4A/2010G579

In situ elemental analysis of distribution and degradation of QDs in a model organism *Caenorhabditis elegans*

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Introduction

In vivo characterization and quantification of nanomaterials are always challenging, because their physicochemical properties are highly susceptible to the complex biological microenvironments. When it comes to Quantum Dots (QDs), possible oxidation, aggregation and degradation in biological environment largely hinder their quantification by conventional fluorescence technique. Microbeam synchrotron radiation X-ray fluorescence (µ-SRXRF) technique can provide precise information with subcellular spatial resolution, high sensitivity and simultaneous distributions of various elements, while microbeam X-ray absorbance near edge structure (µ-XANES) technique allows the analysis of the physicochemical changes of chemical species in vivo. In this study, in combination of the two synchrotron radiation based analytical techniques, the in situ metabolic process of QDs at the elemental level in a model organism Caenorhabditis elegans (C. elegans) was successfully explained in detail^[1].

Experiments

Worms were washed ten times and fixed with liquid nitrogen on mylar films for μ -SRXRF mappings and *in situ* μ -XANES spectra. Optical images were acquired before elemental analysis. The elemental analysis was carried out at BL-4A in Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. The incident beam was focused using Rh-coated Kirkpatrick– Baez focusing optics to an approximate size of 5 μ m × 5 μ m. The sample platform was moved along the X and Z directions at an interval of 5 μ m for each steps. XANES spectra were normalized using a linear function for the pre-edge and a second-degree polynomial function for the postedge region.

Results and Discussions

Selenium in CdSe@ZnS QDs was chosen for XRF and XANES analysis due to its obvious advantages: Se locates in the core encapsulated by ZnS shell, so its chemical state changes only if the ZnS shell structure is degraded. In worms exposed for 24h, there is no optical fluorescence signal at the retral part of the intestine, where Se and Zn elements are largely present (arrows in Fig.1 C). *In situ* Se K-edge μ -XANES spectra of QDs within the worm where QDs fluorescence quenched (Point b and c) show obvious changes: 1) Intensity of white line peak (peak I) increases strongly; 2) Position of peak I shifts to higher energy by about 2 eV; 3) Intensity of shoulder II gradually decreases and disappears, which were together assigned to a transition to oxidized Se.

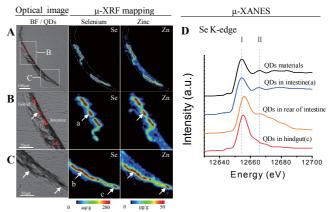


Fig.1 In situ elemental analysis and degradation of QDs.

The changes of Se XANES spectra may be attributed to the collapse of core/sell structure after digestion, and the efficient protection of the CdSe core by ZnS shell is destroyed. Such oxidation of CdSe core gives rise to dramatic decrease of QD fluorescence. These results suggest that the imaging method based upon QD optical fluorescence may not reflect the actual distribution *in vivo*. Synchrotron radiation based analytical techniques are thus more accurate ways to understand QD fate in organism.

Acknowledgement

This work was supported financially by the National Basic Research Program of China (973 Program, Nos. 2011CB9334000 and 2010CB934004), National Natural Science Foundation of China (Grant No. 10975040, 20931160430 and 31070854). This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2008G189 and No. 2010G579). We thank Prof. Atsuo Iida for his kind help at BL-4A, PF, KEK, Japan.

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