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Ligand Exchange Reaction from Cl to Br on the Brust-Schiffrin Gold Nanoparticle Synthesis

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1. Introduction

The publication by Brust and Schiffrin et al. [1], describing a simple two-phase i.e., water and toluene, reaction to produce alkane thiol coated nanoparticles was a landmark in the field of metal nanoparticle synthesis. However, further investigation has been required to understand the possible complications at each stage of the reaction. Mechanistic studies have now led to a consensus on the reactions involved in each step of the original synthesis. Initially tetraoctylammonium bromide, TOA^+Br^-, often written as TOAB, in toluene is brought into contact with the aqueous tetrachloroaurate, $[AuCl_4]^-$, solution to facilitate transfer into the organic phase. In the present study, the ligand exchange reaction of $[AuCl_4]^-$ in the presence of TOAB in organic phase was analyzed quantitatively to calculate concentration ratio of $[AuCl_4]^-$ and $[AuBr_4]^-$ based on principal component analysis (PCA) of EXAFS spectra.

2. Experimental

Sample preparation

Organic toluene solution of $TOA[AuCl_4]^-$, which was preliminary prepared, was mixed with TOAB in toluene. Further details for the preparation of $TOA[AuCl_4]^-$ were described in ref 2.

EXAFS data acquisition

Au L_{III}-edge XAFS measurements were performed at the beamline BL27B, beam-line of the Photon Factory. For each measurement, the sample was placed in a hole on an PTFE plate enclosed in polyethylene bags. All the measurements were performed under ambient conditions at room temperature. A suite of PCA including target transformation and iterative target transformation was performed both on the acquired EXAFS spectra using the program code ITFA developed by A. Rossberg [3].

3. Results

This ligand exchange has been widely reported, although the extent of halide exchange and its significance for the reaction has not been determined. Here, we probe the exchange process by examining the EXAFS response on increasing the TOAB : $[AuCl_4]^-$ ratio (Fig. 1). The EXAFS response for $[AuCl_4]^-$ and $[AuBr_4]^-$ is similar as they both form a square planar structure. As mentioned in the introduction, however, it is possible to differentiate the two species as there is a significant change in oscillation pattern. The fitted EXAFS data show a clear increase in the exchange of Cl for Br at higher TOAB concentrations. Based on the standard sample of $[AuCl_4]^-$ and $[AuBr_4]^-$, mole fractions of $[AuCl_4]^-$ and $[AuBr_4]^-$ were calculated. It was found that the main species of Au in the presence of excess TOAB was $[AuBr_4]^-$, resulted in forming the different size of gold nanoparticles[4].

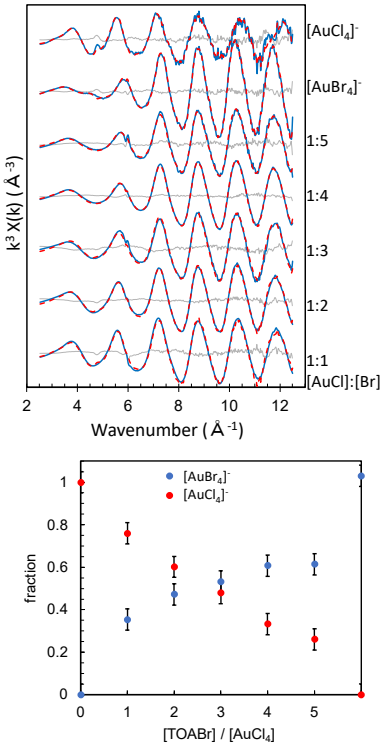

Fig. 1. (a) Fitted EXAFS response following the phase transfer of $[AuCl_4]^-$ by increasing equivalents of TOAB. (b) mole fraction of $[AuCl_4]^-$ and $[AuBr_4]^-$ calculated by PCA analysis.

References

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