Silver Nanoparticles Enhanced Luminescence from the Europium(III)-Doxycycline Complex and Its Analytical Application

Mohammad Kamruzzaman, Al-Mahmnur Alam, Sang Hak Lee, Sang-Hyub Oh, Young Ho Kim, ANM Hamidul Kabir

Department of Chemistry, Kyungpook National University, Daegu, 702-701, Korea
*Center for Gas Analysis, Korea Research Institute of Standards and Science, Daejeon, 305-600, Korea
**Research Institute of Advanced Energy Technology, Kyungpook National University, Daegu, 702-701, Korea
***Department of Applied Chemistry & Chemical Engineering, University of Dhaka, Bangladesh

Abstract

A simple and sensitive fluorometric method has been proposed by the enhanced luminescence from the europium (Eu³⁺)–doxycycline (DC) complex in the presence of silver nanoparticles (AgNPs). The enhancement of the luminescence from the Eu³⁺–DC complex by AgNPs was accredited due to the transfer of resonance energy to the fluorophores through the interaction of the excited-state fluorophores and surface plasmon electron in the metal nanosurface. The enhanced luminescence intensity was linearly proportional to the concentration of DC in the range of 3.0×10⁻⁹–1.7×10⁻⁷ g mL⁻¹. The limit of detection was found to be 4.0×10⁻¹⁰ g mL⁻¹. The proposed method has been applied successfully to determine DC in pharmaceuticals and biological samples.

Keywords: luminescence, europium, silver nanoparticles, doxycycline.

1. Introduction

Doxycycline (DC) is a member of tetracycline antibiotics containing β−diketonate configuration. It is a broad spectrum anti−bacterial agent with a wide range of activity against gram positive and gram negative organisms. DC is used frequently in the treatment of chronic prostatitis, sinusitis, syphilis, chlamydia, pelvic inflammatory disease, acne, rosacea, and rickettsia infections. Therefore, the determination of DC in human body fluids and pharmaceuticals is very important. Numerous analytical methods have already been reported to determine DC including, liquid chromatography[1], spectrophotometric[2], thin layer chromatography[3], sequential injection chromatography[4], fluorometry[5]. Among the above method, lanthanide (Eu³⁺, Tb³⁺) sensitized fluorometric method has been extensively
used because lanthanide ions are used as fluorescent probe due to their high fluorescence quantum yield, large stocks shifts, narrow emission bands and long lifetime. In the present study, we proposed a simple and sensitive fluorometric method for the determination of DC based on the enhanced luminescence intensity of Eu\(^{3+}\)-DC complex by AgNPs. The proposed method is simple and sensitive to determine DC which showed wide linear range, low limit of detection with satisfactory results.

**Fig. 1.** Fluorescence emission spectra. Conditions: Eu\(^{3+}\), 4.2×10\(^{-6}\) mol L\(^{-1}\); DC, 1.5×10\(^{-7}\) g mL\(^{-1}\); AgNPs, 3.5×10\(^{-4}\) mol L\(^{-1}\); pH, 8.5; Tris-HCl, 0.1 mol L\(^{-1}\).

### 2. Experimental

#### 2.1. Reagents

Stock solutions of DC, AgNO\(_3\) and EuCl\(_3\) (Sigma–Aldrich, St. Louis, USA) were prepared using distilled water and stored at refrigerator. All working solutions at desired concentration were prepared daily from the stock solution just before use.

#### 2.2. Apparatus and Procedures

A spectrofluorometer (F–4500, Hitachi, Japan) equipped with a 150 W Xenon lamp (Model XBO 450 W/1, Osram, Germany) and a photomultiplier tube (Model R928, Hamamatsu, Japan) powered at 950 V was used to collect all the fluorescence spectra.

#### 2.3. Preparation of AgNPs

AgNPs were prepared in accordance with the procedure described in literature[6]. The prepared AgNPs were characterized by transmission electron microscope (TEM) which illustrated the morphology of AgNPs with quite uniform size and average diameter of approximately 8±2 nm (Fig. 2).
3. Results and Discussion

3.1. Spectral Characteristics of Fluorescence

The weak FL intensity of Eu\(^{3+}\) was enhanced at 591 and 614 nm when DC was mixed with Eu\(^{3+}\) corresponding to the \(^{5}D_{0} - ^{7}F_{1}\) and \(^{5}D_{0} - ^{7}F_{2}\) transitions of Eu\(^{3+}\) ion and the highest intensity was obtained at 614 nm. The FL intensity of the Eu\(^{3+}\)-DC complex was enhanced significantly at 614 nm by AgNPs due to the plasmonic interaction between the excited-state fluorophores and surface plasmon electron in the metal nano surface.

3.2. Optimization of the Experimental Conditions

The effect of the experimental conditions was investigated. The FL intensity was increased with the pH over the range of 7.0 to 8.5 and decreased above pH 8.5. The effect of the concentrations of Eu\(^{3+}\) and AgNPs was examined in the range of 6.5×10\(^{-6}\) to 7.0×10\(^{-6}\) and 6.0×10\(^{-4}\) to 3.5×10\(^{-3}\) mol L\(^{-1}\) respectively. The highest FL signal was obtained using 4.2×10\(^{-6}\) mol L\(^{-1}\) of Eu\(^{3+}\) and 3.5×10\(^{-4}\) mol L\(^{-1}\) of AgNPs and chosen for the whole experiment.

![Fig. 2. TEM image of the AgNPs.](image)

![Fig. 3. Calibration curve for the determination of DC.](image)
3.3. Analytical Performance

At the optimum conditions, a calibration curve was constructed by plotting the FL intensity against DC concentration in the range of $3.0 \times 10^{-9} - 1.7 \times 10^{-7}$ g mL$^{-1}$ of DC ($r=0.9992$). The limit of detection was found to be $4.0 \times 10^{-10}$ g mL$^{-1}$ with the relative standard deviation (RSD) of 0.77% for the determination of $1.5 \times 10^{-7}$ g mL$^{-1}$ DC (Fig. 3).

4. Conclusion

A simple, sensitive and selective fluorimetric method has been presented to determine DC in pharmaceuticals and biofluids based on the enhanced luminescence of Eu$^{3+}$–DC complex by AgNPs which offers wide dynamic range and low limit of detection.

Acknowledgement

This work was supported by the Korea Research Council of Fundamental Science and Technology (KRCF) through Basic Research Project managed by the Korea Research Institute of Standards and Science (KRISS). This research was supported by Dual Use Technology (08-DU-EB-02) Research Fund.

References