NANOCRYSTALS AND SMALL CLUSTERS INVESTIGATED BY SYNCHROTRON RADIATION AND MICROFLUIDICS

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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 nanocrystals (NC'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 ($v_0 < 1$ mm^3) *in-situ*. Microfluidic cell [1] is a microchannel device along which a chemical reaction occurs in a lamilar flow [2]. For investigating time-dependent structures of NCs, "monomers" or SCs, a high-sensitivity is needed which is realized by high brilliance x-ray beam available from insertion devices at the 3^{rd} generation facilities (*ca.* 10^{12} photons per sec) and modern x-ray detectors. 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 NCs [3] and *ii*) copper SCs ($N = 13 - 19$) photo-induced by intense x-ray beam.

Colloidal semiconductor NCs, 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., NC size and density if bond formation kinetics is analyzed [4, 5]. 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 *as-grown* 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. 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.

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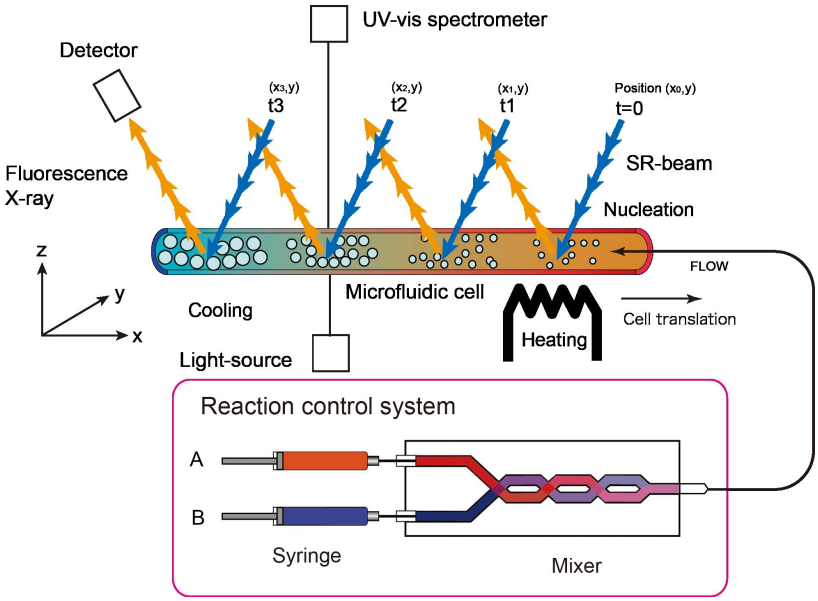

Figure 1: Schematic principle of *in-situ* XAS.