flow (5.0 purity) of 300 sccm was used for a sufficient fluidization of the materials. The samples were plasma treated under the further specified conditions (cf. [Supporting Information](#)) in a fluidized bed for 30 min and the recovered samples were stored in a desiccator.

Gas adsorption analysis was performed using Micromeritics ASAP 2420 Surface Area and Porosity Analyzer. Raman spectra were measured with a NT-MDT NTEGRA spectrometer using 488 nm excitation wavelength (2.54 eV), a 600/mm grating and a 20× objective if not stated otherwise. A Physical Electronics PHI 5000 Versa Probe and Al $K_{\alpha 1,2}$ radiation ($h\nu = 1486.6$ eV) was used for photoelectron spectroscopy (XPS). Elemental analysis was performed with an Elementar vario Micro cube system. The oxygen content was determined by a HeKaTech Euro EA Elementaranalysator. Scanning electron microscopy (SEM) was performed with a Zeiss LEO 1530 Gemini at 1.0 keV and Hitachi SU8000 at 1.0 keV. Powder diffraction measurements (XRD) were obtained with a Bruker D8 diffractometer. Contact angle measurements were obtained by a DataPhysics OCA35 contact angle meter from deionized water. Further detailed description is provided in the [Supporting Information](#).

3. Results and discussion

The samples of both SPG and FG were modified in a reactor [28] in a nitrogen RF-plasma using excitation energies of approx. 0.8 kW (denoted as “N₂ plasma LP”) and 1.6 kW (denoted as “N₂ plasma HP”). A strong interaction of the materials with the excited gas phase was observed for high excitation energies as evidenced by Raman spectroscopy, XPS and SEM analysis.

All starting materials reveal the typical Raman spectroscopic features of graphitic carbons, i.e. the D-band, the graphitic G-mode, the D'-mode and the 2D-band (cf. [Fig. 1](#) and [Table 1](#)). The D-mode is generally attributed to disorder and defects within the graphite lattice and is commonly observed in Raman spectra of modified or doped carbon materials displaying perturbations within the crystal lattice. [29] The Raman spectra of the starting materials indicate a better crystallinity and graphite quality for the untreated natural FG as compared to the sample of the untreated artificial SPG graphite in terms of defects and disorder (cf. intensity of the D-mode), which is also evidenced by the lower I_D/I_G ratio and smaller full width at half maximum (FWHM) values of the Raman G- and 2D-modes (for details see [SI](#)).

The Raman spectra of the nitrogen plasma treated samples indicate modifications of both materials already at low excitation energies, which become more dominant at higher energies. For the low energy treated SPG and FG graphites, an increase of the I_D/I_G ratio of about twofold in the former case and about tenfold in the latter case is observed. The I_D/I_G ratio is in line with this observation and follows the same trend. Another indicator for the decrease of the crystalline perfection of the material is the full width at half maximum (FWHM) of the corresponding Raman modes. The FWHM values increase after low energy nitrogen plasma treatment for both graphites. The Raman spectra of the high energy nitrogen plasma treated samples indicate a much

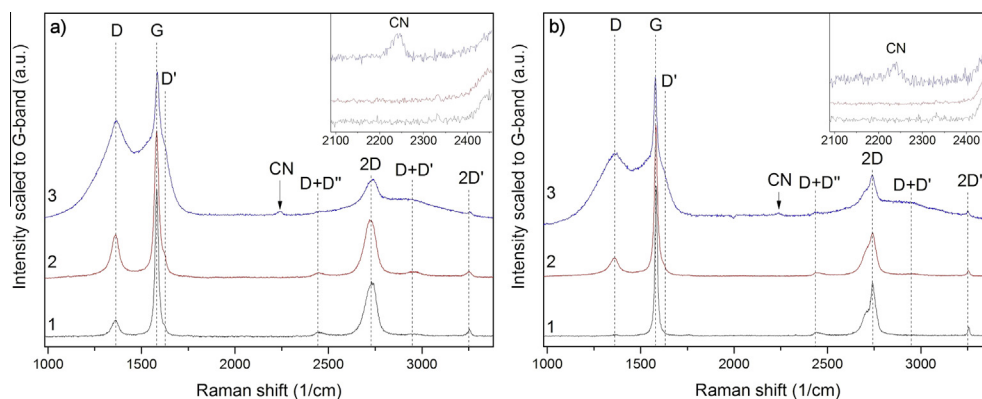


Fig. 1 – Raman spectra of pristine (1), N₂ plasma LP (2) and N₂ plasma HP (3) SPG (a) and FG (b). 488 nm excitation (2.54 eV), 20× objective, laser power 2.1 mW. Spectra are offset in y-direction for better clarity. (A color version of this figure can be viewed online.)

Table 1 – Important Raman spectroscopic data of pristine and plasma treated graphite samples. Values presented have been obtained by analysis of the spectra shown in Fig. 1. Additional data including mean values derived from multiple measurement spots can be found in the SI (Tables S1–S4).

Plasma treatment	Peak position (cm ⁻¹)/FWHM (cm ⁻¹)				Intensity ratio	
	ν_D/D_{FWHM}	ν_G/G_{FWHM}	$\nu_{D'}/D'_{FWHM}$	ν_{CN}/CN_{FWHM}	I_D/I_G	$I_{D'}/I_G$
Pristine SPG	1361.7/44.9	1584.0/20.9	1626.2/7.5	–	0.233	0.008
N ₂ plasma LP (0.75 kW)	1362.0/54.6	1583.7/27.4	1625.2/19.5	–	0.564	0.051
N ₂ plasma HP (1.5 kW)	1365.6/178.1	1586.6/52.9	1634.3/54.7	2242.3/24.9	4.272	0.449
Pristine FG	1364.5/35.5	1584.1/14.8	–	–	0.019	–
N ₂ plasma LP (0.8 kW)	1360.3/71.9	1584.1/19.1	1618.5/37.2	–	0.421	0.063
N ₂ plasma HP (1.6 kW)	1367.8/174.0	1584.1/20.8	1624.7/61.0	2239.2/26.9	5.164	0.808

stronger modification of both graphites. This is evidenced by a high, up to tenfold, increase of the I_D/I_G and $I_{D'}/I_G$ ratio as well as by a further increase of the FWHM of the G-modes.

Importantly, for high energy nitrogen plasma modified SPG and FG samples (cf. Fig. 1), a new spectroscopic feature is observed for both materials centered at about 2240 cm⁻¹ (FWHM of about 26 cm⁻¹) which can be ascribed to an aromatic nitrile type signature [27,31]. This Raman mode is not observed for samples treated at low energy plasma excitation. According to theory, nitriles give rise to relatively low intensities in Infrared spectroscopy due to small changes in the dipole moment, whereas their Raman modes are strongly active due to a comparatively large change in the polarization resulting from the linear stretching mode. Therefore, Raman spectroscopy is the more sensitive tool to detect small traces of nitriles. This can be unambiguously done by the Raman mode detected here at approx. 2240 cm⁻¹ (cf. e.g. [27]). Since we observe small signal intensities of nitrile bands by Raman spectroscopy, this explains why FT-IR spectroscopy is not sensitive enough for a detection of minor amounts of nitrile groups on surfaces and thus does not lead to appropriate infrared spectra. In addition, the use of a Raman microscope with a 100x objective enhances the signal due to the focused laser excitation and scattered light accumulation.

The general influence of the nitrogen incorporation in the carbon lattice can furthermore be noticed by changes in the G- and D-bands of the Raman spectra of both plasma

modified SPG and FG samples since they can no longer be fitted by a single Lorentzian. A second low frequency component has to be added for each Raman mode (cf. example fit in Fig. S1) which can be attributed to strongly disordered, nitrogen containing amorphous carbon at the graphite particles surface in agreement with literature reports [29,30].

The formation of the observed aromatic nitrile groups can be explained by the reaction of highly activated nitrogen atoms breaking up the graphene lattice at reactive rim and top positions. They can be formed by the reaction of the carbon atom lattice with highly activated nitrogen species (e.g. N₂⁺, N⁺ etc.) provided by a reactive nitrogen plasma and finally form e.g. nitrile radicals (CN[•]) or dicyane [(CN)₂] and are thus being prone to cleavage once formed on the surface. The weak intensity of the nitrile Raman signal at even high excitation energies implies that nitrile groups may only be formed up to an equilibrium concentration on the surface. This would be in accordance to the chemical reactivity of nitrile radicals as a pseudohalogen [31].

The morphological changes of the graphite samples were also studied by SEM (Fig. 2). The major morphological changes observed after the plasma treatment in the case of SPG samples are the formation of significant changes in the layer stacking and the formation of micron sized pores (cf. SI Fig. S8). While the pristine material exhibits regularly stacked graphite layers, an expansion can be observed after the plasma treatment. In addition, a treatment with highly

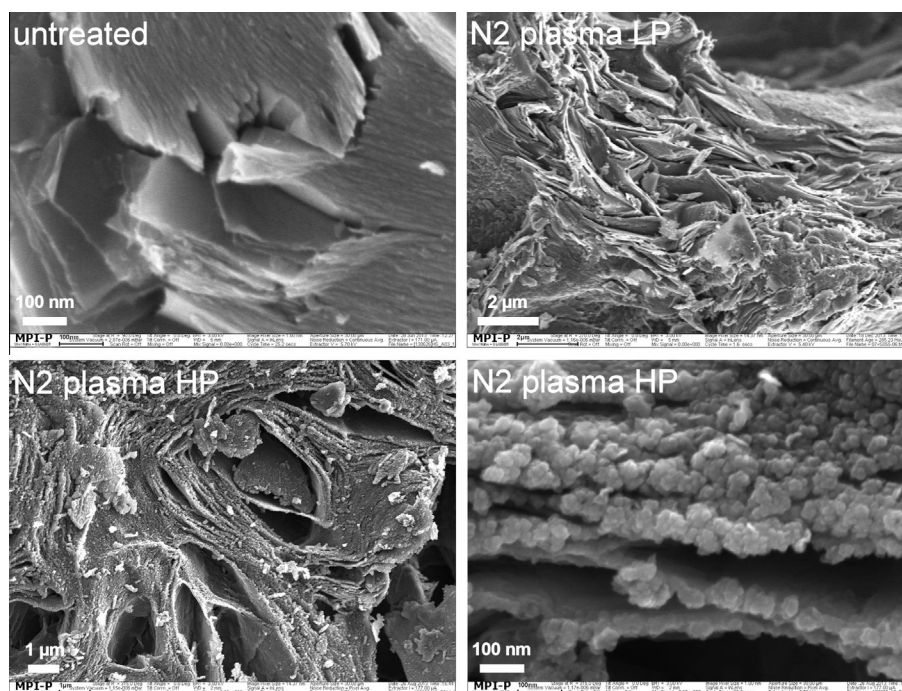


Fig. 2 – SEM images of untreated and N₂ plasma modified SPG.

excited nitrogen plasma results in a strong chemical attack and modification leading to the formation of globular structures. The more regular FG graphite sample shows much less morphological changes and thus higher structural stability to the surrounding plasma atmosphere. While a low energy plasma treatment results in no significant visible changes, a high energy plasma treatment indicates an attack at the graphite layer edges (cf. SI Figs. S9 and S10).

The observed morphological changes thus reveal that the more disordered SPG is more prone to degradation by a reactive plasma treatment as compared to a FG sample of higher crystalline perfection.

The atomic composition of the surface of the pristine and plasma treated samples was characterized by XPS (cf. Fig. 3). No N1s signals were detected for both pristine materials, whereas low oxygen levels were detected. The untreated, structurally less perfect SPG sample has a surface oxygen content of about 1.9 at.% compared to the FG starting material with 0.9 at.% oxygen (cf. SI Tables S5 and S6). This analysis correlates to the interpretation of the Raman data, evidencing the better graphite quality for the FG sample. A moderate increase of the oxygen content by up to approx. 2 at.% is observed for the plasma treatments. This effect is attributed to the natural leak rate of the reactor (less than 0.2 mbar/h) as well as to potential abrasion from parts of the quartz reactor.

The successful incorporation of nitrogen into the surface of the samples by plasma treatment is confirmed by the pronounced N 1s signals in the corresponding XPS spectra for both graphite substrates (cf. Fig. 3). While a low power plasma modification leads to a moderate nitrogen content of about 3 at.%, the high power treatment results in a surface nitrogen content of about 11 at.% for SPG and about 9 at.% for FG. The N1s XPS signals of nitrogen atoms incorporated in a sp² type

carbon lattice are assigned by deconvolution of the spectra, with a commonly used peak assignment for pyridinic N (398.8 eV), pyrrolic N (400.7 eV) and graphitic N (402.3 eV) species. The signal at 399.3 can be assigned to amide, amine, cyano, and nitrile groups. [22]

Besides the signal for sp² type carbon (284.3 eV), an increase of species at higher binding energies is observed for low power plasma treated materials, which is even more pronounced for high power modified samples (cf. Fig. 3). The signal at 285.1 eV can be attributed to sp³ type carbon. Its increase by plasma treatment evidences the introduction of defects and disorder and correlates perfectly with the Raman spectra and SEM analysis. The other signals at higher energies (286.3 eV, 287.9 eV, 289.3) can result from carbon atoms bonded to either oxygen or nitrogen species. Since the total increase of oxygen content upon plasma modification is rather low but the increase of the N1s signal is rather high, we correlate these features to C–N, C=N and CN (nitrile) type bonds.

The pristine materials as well as the plasma treated samples of both graphite grades were analyzed by elemental analysis, X-ray diffraction and nitrogen sorption measurements to elucidate any bulk changes. No significant differences between untreated and treated materials were observed for the bulk elemental composition, the BET surface area and the graphite interplanar distances. This indicates that the employed plasma chemical process results mainly in a surface modification of the graphite materials investigated in this study.

In order to elucidate the material properties of these fluidizable graphites, contact angle measurements were performed on compressed samples to study the changes of the hydrophilic character by nitrogen functionalization (cf. Fig. 4). The contact angle of the nitrogen treated FG samples

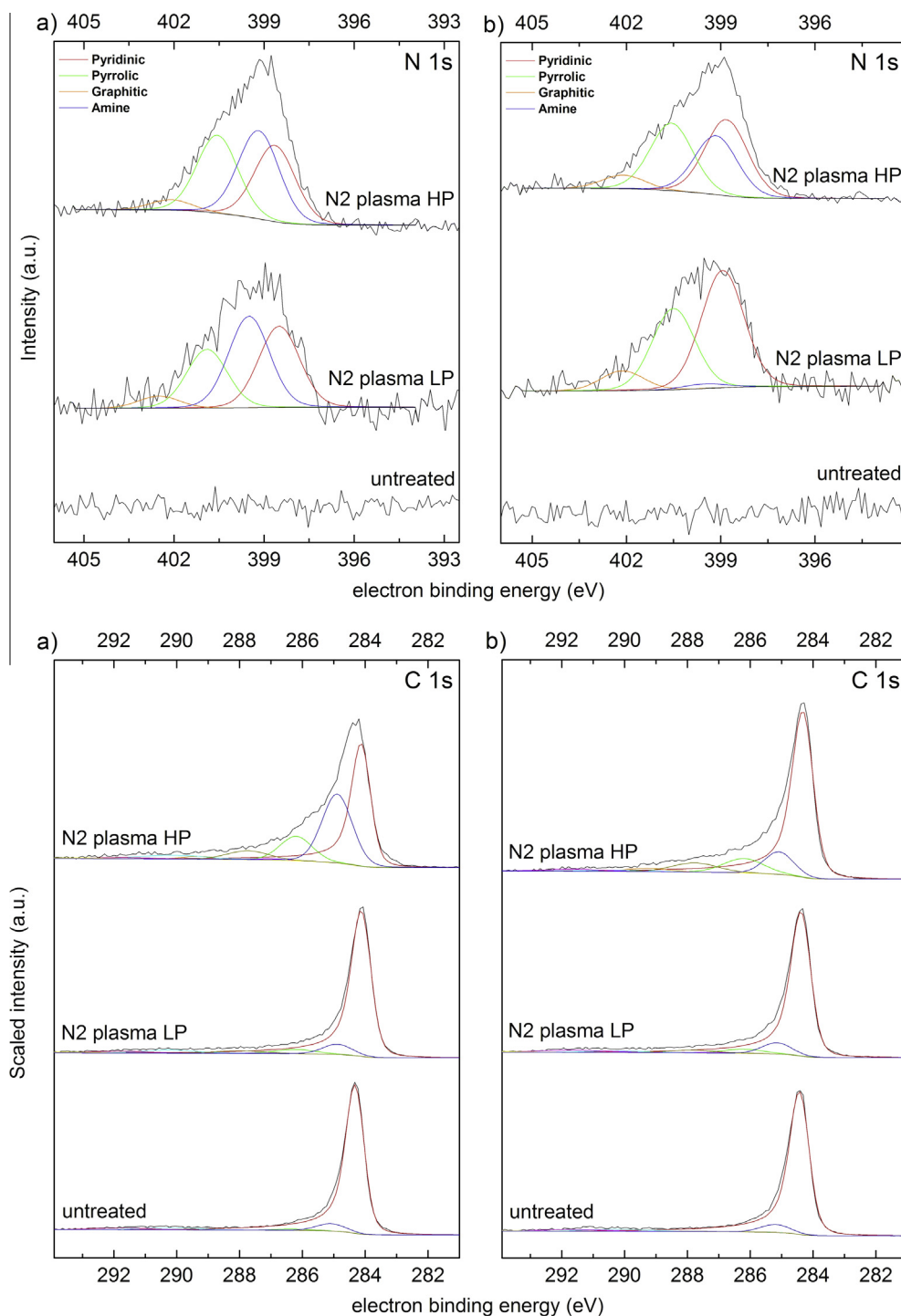


Fig. 3 – N 1s and C 1s XPS spectra of N₂ plasma modified SGP (a) and FG (b). Nitrogen incorporation is confirmed by the observed N 1s signal after plasma treatments. (A color version of this figure can be viewed online.)

is decreased what can be explained with a higher hydrophilic character of this sample. Since the particle graphite sample needs to be compressed prior to measurement resulting in breaking of the particles, here unavoidably a new surface is generated leading to contact angles similar to the starting material. It is noteworthy to mention that the samples are highly hygroscopic although they were stored directly after

the synthesis under inert conditions (cf. variation of the contact angle measurements see SI Fig. S11).

The increased hydrophilic character of the nitrogen modified graphites materials will be beneficial for e.g. common exfoliation techniques to prepare graphene nanoplatelet dispersions in polar solvents, metal ion decoration for catalytic applications or preparation of composite materials. While a

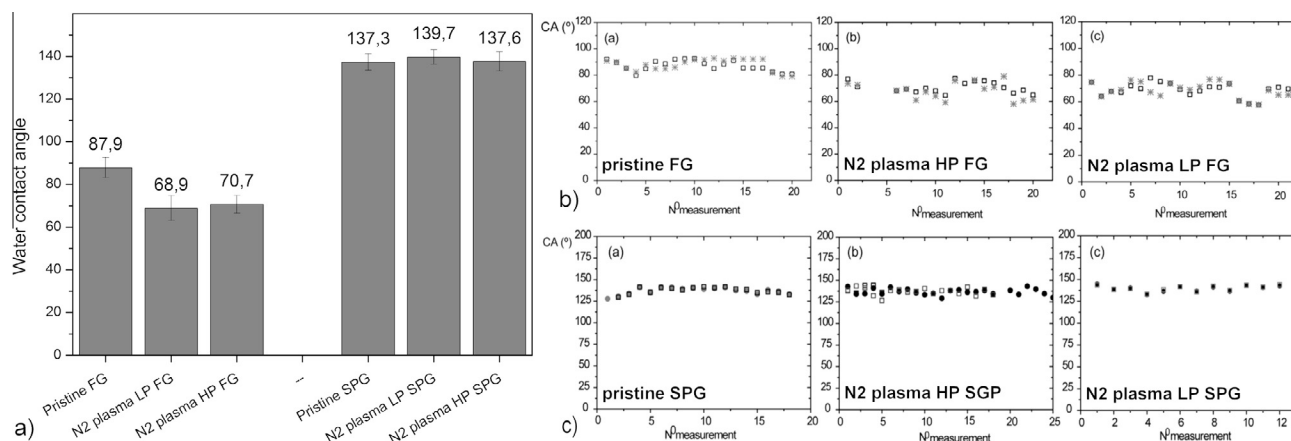


Fig. 4 – (a) Water contact angles of pristine and modified FG and SPG samples. (b) Measurement statistics for pristine and modified FG samples. (c) Measurement statistics for pristine and modified SPG samples.

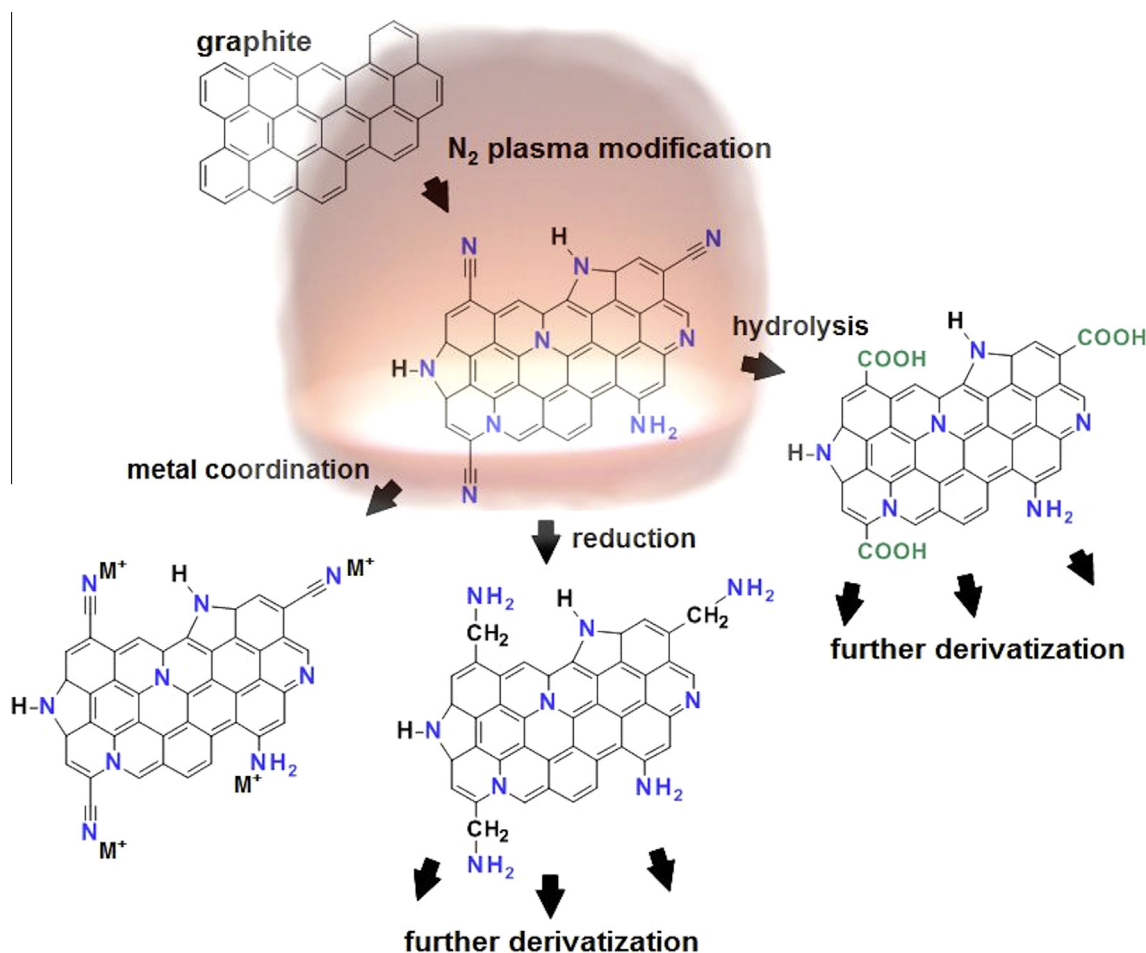


Fig. 5 – Illustration of the N_2 plasma modification of graphite and examples for possible subsequent derivatization steps exploiting the grafted nitrogen and nitrile groups. (A color version of this figure can be viewed online.)

nitrile functionalization of carbon materials is so far only achieved by wet chemical methods, a treatment of these materials in a highly excited nitrogen plasma enables a modification in a dry and clean atmosphere without post processing steps [13–16]. In addition, other co-formed nitrogen

functional groups together with the nitrile groups can be further chemically modified by standard organic reactions for various further derivatisation, e.g. by reduction to uniform functional amine groups or by hydrolysis to carboxylic acid groups (cf. Fig. 5).

4. Conclusion

We demonstrated that bulk samples of graphitic carbon can be strongly nitrogen functionalized at the surface by a RF-plasma CVD reaction, leading to nitrile groups at high plasma excitation as evidenced by Raman spectroscopy. A surface nitrogen content of up to 11 at.% was achieved as per XPS and is accompanied by a certain degree of surface amorphization as indicated by an increased D-band and sp^3 -carbon content. No nitrile formation was detected by Raman spectroscopy at low plasma excitation energies, resulting in a nitrogen content of only about 3 at.%. These findings are in accordance with a strong surface erosion and modification by the plasma treatment, leading to the formation of volatile nitrogen containing species (such as e.g. CN radicals, dicyane $[(CN)_2]$, and HC_xN etc.). The decrease of water contact angle indicates a higher surface polarity for the nitrogen modified graphites. The obtained nitrogen and nitrile modifications can be further used for metal decoration and subsequent chemical modification to obtain uniform chemical groups.

The presented process gives quick and scalable access to new nitrile functionalized carbon materials for solution processing, catalyst supports and composites and an even stronger modification is expected for carbon particles of smaller size or high surface area.

The aspects of this work are furthermore of importance regarding erosion of carbon materials in severe environments, e.g. space applications and re-entry aspects in the atmosphere.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2014.11.054>.

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