DOCTORAL THESIS

Synthesis, Photoluminescence, chromatographic and electrophoretic studies of monolayer-protected gold nanoparticles

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Abstract

This thesis mainly consists of three parts. This first part is the synthesis of ultrasmall (< 2.0 nm) thiolated α-cyclodextrin-capped gold nanoparticles (α-CD-S-AuNPs). Per-6-thio-α-cyclodextrins were firstly synthesized and were employed to protect gold nanoparticles (AuNPs) from aggregation. These α-CD-S-AuNPs (core size < 2.0 nm) display remarkably strong blue emissions at 478 nm when excited at 400 nm. The 1.4 nm-sized α-CD-S-AuNP shows photoluminescence enhancement in the presence of tetraalkylammonium ions but is strongly quenched by Hg(II). We found that the α-CD-S-AuNP possesses ultrahigh sensitivity and good selectivity for the determination of Hg (II) with the limit of detection at 49 pM (9.7 ppt).

In the second part of this work, two liquid chromatographic methods have been developed and their efficiencies in separating samples of polydisperse gold nanoparticles protected with *N*-acetyl-L-cysteine ligand (NAC-AuNPs) and other ultrasmall ligand-protected gold NPs are compared. The total elution time for analysing a NAC-AuNPs sample by ultra high-performance liquid chromatography (UHPLC) is ten times shorter than that of high-performance liquid chromatography. The major attributes of UHPLC are smaller sample volume (1–2 μL) and better

separation efficiency. More importantly, our proposed UHPLC method has been successfully applied to evaluate and compare polydisperse NAC-AuNPs products synthesised with the one-phase and two-phase Brust-Schiffrin methods. The results indicate that the two-phase method would harvest AuNPs product with smaller core size and less dispersity.

The third part of this work is to describe a novel and effective capillary electrophoretic method to study positively charged, sub-nanometer-sized, water-soluble gold nanoclusters protected by *N*,*N*′-dimethylformamide (DMF-AuNC). The effects of buffer concentration, pH, and % ethanol (EtOH) on the electrophoretic mobility of the cationic DMF-AuNC are investigated. The optimum CE conditions are found to be 30 mM phosphate run buffer in 20 *v*/*v* % EtOH (pH 7.0) and an applied voltage of 15 kV. We find that the addition of SDS to the run buffer can enhance the separation of cationic DMF-AuNC, attributing to the attachment of the charged SDS to the AuNC surface with a concomitant effect on changing the charge-to-size ratio of the cationic DMF-AuNC.

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