

Resolving short-range order in Carbon Nitride-based catalysts using EELS

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Background and aims

Carbon Nitrides (CNs) attract great attention as promising materials for water remediation, gas sorption, energy storage devices and photocatalysis, among others. This variety of applications stems from a set of specific properties of CNs: chemical inertness, biocompatibility, high thermal and mechanical stability, and non-toxicity [1,2]. Tuning the functionalities of carbon nitrides requires precise control over their structure and composition. Many CNs are poorly crystalline or even amorphous materials, thus requiring specific methods to describe their local structure (short- and medium-range order). In this work, we explore the possibility of obtaining quantitative information about the local structure of CN-based compounds using electron energy loss spectroscopy (EELS) in (S)TEM. Element-specific radial distribution functions (RDFs) can be derived from the extended energy loss fine structure (EXELFS) of EELS spectra [3]. Taking into account that modern analytical microscopes are much easier to access than spectroscopic beamlines at synchrotrons, this method holds great potential for fast analysis and prescreening of high amounts of samples. Here we investigate two challenging CN systems to establish the limitations of RDF analysis from EELS spectra in application to polymeric compounds: (1) the heterojunction of two photocatalysts (poly(triazine imide) (PTI) and potassium poly(heptazine imide) (K-PHI)) is used to check the ability to distinguish between two structurally closely related polymeric materials; (2) Ce-doped CNs (Ce-CNs) are used to check the limitations regarding sensing the local environment around single-atom catalysts.

Methods

All samples were first investigated using high-resolution (scanning) transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) using a double aberration-corrected Jeol JEM ARM200F equipped with a cold field emission gun and a Gatan Imaging Filter (GIF) Quantum spectrometer. HRTEM images were acquired on an Oneview (4k × 4k) camera, EELS spectra were collected on a US1000 (2k × 2k) camera. EELS spectra for the PHI/PTI sample were collected using a monochromated TFS Themis Z 80-300 microscope operated at 80 kV and equipped with a GIF Continuum 1065ER spectrometer (convergence and collection angles of 22 mrad) at energy dispersion of 0.15 eV/ch. For all EELS spectra, a power law

model was used for background subtraction. Multiple scattering effects were removed using the Fourier-ratio method, implemented in the Gatan Digital Micrograph Suite (GMS), version 3.4. EXELFS data were normalized and Fourier-transformed using the Athena software package. FEFF9 was used for fitting of the experimental data.

Results

The results will be described in two sections following the scientific questions defined above.

(1) Samples of PTI, K-PHI and a heterojunction between them (PTI/K-PHI) were analyzed [5]. Our study confirmed the formation of a heterojunction between the PTI and the K-PHI phase. The RDF obtained from the EXELFS part of the N K-edge of the PHI/PTI sample shows five prominent peaks. The first peak at around 1.3 Å arises due to scattering from the nearest carbon neighbors in both PTI and K-PHI. The second and third peaks correspond to the N-N (2.1 Å) and N-C (2.75 Å) distances within the aromatic rings. The fourth peak represents the summed contribution of the shortest N-N (3.3 Å) and N-C (3.58 Å) distances between adjacent layers of K-PHI. The fitting of RDFs obtained from individual phases and the heterojunction is in progress and should allow us to quantify the amount of each phase.

2. We investigated Ce-CNs employed in photocatalytic wastewater dephosphorylation. By varying the amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor, samples with different concentration of Ce were obtained (9.5, 17.0, 30.5 and 39.8 wt.%). HAADF-STEM images of the samples showed that Ce is present in the CN matrix in different forms: single atoms, clusters and nanoparticles. To resolve the average coordination around Ce atoms and distinguish between the aforementioned types of structures, RDFs obtained from the EXELFS part of the M_{4,5}-edge of Ce and from EXAFS at the Ce L_{2,3}-edge were compared. The EXELFS signal obtained from the 9.5 wt.% doped sample was found to be too low in intensity to perform reliable RDF analysis. The position (~2.5 Å) and the high intensity of the first peak on RDFs obtained from the Ce-CNs samples with 17.0, 30.5 and 39.8 wt.% suggest that Ce atoms bind to C or N and that a considerable fraction of Ce forms single atoms. On the RDFs from the CeO₂ reference the most intense peak, at 3.5 Å, corresponds to the Ce-Ce distance. Different structural models for Ce incorporated into the CN matrix were constructed and the refinement of these models is currently in progress. In addition, we collected X-ray absorption spectra from these samples in order to compare RDFs obtained from bulk samples and locally from EXELFS spectra.

Conclusion

The local structure in two soft polymeric systems utilized in energy-conversion (K-PHI/PTI heterojunction) and photocatalytic water treatment (Ce-doped CNs) was studied using element-specific RDFs obtained from EELS spectra. The results suggest that a clear discrimination between the structurally closely related PHI and PTI phases is challenging; accurate data fitting (which is currently in progress) is required to make a final conclusion. The formation of Ce single atoms manifests itself by considerably higher intensity of the C/N-Ce peak on RDFs. Conclusions about the possibility to quantify the amounts of co-existing phases (CeO₂, Ce-clusters and Ce-single atoms) can only be made after accurate fitting of RDFs.

Keywords:

EELS, Carbon Nitrides, short-range order.

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