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Nanocrystals and small clusters investigated by synchrotron radiation and microfluidics

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1 Introduction

Recently, small clusters (SCs) formed by N atoms where N<50 attract keen attention, associated with recent demands on understanding microscopic mechanisms of initial growth (nucleation) of nano particles (NP's) and state of "monomers". Combining synchrotron radiation and x-ray absorption spectroscopy (XAS) with microfluidics allows us to study the initial process within a limited volume (<1 mm^3) *in-situ*. Microfluidic cell[1] is a microchannel device along which a chemical reaction occurs in a laminar flow.[2] For investigating time-dependent structures of NPs, "monomers" or SCs, a high-sensitivity is needed which is realized by high brilliance x-ray beam available from insertion devices at the 3rd generation facilities (*ca.* 10^{12} photons per sec) and modern x-ray detectors.

2 Experiment

Here, we describe *in-situ* XAS studies using microfluidics to illustrate the capability described above, demonstrated by a couple of applications, *i.e.*, i) the structural and kinetics studies during the initial stage of CdSe NPs[3] and ii) copper SCs (N=13-19) photo-induced by intense x-ray beam. Colloidal semiconductor NPs, sometimes called quantum dots, became popular due to their size-tunable optical properties and a variety of industrial applications. We demonstrated that time-dependent EXAS (conventionally used as an average local probe) is informative on higher order structures, *i.e.*, NP size and density if bond formation kinetics is analyzed.[4] The second application is copper SCs formed by a reducing reaction in organic solvent under photo-irradiation. The local structure of SCs prepared in organic solution by reducing Cu(II) hexafluoroacetylacetonate [$Cu(hfac)_2$] was studied by XANES and EXAFS. The Cu K-XANES spectra indicated the formation of copper SCs by ligand-exchange with oleylamine and a subsequent reducing by diphenylsilane.

3 Results and Discussion

Our *in-situ* EXAFS study on CdSe NPs found discrepancy with the optical spectroscopy that implies that at the initial stage of the nucleation and growth, most of the particles are in the amorphous state, contrary to hypothesis of the classical nucleation theory. These amorphous nuclei would crystallize rapidly over time, with the rate depending on the reaction conditions such as growth temperature, reaction time, surface ligand, and so on. The effect of surfactant (amine) was also studied through a comparison of the growth and crystallization processes in the presence of DDA with different concentrations. The results show a strong non-linear effect in surfactant concentration. The results indicate that surfactants play two competitive roles: accelerating the formation of amorphous nuclei, and hindering the subsequent crystallization and growth when the ligand concentration exceeds a critical limit. The multiple-scattering (MS) XANES calculation for various model SCs suggests that the SCs consist of 13-19 atoms that are characterized by a similar fcc-like local structure although the SCs are expected to be insulating based on the electronic state calculated by DFT on possible models.

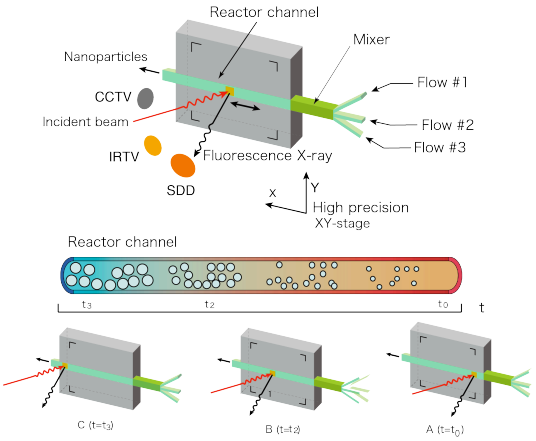

Fig. 1: Schematic representation of in-situ XAS using a microfluidic cell

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