XANES Investigation of ZnO/TiO_2 Core-shell Nanoparticles in the Exposure of Human Lung Epethelial Cells

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In vitro cytotoxicity studies for nanoparticles have been popular for recent years. For titania nanoparticles, studies have found that different crystalline structures of TiO_2 can mediate its toxicity. In general, the order of TiO_2 toxicity in various forms is amorphous > anatase > rutile. The reason might be because amorphous TiO_2 can induce more reactive oxidative species (ROS) from cell and produce ROS in ex vivo situation. As we known, differnt levels of ROS generate by intracellular and materials could be easily detected by fluorecent methods. However, a little reports discuss the variety from material aspect. In the study, XANES was tried to determine the variation of oxidation state of ZnO/TiO_2 core-shell nanoparticles as they exposed to human lung epithelial cells (A549) and the relation between various thickness of TiO_2 shell and potential toxicity.

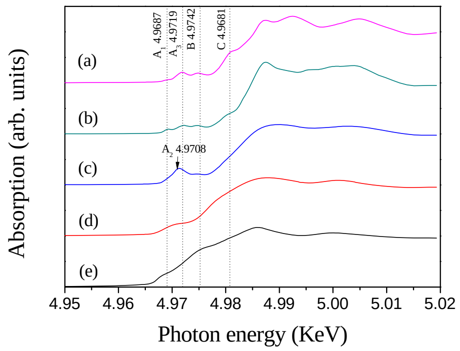

Fig. 1: Experimental XANES spectra of (a-c) different phases of TiO_2, (a) rutile, (b) anatase, (c) amorphous nano-TiO_2, (d) Ti_2O_3 and (e) TiO

The Ti K-edge XANES curves in different phases and oxidation state of titania oxides shows in Fig. 1. These curves served as standard samples in this experiments and future works that the ability to detect ROS in exposure of various phases of TiO_2. In bulk titania, peak A1 is from an electronic quadrupolar t_{2g} transition, A3 from the sum of a dipolar transition and a weak quadrupolar e_g transition, and B from a dipolar transition and peak A2 is specific for amorphous TiO_2 [1]. Thus, Fig. 2 shows the XANES curves of fresh (powder) and on-site measurement of amorphous TiO_2 and ZnO/TiO_2 nanoparticles in A549 cells after 24 h exposure. All core-shell nanoparticles revealed the amorphous phases spectra, while the peak height at the pre-edge and post-edge were all different compared to pure amorphous TiO_2. The decreasing peak height of core-shell nanoparticles which are attributed to some five-coordinated Ti atoms transform to four-cordinated Ti atoms in a material [2], which confirmed the core-shell structure. Peaks > 4980 eV are not very specific of the Ti coordination environment due to the multiple scattering of Ti photon electrons by atoms in several neighboring shells. Figure 3 shows different fitting components of core-shell nanoparticles after cell exposure. Only the thicker one could be discovered the Ti (III) state, which meant thinner TiO_2 shell might produce more ROS simultaneously and cause more toxic to A549 cell. The cytotoxicity results have been confirmed in our previous study. The estimated chemical function in the cell culture medium was as below:

$H_2O + ZnO/TiO_2\ (IV) \rightarrow H_2O_2 + ZnO/TiO_2\ (III)$ - Equation (1)

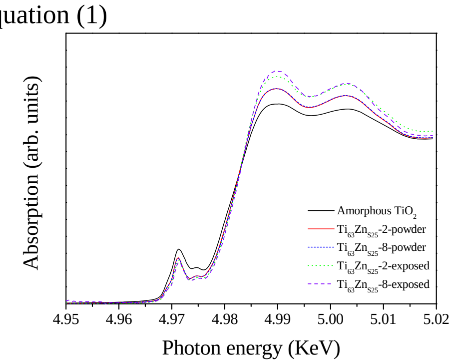

Fig. 2: XANES Ti K-edge spectra of fresh (powder) and on-site measurement of amorphous TiO_2 and various TiO_2 shell thickness of ZnO/TiO_2 nanoparticles in A549 cells after 24 h exposure.

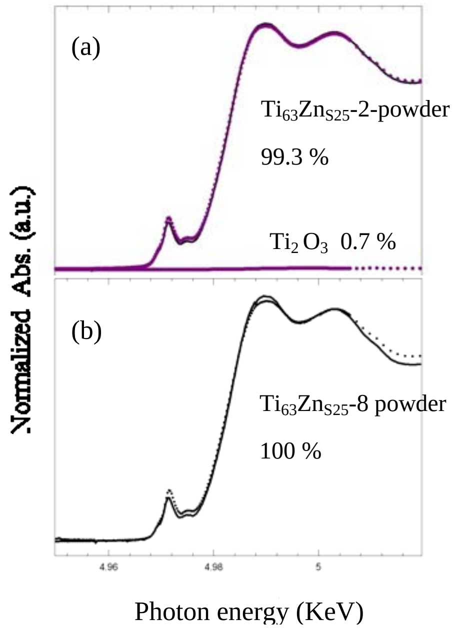

Fig. 3: The components fits of XANES spectra of on-site measurement of (a)$Ti_{63}Zn_{S25}$-2 and (b) $Ti_{63}Zn_{S25}$-8* in A549 cells after 24 h exposure.. The dotted line denotes the best fittings of XANES spectra.

* molar Ti/Zn:63; size of ZnO: 25 nm; number after dash line: shell thickness (nm)

[1] H. Zhang, B. Chen, and J.F. Banfield, Physical review B **78**, 214106 (2008).

[2] F. Farges, G. E. Brown, and J. J. Rehr, Geochim. Cosmochim. Acta **60**, 3023 (1996).