DOCTORAL THESIS

Growth of silver dendrite crystals and liquid chromatographic analysis of water-soluble gold nanoclusters

Xie, Shunping

Date of Award:
2012

Growth of Silver Dendrite Crystals and Liquid Chromatographic Analysis of Water-Soluble Gold Nanoclusters

XIE Shunping

A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Principal Supervisor: Dr. Martin M. F. Choi

Hong Kong Baptist University

August 2012

Abstract

This thesis mainly consists of two parts. The first part focuses on exploring the growth of silver (Ag) dendrite crystals. The fast growth synthesis of Ag dendrite crystals on a copper (Cu) substrate assisted by sulfate (SO_4^{2-}) ions based on an electroless galvanic displacement reaction between solid Cu and Ag^+ ion is presented. The growth of Ag dendrites is succeeded by using an aqueous solution of Ag^+ ion and a Cu foil. Interestingly, the morphology, apparent color, and growth rate of Ag dendrites on Cu foil using 2.5 mM Ag_2SO_4 aqueous solution are different from that of 5.0 mM $AgNO_3$ aqueous solution even though they contain the same concentration of Ag^+ ion. The growth rate of Ag dendrites is proved to be much accelerated for a solution of Ag^+ ions with SO_4^{2-}. The diffusion-limited growth and oriented attachment explain the formation of the Ag dendrites under the non-equilibrium growth conditions. The effect of SO_4^{2-} ion on the growth of Ag dendrites on Cu foil has been investigated in detail. In addition, Liesegang rings (LR) of various types of Ag dendrite crystals are observed from an aqueous solution based on a simple galvanic displacement reaction between Zn plate and Ag_2SO_4. The formation of LR of Ag dendrite crystals is attributed to the concentration gradient and diffusion of Ag^+ ions in aqueous solution. The entire growth process and formation mechanism of LR of Ag dendrites are investigated in detail. The growth process of Ag dendrites can be readily observed under a microscope. The resultant Ag dendrites are characterized by scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction, energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. Finally, the synthesized Ag dendrites have been successfully employed as a Raman probe for

surface-enhanced Raman spectroscopic (SERS) analysis of melamine. The SERS results demonstrate that Ag dendrites can be a useful solid substrate for SERS analysis.

The second part is to separate, analyze and characterize polydisperse water-soluble gold nanoclusters (AuNCs) stabilized with *N*,*N*′-dimethylformamide (DMF) by reverse-phase high-performance liquid chromatography (RP-HPLC) in conjunction with photodiode array (PDA) detector and fluorescence detector. Under optimal elution gradient condition, the separation of DMF-AuNCs is monitored by absorption and fluorescence spectroscopy. The UV-vis spectral characteristics of the separated DMF-AuNCs have been captured and do not possess distinct surface plasmon resonance band, indicating that all DMF-AuNCs are small AuNCs. The photoluminescence emission spectra of the separated DMF-AuNCs are in the blue-light region. Moreover, cationic DMF-AuNCs are identified by ion chromatography. Our proposed RP-HPLC methodology has been successfully applied to separate AuNCs of various Au atoms as well as DMF-stabilized ligands. Finally, the composition of the separated DMF-AuNCs is confirmed by mass spectrometry, proving that the as-synthesized DMF-AuNCs product consists of Au_{10}^{+}, Au_{10}, Au_{11}, Au_{12}, Au_{13}, and Au_{14} NCs stabilized with various numbers of DMF ligands. In addition, the growth of individual DMF-AuNCs in polydisperse AuNC samples using similar RP-HPLC methodology. Their growths at various reaction times are offline monitored by HPLC-PDA. The DMF-AuNC reaction products are effectively separated into different elution peaks, indicating that various kinds of AuNC species are formed on the course of the synthesis reaction. Finally, the chemical compositions of the separated DMF-AuNCs are confirmed by matrix-assisted laser desorption/ionization time-of-flight

mass spectrometry, showing that ultrasmall NCs including Au_8, Au_{10}^+, Au_{12}, and Au_{13}-protected with various numbers of DMF ligand are simultaneously generated over the course of the reaction. The $Au_{13}(DMF)_9$ is unstable in the dry state since it vanishes after the excess DMF has been removed. Our established HPLC methodology provides a viable approach to study the growth of various AuNCs species over the course of the reaction.

Table of Contents