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Observation of Binding Mode of a Sulfur-Containing Compound with Ferrite Nanoparticles

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Introduction

Ferrite is a class of ceramic material that iron oxide is main component. Most of ferrites show ferromagnetism and are used widely as magnetic material. Among ferrites, magnetite is biocompatible magnetic iron oxide represented by formula Fe_3O_4 and has been noted as an attractive material in the field of biotechnological and medical application. Our group focused on a development of functional ferrite nanoparticle (FP) applicable to biotechnology and medical science, such as bioseparation, MRI contrast agent, hyperthermia agent, magnetic probe for biosensor, and so on [1]. In progress of our research on development of functional FPs, we found that sulfur-containing compounds bound to FPs specifically [2]. Thus, our interest focused an analysis of binding configuration of sulfur-containing compound with FPs. In this report, we describe significant binding mode of sulfur-containing compounds on FPs.

Results and Discussions

Recently, we reported oxidation of cysteine on FPs based on X-ray adsorption near edge structure (XANES) measurements [3]. This finding prompted us to examine a binding mode of compounds conjugated on FPs, which possess both thiol and carboxylic acid. Thus, we selected a series of mercaptocarboxylic acid (thioglycolic acid, 3-mercaptopropionic acid, and DL-homocysteine) for analyzing each binding mode on FPs. Oxygen-purged mercaptcarboxylic acid aqueous solution (pH 7) was added to a suspension of FPs (around 8 nm) in aqueous solution (pH 7). After mixing for 1 h at room temperature, mercaptocarboxylic acid-conjugated FPs were collected by magnet and were dried under vacuum to give samples for XANES measurement. The XANES spectra of mercaptocarboxylic acid-conjugated FPs and original mercaptocarboxylic acid are shown Fig. 1. Main peak of XANES spectrum of thioglycolic acid-FPs was mostly same as that of thioglycolic acid and was also exactly same energy position as cysteine (2473.4 eV). Thus, the thiol group in thioglycolic acid did not oxidize to disulfide and intact thioglycolic acid was conjugated with FPs. On the other hand, XANES spectra of 3-mercaptopropionic acid- and DL-homocysteine-conjugated FPs showed two distinct peaks, different from that of 3-mercaptopropionic acid or DL-homocysteine. These peaks corresponded with those of cystine (2472.7 and 2474.2 eV). From these results, we speculated that slight structure difference in mercaptocarboxylic acids affected their oxidation on FPs. In thioglycolic acid, short distance between thiol and carboxylic acid may prevent the thiol from oxidizing into disulfide on FPs. By contrast, for 3-mercaptopropionic acid and DL-homocysteine, the thiol would be subject to oxidizing into disulfide on FPs due to long distance between thiol and carboxylic acid.

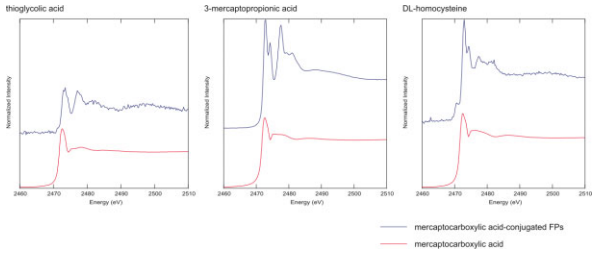

Figure 1. Sulfur K-edge XANES spectra of mercaptcarboxylic acid-conjugated FPs: (a) thioglycolic acid; (b) 3-mercaptopropionic acid (c) DL-homocysteine as well as reference spectra of unconjugated parent compounds.

In conclusion, we observed interesting XANES spectra change of mercaptocarboxylic acid-conjugated FPs, dependent on distance between thiol and carboxylic acid in mercaptocarboxylic acid. Currently, we are investigating full mechanism to oxidize thiol into disulfide in mercaptocarboxylic acid on FPs.

References

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