In-situ UV-Vis and EXAS Measurements of Oxidation States and Structural Changes of Metal Complexes in Non-aqueous Solution During the Formation of Ni-coated Cu Nanowires

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Introduction

Authors have developed a technique to synthesize of Ni-coated Cu NWs using alcohol reduction technique[1]. However, the control over their size, shape and composition to be used in transparent electrode applications is considered difficult due to poor understanding of the formation mechanism, especially in the solution state. Here, an attempt has been made to determine the reaction scheme in the solution state by measuring the oxidation states and complex formation of metals. This was carried out by observing the changes of the oxidation states and the complex structures using the *in situ* UV-vis and XAFS measurements.

Experimental

$CuCl_2$ (1.25 mmol) and $Ni(OAc)_2$ (1.25 mmol) were dissolved in 25 ml of 1-heptanol in the presence of 20 mmol of oleylamine. Then, this solution was introduced into an aluminum-based alloy (A5052) cell specially designed for *in situ* UV-vis and XAFS measurements and heating to 177 °C at a heating rate of 0.4 °C/min. The cell has a Kapton film window to expose the solution to the incident X-ray beam and extract the fluorescent X-ray from the target elements. In addition, two quartz windows are placed on the walls of the cell for UV-Vis measurements. The XAFS measurements at Cu and Ni-K edges were carried out at BL14B2 of SPring-8 by the fluorescence yield method using 19 element SSD.

Results and discussion

From the UV-vis, XANES and XAFS analysis, the formation mechanism of Ni-coated Cu NWs was elucidated to be as follows: At low reaction temperatures Ni and Cu form complexes with oleylamine. Then during heating, Ni^0 is formed via the reduction of $Ni(OH)_2$. In the case of Cu, XANES and XAFS measurements suggested the formation of Cu^{2+}-oleylamine complex, decomposition of this complex and subsequent reduction of Cu^{2+} to Cu^+ that formed a complex with chloride at temperatures higher than 60° C[2]. After that Ni atoms donated electrons to Cu ions to form Cu^0 through galvanic reaction to generate Cu NPs that underwent etching to form multiply twinned particles (MTPs), which subsequently grew unidirectionally to form NWs. Once Cu ions were completely reduced, Ni ions that remained in the solution underwent reduction and inhomogeniously nucleated on the surface of Cu NWs to produce Ni-coated Cu-NWs.

Conclusion

Cu and Ni metallic complexes formed in 1-heptanol-oleylamine system was successfully elucidated using *in situ* UV-vis and XAFS measurements in the specially designed cell. Results suggested that the complexation of Cu with amine and chloride ions is the key for the formation of Cu NWs.

[1] M. Ishijima, Master's Thesis, The University of Shiga Prefecture, 2016
[2] SPring-8 Implementation Report of the Industrial Application Topic 2016B1865