Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 153 (2016) 445–450

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectral study of interaction between chondroitin sulfate and nanoparticles and its application in quantitative analysis

Yi Ma [a], Maojie Wei [a], Xiao Zhang [b], Ting Zhao [c], Xiumei Liu [c,*], Guanglian Zhou [a,*]

[a] School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, China
[b] Quality Assurance Department, Shandong Lukang Pharmaceutical Co., Ltd., Jining 272021, China
[c] School of Pharmaceutical Sciences, Shandong University, Jinan 250012, China

ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form 14 July 2015
Accepted 29 August 2015
Available online 2 September 2015

Keywords:
Spectrum
Chondroitin sulfate
Nanoparticles
Interaction
Quantitative analysis

ABSTRACT

In this work, the interaction between chondroitin sulfate (CS) and gold nanoparticles (GNPs) and silver nanoparticles (SNPs) was characterized for the first time. Plasma resonance scattering (PRS) and plasma resonance absorption (PRA) were used to investigate the characteristics of their spectrum. The results suggested that the CS with negative charge could interact with metal nanoparticles with negative charge and the adsorption of CS on the surface of SNPs was more regular than that of GNPs. The resonance scattering spectra also further confirmed the interaction between CS and SNPs. A new method for detection of CS based on the interaction was developed. CS concentrations in the range of 0.02–3.5 μg/mL were proportional to the decreases of absorbance of SNPs. Compared with other reported methods, the proposed method is simple and workable without complex process, high consumption and expensive equipments. The developed method was applied to the determination of the CS contents from different biological origins and the results were compared with those obtained by the method of Chinese Pharmacopeia. The effects of matrix in plasma and other glycosaminoglycans on the determination of CS were also investigated. The results showed that a small quantity of blood plasma had no effect on the determination of CS and when the concentration ratio of CS to heparin was more than 10:1, the influence of heparin on the detection of CS could be ignored. This work gave a specific research direction for the detection of CS in the presence of metal nanoparticles.

1. Introduction

Glycosaminoglycans (GAGs) are a kind of heterogeneous polysaccharides with various relative molecular mass, charge density and physico-chemical properties. Chondroitin sulfate (CS) is an important polyanion GAG with many physiological functions, consisting of an alternate sequence of D-glucuronic acid (GlcA) and aminohexose linked by β (1 → 3) bonds [1], its structure is shown in Fig. 1. Currently, CS is widely used as nutraceutical and pharmaceutical raw materials. It is mainly used for the treatment of sensorineural headaches, migraine, osteoarticular disease, coronary disease and angina pectoris [2]. It also has significant effect on hearing impairment caused by streptomycin [3].

At present, the enzymolysis method is mostly used for the determination of CS by analyzing the unsaturated disaccharides produced by chondroitin lyases and detection at 232 nm [4–7]. This method, however, requires complex degradation process and expensive reagents. Recently, the CE method [8,9] and near infrared spectroscopy (NIRS) method [10] were used for the analysis of intact CS, however, CE has poor peak shape and low sensitivity besides expensive equipment, NIRs needs a large amount of samples and complex data processing. Therefore, it is necessary to develop a simple and sensitive analytical method for CS detection.

Lately, nanoparticles, especially noble metal nanoparticles, such as gold nanoparticles (GNPs) and silver nanoparticles (SNPs), were applied widely to analytical chemistry because of its special characters: large specific surface area, chemical stability and biological applicability. For example, GNPs were used for determination of protein [11,12] and urea [13]. SNPs are ideal inorganic chromospheres because of their remarkable photo-physical and photochemical properties. Particularly, due to their characteristic surface plasmon resonance, SNPs are often used in bio-sensing and imaging applications [14]. For example, SNPs were used for detection of anions in aqueous solution [15] and determination of flavonoids in biologically active food additives [16]. The applications of nanoparticles in GAG analysis have emerged slowly in recent years. Liu et al. [9] used GNPs as additive of buffer in CE to improve the separation of CS and dermatan sulfate. Mausam Kalita developed a rapid, ultrasensitive method to detect oversulfated chondroitin sulfate (OSCS) in heparin using a nanometal surface energy transfer (NSET) based gold-heparin-dye nanosensor [17].

The optical properties of metal nanoparticles have fascinated many scientists since the recent past because of the phenomenon known as the localized surface plasmon resonance (LSPR), which is a result of collective oscillation of conduction electrons induced by an electromagnetic

* Corresponding authors.
E-mail addresses: liuxium@sdu.edu.cn (X. Liu), guanglianzhou@126.com (G. Zhou).

http://dx.doi.org/10.1016/j.saa.2015.08.045
1386-1425/

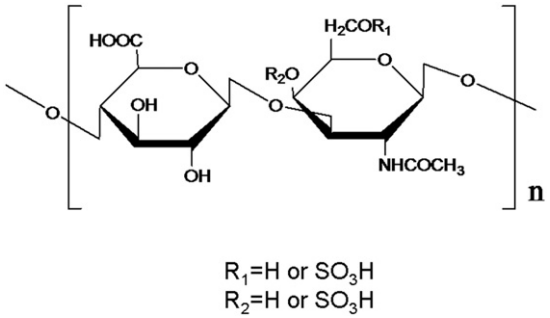

Fig. 1. Repeat disaccharide unit of CS.

field [18,19]. The selective photon absorption and scattering allow the optical properties of LSPR of the NPs to be monitored, including localized surface Plasmon resonance absorption (LSPR-A) and localized surface Plasmon resonance light scattering (LSPR-LS). The characteristics of metal nanoparticles have been used to detect salmeterol xinafoate [20] and hydroquinone [21] sensitively.

The aim of this study is to investigate the interaction between CS and metal nanoparticles (GNPs and SNPs) using plasma resonance scattering (PRS) and plasma resonance absorption (PRA). Furthermore a method of spectra for CS quantitative analysis was developed and used to detect the CS content from different sources successfully. The effects of matrix in plasma and other GAGs on the determination of CS were also investigated.

2. Materials and methods

2.1. Chemicals and reagents

CS from porcine cartilage was purchased from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). CS from bovine cartilage was donated by Zaozhuang Sainuokang Biochemistry Co. (Zaozhuang, China). Chondroitinase ABC and GNPs (stabilized suspension in 0.1 mM PBS, reactant free, 40 nm: 6.44E + 10–7.87E + 10 particles/mL, TEM image is shown in Fig. 2b) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Tris (hydroxymethyl) aminomethane (99%) and sodium acetate trihydrate were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium phosphate monobasic dihydrate and phosphoric acid (85%) were supplied by Tianjin Guangcheng Chemical Factory (Tianjin, China). Deionized water was obtained from a Millipore Milli-Q Biocell purification system.

SNPs were synthesized according to the method of Meisel [22]. Its property was characterized by UV–vis spectrum and TEM image (shown in Fig. 2a). The average size was 40 nm.

2.2. Preparation of samples

The phosphate buffer was prepared by dissolving a quantity of Na_2HPO_4 into the desired concentration, and the pH was adjusted with phosphoric acid. Standard stock solution of 10 mg/mL CS was prepared with purified water. A working standard solution containing 3.5 μg/mL CS was obtained by diluting the corresponding stock solution to the desired concentration with purified water.

To the detection of CS by HPLC, the CS from porcine and bovine was treated with Chondroitinase ABC in accordance with Chinese Pharmacopeia.

The pretreatment of blood plasma was carried out according to the report of Shuichi Kusano [23]. Then a series of CS in blood plasma was prepared to interact with SNPs.

2.3. Instruments and conditions

A CARY-100 BIO UV–vis Spectrophotometer scans from 200 nm to 800 nm, the slit width was 4 nm. The RLS spectrum was obtained by scanning simultaneously the excitation and emission monochromators

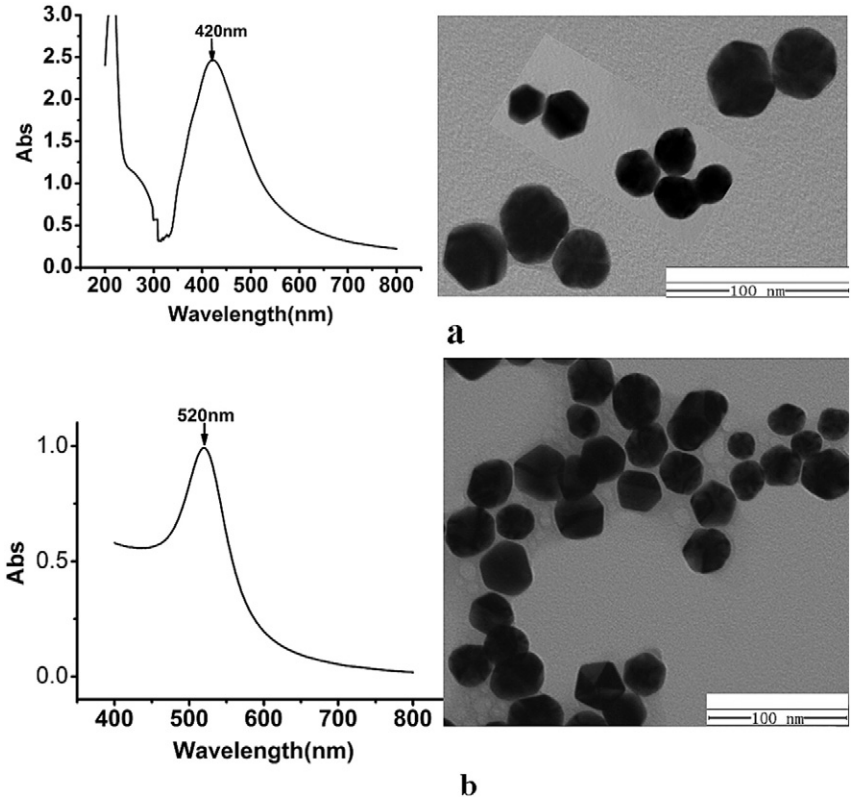

Fig. 2. a: UV–vis spectrum and TEM image of SNPs; b: UV–vis spectrum and TEM image of GNPs.