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Resonance Rayleigh scattering and resonance non-linear scattering method for the determination of aminoglycoside antibiotics with water solubility CdS quantum dots as probe

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ABSTRACT

In pH 6.6 Britton–Robinson buffer medium, the CdS quantum dots capped by thioglycolic acid could react with aminoglycoside (AGs) antibiotics such as neomycin sulfate (NEO) and streptomycin sulfate (STP) to form the large aggregates by virtue of electrostatic attraction and the hydrophobic force, which resulted in a great enhancement of resonance Rayleigh scattering (RRS) and resonance non-linear scattering such as second-order scattering (SOS) and frequency doubling scattering (FDS). The maximum scattering peak was located at 310 nm for RRS, 568 nm for SOS and 390 nm for FDS, respectively. The enhancements of scattering intensity (ΔI) were directly proportional to the concentration of AGs in a certain ranges. A new method for the determination of trace NEO and STP using CdS quantum dots probe was developed. The detection limits (3σ) were 1.7 ng mL^{-1} (NEO) and 4.4 ng mL^{-1} (STP) by RRS method, were 5.2 ng mL^{-1} (NEO) and 20.9 ng mL^{-1} (STP) by SOS method and were 4.4 ng mL^{-1} (NEO) and 25.7 ng mL^{-1} (STP) by FDS method, respectively. The sensitivity of RRS method was the highest. The optimum conditions and influence factors were investigated. In addition, the reaction mechanism was discussed.

1. Introduction

In recent years, quantum dots (QDs), which are semiconductor nanoparticles that have all three dimensions confined to the 2–15 nm length scale [1], have attracted considerable attention [2] because of their unique luminescent properties. QDs have been applied to the detection of biomacromolecules [3,4], metal ions [5], pharmaceuticals [6], and so on. Therefore, it is significant for further developing new analytical application of QDs.

Furthermore, resonance Rayleigh scattering (RRS), second-order scattering (SOS) and frequency doubling scattering (FDS) have been paid more and more attention because of their high sensitivities and simplicities [7]. And these techniques have been applied to determine macromolecules such as inorganic ions [8], organic compounds [9], nucleic acids [10], proteins [11], heparin [12], and some drugs [13,14].

Aminoglycoside antibiotics are composed of a sugar group and an amino group. It works by binding to the bacterial 30S ribosomal subunit (some work by binding to the 50S subunit), inhibiting the translocation of the peptidyl-tRNA from the A-site to the P-site and also causing misreading of mRNA, leaving the bacterium unable to synthesize proteins vital to its growth. They will kill bacteria by inhibiting protein synthesis as they bind to the 16S rRNA and by disrupting the integrity of bacterial cell membrane [15]. Neomycin (NEO) and streptomycin (STP) are the two representative aminoglycoside antibiotics (AGs) used in the treatment of both animals and humans against aerobic gram-negative bacteria [16]. However, it is well known that they will cause damage to the kidneys and cranial nerves [17]. To ensure therapy efficacy and avoid possible risk of toxicity, there is an urgent need for developing detection technologies to monitor AGs. Up to now, many methods have been developed to detect AGs, including microbiological assay [18], high performance liquid chromatography (HPLC) [19,20], spectrofluorescence [21], electrochemical analysis [22], ion-exchange chromatography [23], spectrophotometry [24] and chemiluminescence [25]. However, these methods involved inconvenient and their sensitivities are lower. So, it is very necessary to develop a simple, high sensitive and selective method for the determination of aminoglycoside antibiotics.

In weak acidic medium, AGs positive charge-contained molecules was bounded to the surface of CdS-QDs contained negative charge via electrostatic attraction form complexes, which results in the enhancement of resonance Rayleigh scattering (RRS), second-order scattering (SOS) and frequency doubling scattering (FDS) significantly. At the same time, the spectral characteristics of RRS, SOS and FDS spectra and the reaction conditions and the influ-

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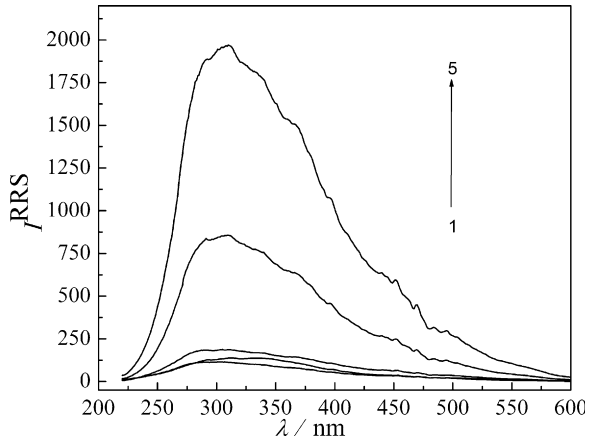

Fig. 1. The RRS spectra of binding products of CdS-QDs with aminoglycoside drugs. (1) STP; (2) NEO; (3) CdS-QDs; (4) STP + CdS-QDs; (5) NEO + CdS-QDs. NEO and STP concentrations: 0.48 μg mL^{-1}; CdS concentration: 2.5×10^{-5} mol L^{-1}.

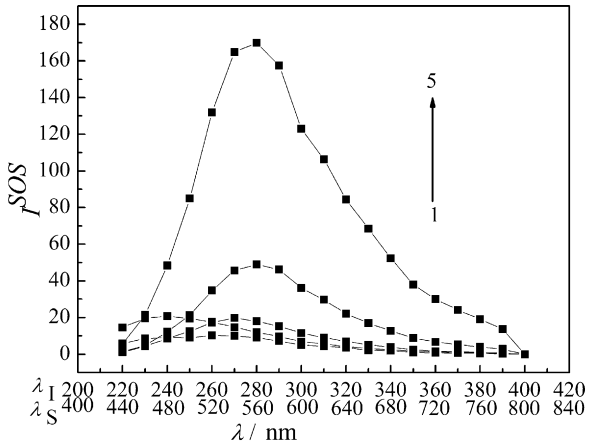

Fig. 3. The SOS spectra of binding products of CdS-QDs with aminoglycoside drugs. (1) NEO; (2) STP; (3) CdS-QDs; (4) STP + CdS-QDs; (5) NEO + CdS-QDs; NEO and STP concentrations: 0.48 μg mL^{-1}; CdS concentration: 2.5×10^{-5} mol L^{-1}.

encing factors were investigated. The results indicated that three methods exhibited higher sensitivities and the RRS method had the lowest detection limit of 1.7–4.4 ng mL^{-1} for the determination of NEO and STP. The sensitivity of the RRS method is not only 1–3 orders of magnitude higher than those of common spectrophotometric methods, but also higher than the sensitivities of many spectrofluorescence, chemiluminescence, HPLC [26], and RRS [27]. Based on these properties, a sensitive, simple, selective method for the determination of aminoglycoside antibiotics with TGA-capped QDs as probe by resonance Rayleigh scattering technique had been developed.

2. Experimental procedure

2.1. Apparatus

A Hitachi F-2500 fluorospectrophotometer (Tokyo, Japan) was used for measuring the scattering intensities with the slits (EX/EM) of 5/5 nm (RRS, SOS and FDS). A PHS-3C digital pH meter (Leici, Shanghai, China) was used to adjust the pH values of the solutions. HITACHI-600 transmission electron microscopy (TEM, Electronic Company, Japan) was used to observe the appearance and size of quantum dots (QDs).

2.2. Materials and reagents

400 μg mL^{-1} stock solutions of neomycin sulfate (NEO, AMRESCO) and streptomycin sulfate (STP, AMRESCO), $CdCl_2 \cdot 2.5H_2O$ (Shanghai Chemical Reagents Co., Shanghai, China), $Na_2S \cdot 9H_2O$ (Chongqing Chemical Reagents Main Workshop, Chongqing, China) and thioglycolic acid (TGA, Station Medicine Group Chemical Reagents Co., Chengdu, China) were prepared by dissolving these commercial products with doubly distilled water. The concentration of NEO and STP was 40 μg mL^{-1} which was prepared by diluting the stock solutions, while that of $CdCl_2$ and Na_2S were 0.1 mol L^{-1}. Britton–Robinson buffer solutions with different pH were prepared according to suitable proportion and adjusted pH values with a pH meter. All reagents used are of analytical grade. Water used throughout was doubly distilled.

Water solubility colloids of CdS-QDs were prepared according to previously published methods [28]. In brief, appropriate amount of TGA was added to nitrogen-saturated $CdCl_2$ aqueous solution, after thoroughly mixing, the pH value of the mixture was adjusted between 10 and 11 by using 0.2 mol L^{-1} NaOH solution, and then an appropriate volume of 0.1 mol L^{-1} Na_2S was added under vigorous stirring. The initial molar ratio TGA:Cd^{2+}:S^{2-} was approximately 1.1:1:0.9. After thoroughly mixing, the mixture was converted to CdS-QDs by refluxing the reaction mixture at 70 °C for 12 h under

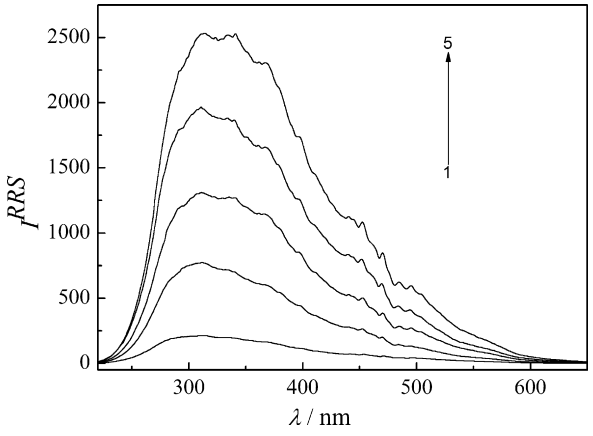

Fig. 2. The RRS spectra of binding products of CdS-QDs with NEO for various concentrations. (1) CdS-QDs; (2–5) NEO + CdS-QDs. NEO concentration: 0.16, 0.32, 0.48, and 0.64 μg mL^{-1}; CdS concentration: 2.5×10^{-5} mol L^{-1}.

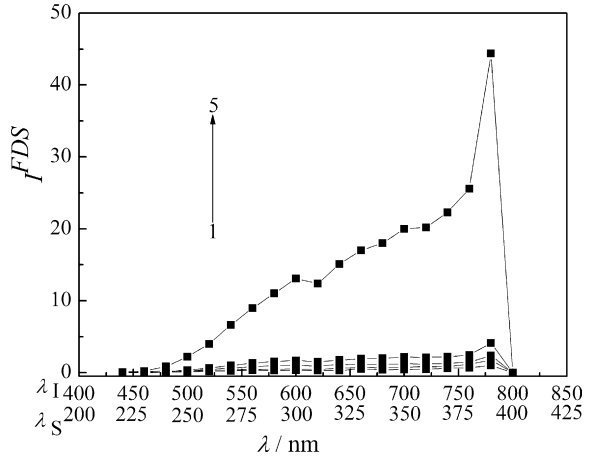

Fig. 4. The FDS spectra of binding products of CdS-QDs with aminoglycoside drugs. (1) NEO; (2) STP; (3) CdS-QDs; (4) STP + CdS-QDs; (5) NEO + CdS-QDs; NEO and STP concentrations: 0.48 μg mL^{-1}; CdS concentration: 2.5×10^{-5} mol L^{-1}.