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Colorimetric recognition of pazufloxacin mesilate based on the aggregation of gold nanoparticles

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ABSTRACT

A novel colorimetric nanomaterial-assisted optical sensor for pazufloxacin mesilate was proposed for the first time. Pazufloxacin mesilate could induce the aggregation of glucose-reduced gold nanoparticles (AuNPs) through hydrogen-bonding interaction and electrostatic attraction, leading to the changes in color and absorption spectra of AuNPs. The effect of different factors such as pH, the amount of AuNPs, reaction time and reaction temperature was inspected. Under the optimum condition, UV–vis spectra showed that the absorption ratio (A_{670}/A_{532}) was linear with the concentration of pazufloxacin mesilate in the range from 9×10^{-8} mol L^{-1} to 7×10^{-7} mol L^{-1} with a linear coefficient of 0.9951. This method can be applied to detecting pazufloxacin mesilate with an ultralow detection limit of 7.92×10^{-9} mol L^{-1} without any complicated instruments. Through inspecting other analytes and ions, the anti-interference performance of AuNP detection system for pazufloxacin mesilate was excellent. For its high efficiency, rapid response rate as well as wide linear range, it had been successfully used to the analysis of pazufloxacin mesilate in human urine quantificationally.

1. Introduction

As a novel chemical drug, pazufloxacin mesilate is one of the fourth generation members of synthetic fluoroquinolone antibacterial agents. It has high antimicrobial activity against both Gram (+), Gram (−) and anaerobic species, resulting from the antagonism of both DNA gyrase and topoisomerase IV [1,2]. It penetrates infectious foci easily and shows lower toxicity, less photosensitivity and broader spectrum than conventional quinolone antimicrobial agents [3,4]. Pazufloxacin mesilate is used for clinical treatment of infectious diseases such as bronchial, lung, skin and soft tissue infections. Nevertheless in recent years, adverse reactions such as drug resistance and accumulation in vivo increase with antibiotic abuse, which may be dangerous for people's health. So therapeutic drug monitoring to guide clinical individualized medication has become a research hotspot.

Existing methods for determining pazufloxacin mesilate comprise ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS–MS) [5], fluorescence method [6,7], chemiluminescence [8], high performance liquid chromatography (HPLC) [9,10] and capillary electrophoresis [11,12]. UPLC–MS–MS and the HPLC method with UV detector all have excellent separation efficiency, but they are time-consuming and high cost. Capillary electrophoresis has poor reproducibility. Although chemiluminescence and fluorescence analysis methods possess high sensitivity, poor anti-interference makes them limited by complex samples. Therefore, a rapid, simple detection technique with excellent selectivity and high sensitivity for analysis of pazufloxacin mesilate is sorely demanded to overcome these limits.

Noble metal nanoparticles (e.g. Au and Ag) have received great attentions; they are widely used as optical nanoprobes for sensitive detection owing to localized surface plasmon resonance phenomena (LSPR) [13–16]. The LSPR band is not only dependent on the refractive index of the surrounding media and the size of the particle, but also gets significant changes with inter-particle distance and shape. Furthermore, AuNPs solution shows a particular color due to collective oscillations of the surface electrons induced by visible light of suitable wavelength, which is also highly dependent on inter-particle distance. When AuNPs aggregate, the LSPR absorption band would change obviously for the decreasing of inter-particles distance, causing color change of AuNPs solution [17–19]. Recently, taking advantages of localized surface plasmon resonance of AuNPs, analytes-induced aggregation of AuNPs accompanied with color changes have recently been used as emerging probes for colorimetric determination. AuNPs have shown some particular advantages and characters compared with AgNPs since AuNPs are more stable and their particle size are more controllable. Additionally, AuNPs own higher sensitivity than

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AgNPs. Gold nanoparticles, as colorimetric sensors, have been developed for facile tracking of proteins [20–22], heavy metal ions [23–28], amino acids [29,30], small molecules [31–36] and oligonucleotides [37–39].

Herein, we describe a rapid and simple colorimetric method for pazufloxacin mesilate detection using glucose-reduced AuNPs. This method does not need any chemical modification and sophisticated operations, even more important, it possesses good sensitivity, selectivity as well as low detection limit. In this work, glucose-reduced AuNPs have electronegative charge and can be dispersed from each other by electrostatic repulsion. However, pazufloxacin mesilate which acts as "molecular bridge" between the AuNPs can induce the aggregation of AuNPs through hydrogen-bonding interaction and electrostatic attraction, causing color and absorption spectra changes of the AuNPs solution. As far as we are concerned, it is the first demonstration for the rapid and simple analysis of pazufloxacin mesilate by colorimetric assay and it has been successfully applied to urine test.

2. Materials and methods

2.1. Chemical and reagents

Pazufloxacin mesilate and $HAuCl_4$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Glucose and sodium hydroxide (NaOH) were obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). All the other chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with Milli-Q water.

2.2. Apparatus

Ultraviolet and visible spectra were recorded on Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) equipped with 10 mm quartz cells. The pH measurements were performed on a pHS-25 digital pH-meter (Shanghai Wei Ye Instrument Factory, China). Transmission electron microscope (TEM) was used to characterize glucose-reduced AuNPs.

2.3. Preparation of glucose-reduced AuNPs

First of all, all glassware was soaked in a bath of freshly prepared aqua regia (3:1, V/V HCl/HNO_3), then rinsed thoroughly with Milli-Q water and dried in oven. Gold nanoparticles were synthesized by a slight modification to the method previously demonstrated by Sastry and co-workers [40]. In a typical synthesis, 18 mL of an aqueous solution of 2.5×10^{-4} M $HAuCl_4$ was put in a conical flask, and then to this solution was added 2 mL of 1 M D-glucose. The mixed solution was heated to 60 °C, 40 μL of 1 M NaOH was added and stirred rapidly for 10 s subsequently. Finally a ruby red solution was obtained, which implied the formation of gold nanoparticles. The particles were believed to be stabilized by a monolayer of gluconic acid on the surface and thus were negatively charged. The obtained solution was cooled to room temperature and then stored at 4 °C for all further experiments.

2.4. Colorimetric detection of pazufloxacin mesilate

For pazufloxacin mesilate sensing, specifically, 0.5 mL appropriate amounts of pazufloxacin mesilate standard solution, 0.3 mL of Britton–Robinson buffer solution (pH 3.29) and 0.6 mL of the prepared glucose-reduced AuNPs aqueous solution were in turn put into the test tube. Mixed solution incubated a period of time under a certain temperature. Then the color changed from ruby red to purple gradually. Finally, the reaction solution was transferred into spectrometric cell to record the absorbance at 532 nm and 670 nm, respectively. The concentration of pazufloxacin mesilate was quantified based on the absorption ratio (A_{670}/A_{532}) or naked eye observation [41].

3. Results and discussion

3.1. Principle of pazufloxacin mesilate detection using glucose-reduced AuNPs

Fig. 1 describes the principle of the colorimetric determination of pazufloxacin mesilate. Under normal circumstances, AuNPs are stable owing to the electrostatic repulsion of the negative capping agent against van der Waals attraction between AuNPs. Pazufloxacin mesilate (Fig. 2) molecule contains one amine group and one carboxyl group. The amino groups of it can make the molecule carry high positive charge at certain pH, which would absorb onto the surface of AuNPs through the electrostatic attraction. The ketonic oxygen and fluorine of pazufloxacin mesilate can form hydrogen bonds with hydroxyl on the surface of AuNPs. So when pazufloxacin mesilate was added into AuNPs, electrostatic stability is broken as well as the interparticle distance decreases through electrostatic interaction and hydrogen bonding. Adjacent gold nanoparticles aggregate and color changes from ruby red to purple. Meanwhile, the absorbance of characteristic peak of AuNPs decreases and a new absorption peak appears at a longer wavelength [42]. This aggregation-based change in color can be developed into a sensitive and rapid colorimetric method detecting pazufloxacin mesilate by naked eyes or UV–vis spectroscopy.

3.2. Characterization of AuNPs

The TEM image (Fig. 3) showed AuNPs were well dispersed from each other in the solution and uniform with the size of around 20 nm. As shown in Fig. 4(a), the absorption spectra of AuNPs exhibited a typical surface plasma resonance absorption peak at 532 nm and presented ruby red. In the presence of pazufloxacin mesilate, the absorbance at

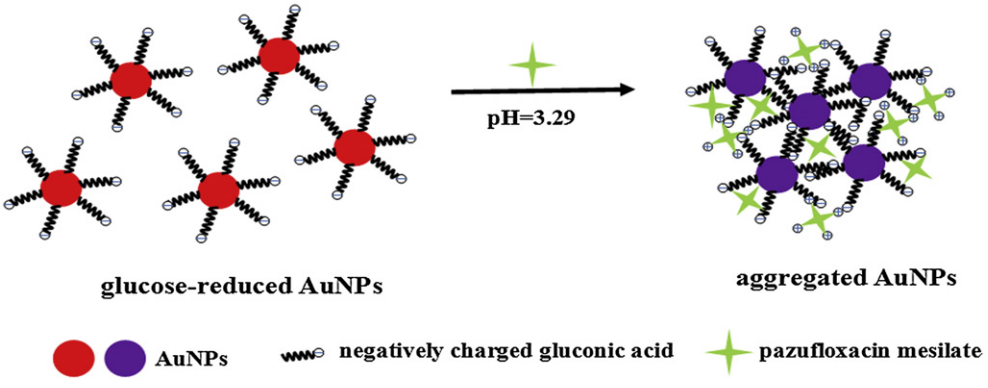

Fig. 1. Schematic mechanism of colorimetric detection of pazufloxacin mesilate.