chem2Dmat

AUGUST 31 – SEPTEMBER 03, 2021 ● ONLINE

TECHNISCHE UNIVERSITÄT DRESDEN

CRC 1415

Solid-state Investigations of 2D Materials

Nikolaj Lopatik, Ankita De, Boya Sun, Andreas Schneemann, Minghao Yu, Silvia Paasch, Xinliang Feng, Eike Brunner

Chair of Bioanalytical Chemistry, Technische Universität Dresden, Dresden, Germany

More than 10 years have passed since the first successful synthesis of graphene. Since then, related two-dimensional materials (2DMs) have attracted increasing interest due to promising physical, electrical, chemical, and optical properties. 2DMs are ultrathin nanomaterials and exhibit unique characteristics such as high surface-to-volume ratio, surface charge, shape, high degree of anisotropy and adjustable chemical functionality. [1] The chemical structure and dynamics of solids and semi-solids can be determined with an atomic-level method - solid-state nuclear magnetic resonance (NMR) spectroscopy. It has proven to be a versatile technique for studying various materials. [2] In this contribution, we investigated two types of 2DMs: MXenes and COFs, using different solid-state NMR experiments.

MXenes

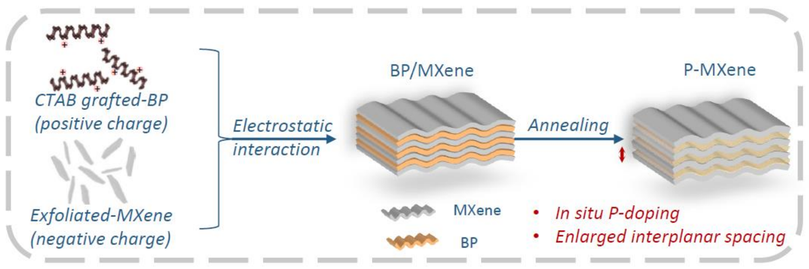


Fig. 1: *PO_x-terminated MXene for Na-ion storage*

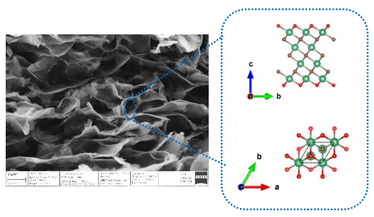


Fig. 2: *SEM image of* $Nb_4C_3T_x$/BP

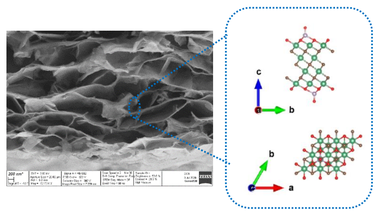


Fig. 3: *SEM image of* PO_x-Nb_4C_3

No.	Sample Name	Status	Elements
1	$Nb_4C_3T_x$/BP	Film	^{1}H, ^{31}P
2	PO_x-Nb_4C_3	Film	^{1}H, ^{31}P

Tab. 1: *Sample information*

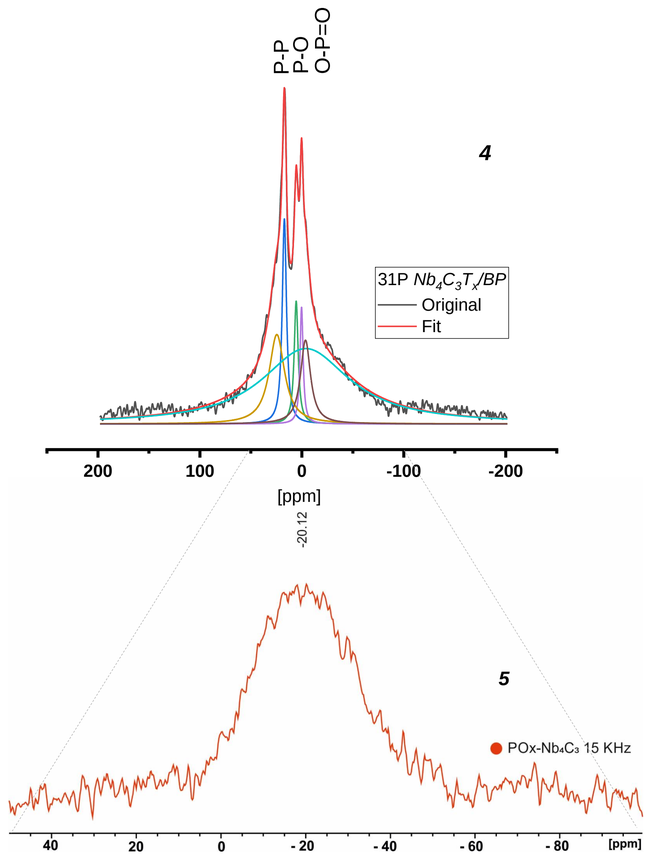


Fig. 4, 5: *^{31}P MAS NMR spectra*

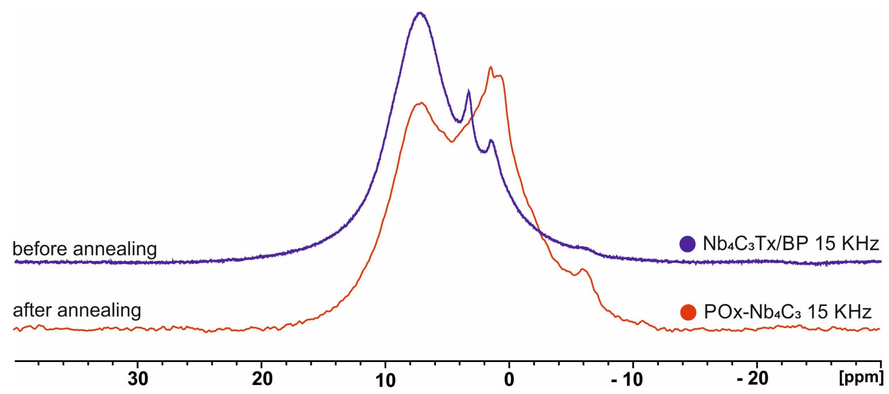
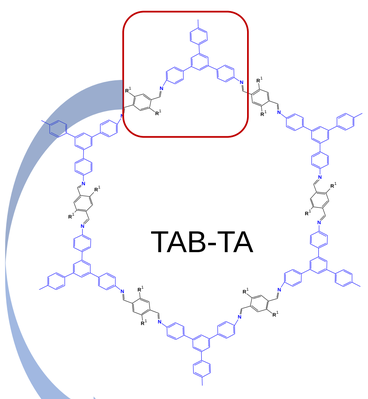


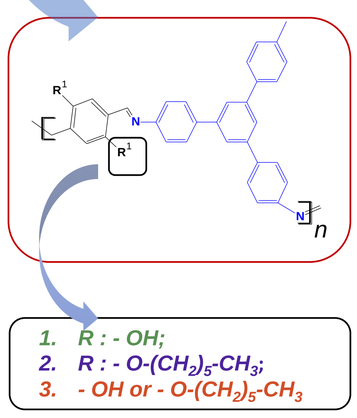
Fig. 6: *^{1}H MAS NMR spectra*

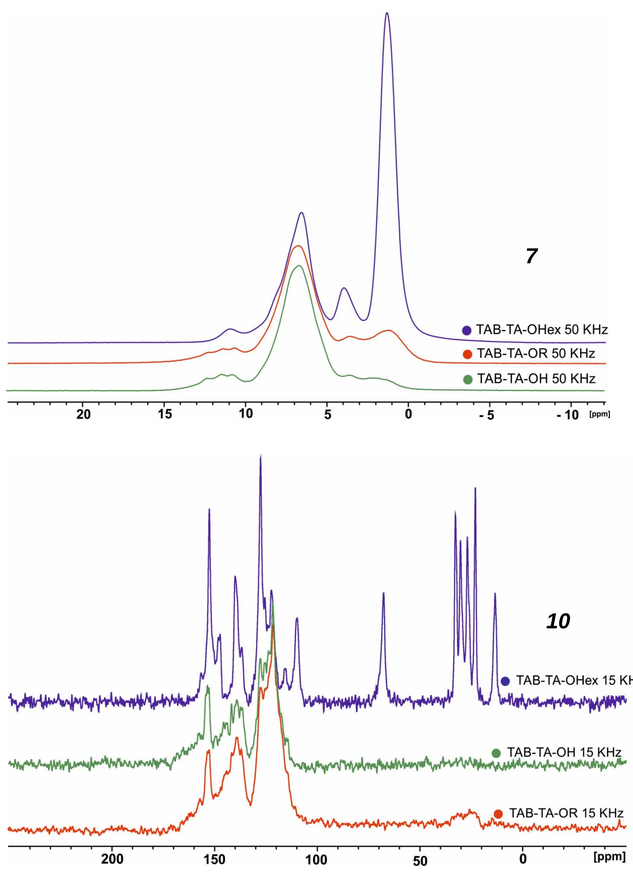
Conclusion:

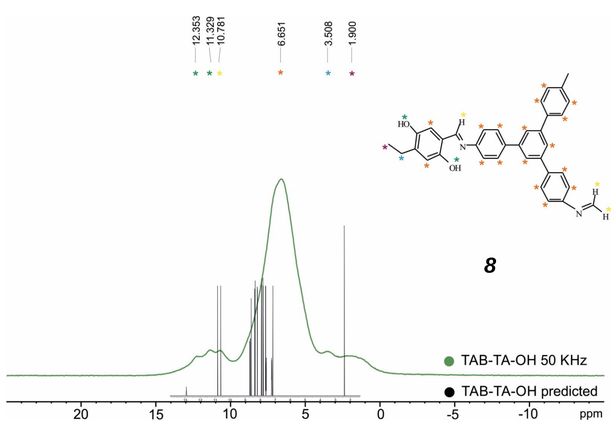
1) Chemical shifts of ^{31}P MAS NMR spectra of $Nb_4C_3T_x$/BP indicate the following groups:
   - 24,54 ppm – [P-P]
   - 17,16 ppm – [P-O]
   - 5,58 ppm – [O-P=O]
2) Annealing transforms phosphorus in an unusual state indicated by the ^{31}P chemical shift of -20 ppm.

COFs









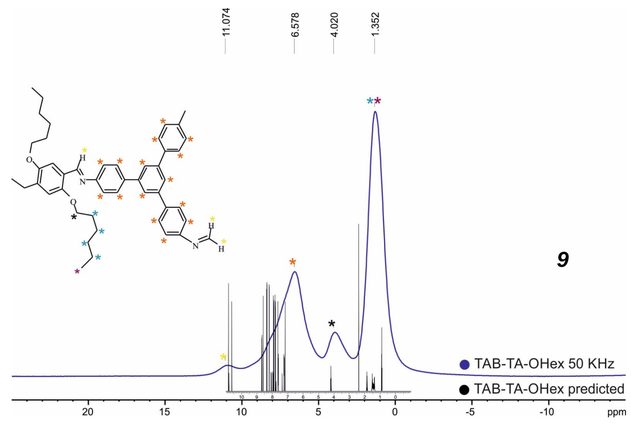
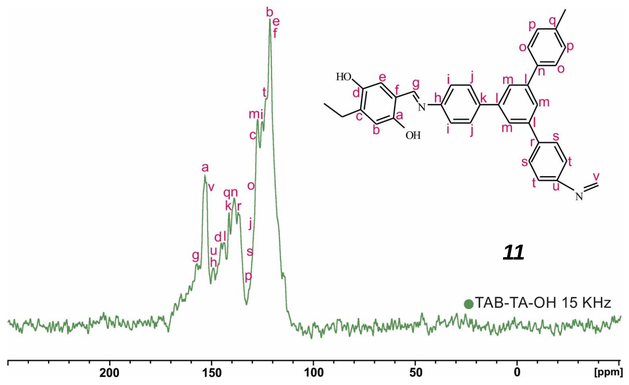


Fig. 7, 8, 9: *^{1}H MAS NMR spectra*



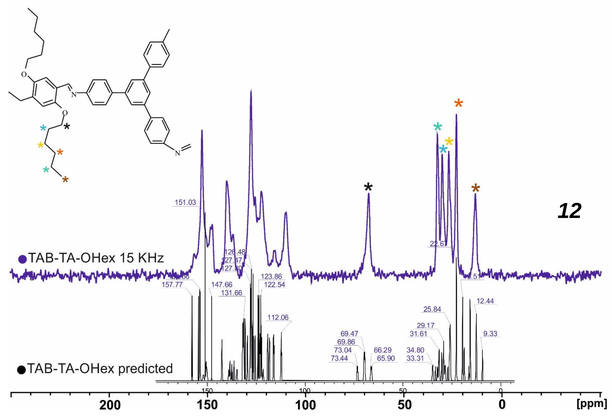


Fig. 10, 11, 12: *^{13}C CP MAS NMR spectra*

Conclusion:

1) MAS NMR spectroscopy sensitively detects the functionalization of 2D COFs.
2) Prediction of the spectrum in the ACDLabs software at the initial stage facilitates the interpretation of the spectrum in the future.

SUMMARY

1. NMR measurements were carried out on 300 MHz and 800 MHz spectrometers with optimization of spinning frequency.
2. We have systematically studied the chemistry of MXenes: $Nb_4C_3T_x$/BP and PO_x-Nb_4C_3 and chemistry of 2D COFs, examined a various of nuclei (^{1}H, ^{13}C, ^{31}P).
3. Black phosphorus is probably partially modified by CTAB solvent in the Nb4C3Tx/BP sample. For Mxene, the annealing transforms phosphorus in an unusual state.
4. In 2D COF samples (TAB-TA-OR), -OH groups and aliphatic chains can be distinguished quantitatively.
5. ^{1}H chemical shifts of OH group in COFs deviate a bit from the common range of 10-11 ppm and occur at 12-13 ppm.

EXPERIMENTAL:

NMR experiments were carried out either on a Bruker Ascend 800 MHz spectrometer using a 1.3 mm MAS NMR probe or a Bruker Avance 300 MHz spectrometer using a 2.5 mm MAS NMR probe. Predicted spectra were made in ACDLabs Software.

CONTACT PERSON

Nikolaj Lopatik

nikolaj.lopatik@tu-dresden.de

Technische Universität Dresden,

Bergstr. 66, Dresden, Germany

REFERENCES

[1] Er D., Ghatak K., in Synthesis, *Modeling, and Characterization of 2D Materials and Their Heterostructures,* 2020. P. 243-255.

[2] Reif B., Ashbrook S. E., Emsley L., Hong M., *Nature Reviews Methods Primers*, 2021, 2.

[3] P. Nakhanivej, X. Yu, S. Park, S. Kim, J. Hong, H. Kim, W. Lee, J. Hwang, J. Yang, C. Wolverton, J. Kong, M. Chowalla, H. Park. *Nature Materials*, 2019, 18, 156–162.

chem2Dmat

AUGUST 31 – SEPTEMBER 03, 2021 ● ONLINE