

# Analysis of electronic states of implanted paramagnetic ions and adsorbed water molecules of nanodiamond MRI contrast agents

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Magnetic resonance imaging (MRI) is widely used as a diagnostic tool in both clinical and biological field. For cell labeling and detection of specific intercellular molecular events, various contrast agents (CAs) have been employed. CAs with paramagnetic metal ions, such as Gd(III) and Mn(II) have been used as T<sub>1</sub>-shortening (positive) MRI CAs with paramagnetic relaxation enhancement (PRE). Unfortunately, these metals are so toxic that chelating agents must be used with their ions. However, chelating substrates have such low molecular weights that large quantities of CAs are required for generating efficient contrast images. To overcome the issues of toxicity and low relative enhancement, researchers have proposed macromolecular CAs, including dendrimers and water soluble carbon nanotubes (CNT).

One of the carbon-based nanomaterials, nanodiamonds (NDs) have been used in the field of biology as optical imaging probes and drug carriers as well as in magnetometers owing to their unique features, including physical stability and high biocompatibility. However, few MRI CAs have been reported. Therefore, NDs implanted with paramagnetic metal ions are candidates for new macromolecular MRI CAs with efficient PRE owing to their high stability within the rigid diamond structure, leading to reduction of their effective toxicity. Recently, we succeeded in the synthesis of NDs implanted with manganese ions to function as MRI contrasts agent. In our previous studies, we performed Mn 2*p* X-ray absorption spectroscopy (XAS) to obtain information about the local coordination and electronic states of the implanted Mn ions. Mn 2*p* XAS spectra of the Mn-implanted NDs were obtained by measuring partial fluorescence yield, which has a probing depth that is typically greater than 10 nm for the 2*p* edge of 3*d* transition metals (ref. 1). Thus, we could obtain information from almost all Mn ions in the 4-nm NDs. Fig.1 shows the Mn 2*p* XAS spectrum of the manganese ions implanted in the NDs with annealing followed by air oxidation (Mn-NDao), which is compared with that of MnO (a typical octahedral Mn<sup>2+</sup> compound). This result indicates that almost all implanted manganese ions were stably localized in the ND structure in Mn<sup>2+</sup> valence states. Atomic multiplet calculations using the CTM4XAS program

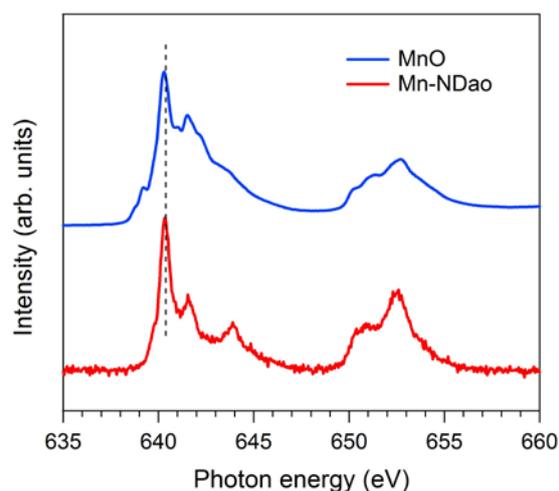


Fig. 1. The Mn 2*p* XAS spectrum of a MnO and Mn-ND with both annealing and air oxidation (MN-NDao) The vertical dot line is the peak energy position in Mn L3 signal.

developed by Professor Frank de Groot and Dr. Eli Stavitski indicate that the spectrum of  $\text{Mn}^{2+}$  located on an octahedral coordinate with a small crystal field splitting parameter accurately reproduces the experimental XAS spectrum.

To understand the electronic properties of the  $d$  orbitals of the Mn ions implanted in the NDs more clearly, Mn  $2p$  X-ray emission spectroscopy (XES) was applied. The experiment was performed using a high-resolution soft X-ray emission spectrometer at the undulator beamline BL07LSU in SPring-8. Mn-implanted ND powder was carefully pressed into a pellet form and mounted on a copper plate using low-emission carbon adhesive tape. Mn  $2p$  XES spectra were measured by tuning the excitation energy at a specific XAS peak structure (the energy indicated by the dotted vertical line in Fig. 1). Fig. 2 shows the XES spectra of both Mn-NDao and MnO plotted relative to the elastic scattering peak. There are sharp  $dd$  excitation peaks from 0 to  $-6$  eV, and a broad charge transfer (CT) tail extends below  $-6$  eV. In the  $dd$  components region, we found nine peaks that are shown as vertical dashed lines (“a”–“i”). We also found two characteristic differences in these peaks between the Mn-NDao and MnO spectra: the energy position of the main peak (“f” for MnO and “e” for Mn-NDao) and the intensity of both “d” and “i” components.

Furthermore, the CT component of Mn-NDao is smaller than that of MnO. The slightly lower symmetry of Mn-NDao might also contribute to the differences. Although the differences in the XAS profile of Mn-NDao when compared with those of MnO strongly support divalent high spin character of the manganese ions in the ND structure., the XAS spectrum of Mn-NDao strongly support divalent high spin character of the manganese ions in the ND structure. For further interpretation of the spectra and identification of possible differences in hybridization between the Mn  $3d$  states and ligand valence states, we plan to perform a configuration–interaction cluster model calculation in the near future.

Recent studies have reported that several paramagnetic ion-doped diamond in which transition metal ions (Ni or Cr) are implanted can form an optical center for various applications, including its utilization as a single photon source and in spintronic devices. High-resolution XES spectroscopy has strong potential as an analytical tool for evaluation of the spin properties of these transition metal-doped NDs.

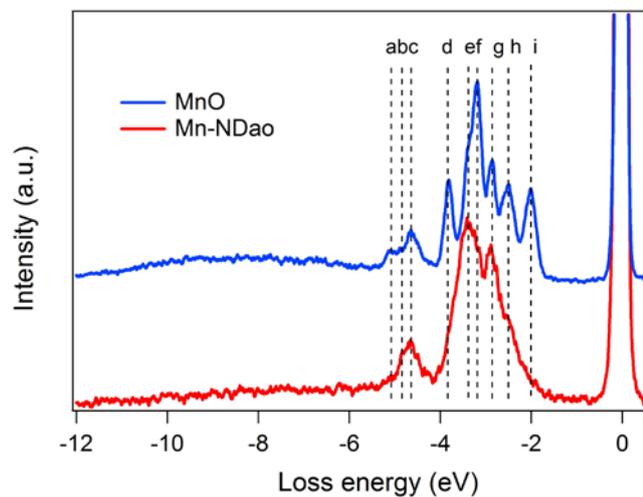


Fig. 2. The emission spectrum of the Mn  $2p$  XES spectrum of a Mn-ND with both annealing and air oxidation (blue) and MnO (red).

## References

- [1] Two-dimensional approach to fluorescence yield XANES measurement using a silicon drift detector. Tamenori Y., Morita M. and Nakamura T., *J. Synchrotron Rad.* 18, 747-752 (2011).