

## Elucidating the local structure of carbon nitride materials using electron energy-filtered radial distribution function analysis

Diana Piankova<sup>1</sup>, Alexander P. Tyutyunik<sup>2</sup>, Hannes Zschiesche<sup>1</sup>, Nadezda V. Tarakina<sup>1</sup>

<sup>1</sup>Max Planck Institute of Colloids and Interfaces, diana.piankova@mpikg.mpg.de, Germany,

<sup>2</sup>Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Russia

Carbon nitrides are green, sustainable organic-based materials, used in various applications including photocatalysis, CO<sub>2</sub> adsorption, and energy storage. Synthesis of well-crystalline carbon nitrides is challenging; often carbon nitride samples possess a high concentration of defects/disorder or do not display long-range order on electron diffraction patterns at all. Still, detailed knowledge about their structure (especially the local ordering) is key to control properties of existing carbon nitrides and designing new members of the CN-family. Here we report the application of energy-filtered electron radial distribution function (eRDF) analysis, combined with transmission electron microscopy imaging and X-ray powder diffraction, for elucidating the crystal structure and describing local order in carbon nitride powders with different degrees of crystallinity: (1) sodium polyheptazine imide (Na-PHI) and (2) amorphous CN covalent network (a-CN).

Na-PHI is a poorly crystalline material, diffraction patterns of which can be indexed in a hexagonal lattice with unit cell parameters:  $a = 12.3739(4)$  Å,  $c = 3.3668(1)$  Å, sp.gr.  $P31m$  (157). We solved its crystal structure using XRPD data. It can be described as a stacking of polyheptazine imide layers with Na atoms placed within and in-between the layers. Long channels are formed in the structure along the  $c$ -direction. The eRDF of Na-PHI has an average coherence length (ACL, marked with arrows) of 48 Å, which can be attributed to the average size of the crystalline domains, Figure 1 (a). Although Na-PHI has a large coherence length value, peak positions in the eRDF coincide with the model obtained from XRD Rietveld refinement only up to 4.2 Å (marked in light orange). As found by Reverse Monte Carlo refinement of the eRDF and HRTEM imaging, the layers are not stacked perfectly but have 2-8 degrees of rotational disorder and also partial disorder of the polyheptazine backbone within the layer, which leads to the abrupt decay of the eRDF at distances larger than 4.2 Å. In spite of this disorder, the channel structure remains.

The XRPD pattern of a-CN has only one broad halo in the  $2\theta \approx 27^\circ$  range. One can see the striking difference in the ACL of Na-PHI compared to a-CN, for which it is around 7 Å, indicating that only short-range order up to the 5<sup>th</sup> (number of the peaks up to ACL value) coordination sphere is present in the amorphous covalent framework. The main C-N, C-C peak positions are common for both Na-PHI and a-CN within 4.5 Å (Figure 1 b), but in the case of a-CN, the peaks are broader (FWHM of the first peak in the eRDF of a-CN is 0.4 Å compared to 0.25 Å of Na-PHI). In both cases the limited size of the ordered regions and crystalline disorder influence the catalytical (for Na-PHI) and adsorption (a-CN) properties. eRDF analysis is found to be a fast, easy accessible tool to quantitatively (using parameters such as ACL, peak broadening, decay of the signal intensity) describe and compare the degree of structural disorder in materials.

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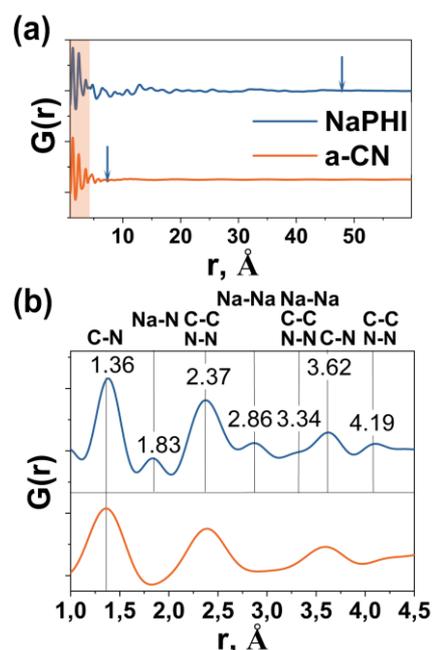


Fig.1. eRDFs of NaPHI and a-CN.