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Detecting glucose by using the Raman scattering of oxidized ascorbic acid: The effect of graphene oxide–gold nanorod hybrid

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ABSTRACT

Surface-enhanced Raman scattering (SERS) activity of oxidized ascorbic acid in the graphene oxide (GO) and gold nanorod (AuNRs) hybrid (GO-AuNR) substrate has been investigated. In the synthesis of AuNRs according to seed-mediated method, ascorbic acid has been oxidized into oxidized ascorbic acid and bonded on the surface of AuNRs via electrostatic interaction. It has been interesting to find the SERS signal of oxidized ascorbic acid shows a linear response to the concentration of the added glucose. This glucose concentration-dependent SERS intensity could be applied for the sensitive detection of liquid glucose. The corresponding mechanism has been attributed to the effect of density and viscosity of liquid glucose on the SERS activity of oxidized ascorbic acid.

1. Introduction

Surface-enhance Raman scattering (SERS) has greatly attracted attention in single-molecule detection and molecular structure investigation due to its unique spectra properties [1]. As a significant spectral analysis technique, the synthesis of SERS-based substrate becomes extremely important. Noble metal nanoparticles have been widely applied in SERS-based substrate preparation and chemical and biological sensing. For instance, gold and silver nanoparticles exhibit a localized surface plasmon resonance (LSPR) induced the coherent oscillation of conduction electrons [2], which results in plenty of hot spots of local electric field when resonantly excited by incident light. Thus the substrate with hot spots in the metal nanostructure exhibits excellent SERS activities [3]. Wang et al. [4] proposed a detection approach of α-fetoprotein based on gold nanoparticles and SERS. The SERS-based immunoassay system could specifically detect AFP with a very low concentration. Unlike gold nanospheres, the gold nanorods (AuNRs) have two LSPR absorption modes, transverse mode and longitudinal mode, due to the oscillation of conduction electrons along two different directions [5]. The aspect ratio-dependent intense longitudinal SPR results in excellent SERS activities, which could be perfectly utilized to detect the single cancer cell [6].

Many previous reports show the mechanism of SERS-based substrate are originated from the local electromagnetic-field enhancement and the charge transfer mechanism [2,7]. In order to improve the SERS abilities, many efforts have been developed to improve the effects of local field enhancement and the electronic transition. Recently, metallic nanoparticles-based substrate decorated with graphene has been recognized as a useful technique, which realizes the combination of these two main effects [8]. The excellent electronic and structural properties have rendered graphene oxide (GO) appropriate candidate for application in SERS-based substrate [9–14]. Because of the intense local electric field, the metallic nanoparticles decorated by GO served as SERS-based substrate could further enhance the SERS activities. Liu et al. [11] offered a successful method of GO grafted on to the Ag nanoparticles, which exhibited excellent SERS enhancement. Du et al. [12] synthesized the hybrid films of graphene and Au nanoparticles. The enhanced electromagnetic hot spots had been found between them, which resulted in the significant improvement of SERS activity.

In recent years, because of severe secondary health complications in diabetes patients, the determination researches of glucose detection have been performed. Thus the simpler and cheaper detection approaches should be aroused in terms of clinical benefit [15,16]. Many previous reports developed indirect SERS detection of glucose by enzymatic oxidation of glucose oxidase and glucose

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[17–19]. For example, Dong et al. fabricated free radical-quenched SERS probes for detecting H_2O_2, which was metabolic product of glucose with glucose oxidase. The SERS probe exhibited excellent properties for detection of glucose [20]. However, lots of environment factors affect the bioactivity of glucose oxidase. Nowadays, plenty of researchers make great effort to synthesize nonenzymatic glucose biosensor to refrain from interference factors. The normal Raman spectroscopy (NRS) has been shown the capacity of addressing glucose. However, due to the inherently small normal Raman scattering cross section and weak or nonexistent binding to bare metal surfaces, it's hard to carry out direct SERS detection of liquid glucose [21,22]. Some reports utilized the SERS signal probes served as the molecular recognition agent in response to the concentration of glucose [15,23–26]. Torul et al. fabricated the SERS substrate by modifying two component self-assembled monolayers (SAMS) on the surface of gold nanorod particles [24]. The variation of the SERS signal of SAMS showed the response to the concentration of glucose, and a low detection limit of 0.5 mM was obtained. Kong et al. proposed a novel glucose binding mechanism by using phenylboronic acid as the receptor for saccharide and forming a glucose-alkyne-boronic acid complex on SERS substrate, which exhibited a new Raman peak at 1996 cm^{-1} [26]. Thus, the novel technology offered a high sensitivity for SERS glucose sensing.

In our previous study [8], AuNRs have been successfully decorated on graphene oxide via electrostatic interaction. Because of some dissociative CTAB in the GO-AuNR hybrid, the electronic transition efficiency of the hybrid film had been greatly enhanced, which resulted in excellent SERS activity. When AuNRs were prepared by seed-mediated method, and ascorbic acid was added as reductive agent, what will happen to ascorbic acid after oxidized? In this paper, we studied the interaction between AuNRs and oxidized ascorbic acid. The SERS activity of oxidized ascorbic acid in the GO-AuNR substrate had been also investigated. Furthermore, by utilizing oxidized ascorbic acid as SERS signal probe, a glucose sensor had been designed and exhibited response to the concentration of liquid glucose.

2. Experimental

Cetyltrimethyl ammonium bromide (CTAB) and D-Glucose anhydrous were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH), sodium borohydride ($NaBH_4$), silver nitrate ($AgNO_3$) and ascorbic acid were purchased from Aladdin. Gold chloride trihydrate ($HAuCl_4$, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and hydrochloric acid (HCl, Beijing Chemical Works, China) were used as received.

The absorption spectra of the prepared simples were collected on a UV-3600UV-VIS-NIR spectrophotometer (Shimadzu, Japan). The Raman spectra were collected in a back scattering geometry through a 50 × (NA = 0.75) objective HORIBA JOBIN YVON Raman spectrometer (HORIBA, France), and the wavelength of laser excitation was 532 nm.

In this study, the preparation of aqueous graphene oxide dispersions, AuNRs and GO-AuNR hybrid refers to our previous paper [8]. AuNRs were synthesized using the seed-mediated method with slight modification. The growth solution was prepared by mixing $HAuCl_4$, $AgNO_3$, CTAB and HCl. Ascorbic acid was then added as reductive agent. In this experiment, the prepared AuNRs have a major longitudinal plasmon resonance wavelength at 730 nm. Whereas the absorption peak at 512 nm corresponds to the transverse plasmon resonance. Aqueous graphene oxide dispersions were prepared by dissolving the solid graphite oxide powder in the ultra-pure water under ultrasonic for 2 h. The sample was taken for centrifugal (12,000 rpm, 25 °C,10 min) twice. The single-layered GO was obtained from the supernatant liquor.

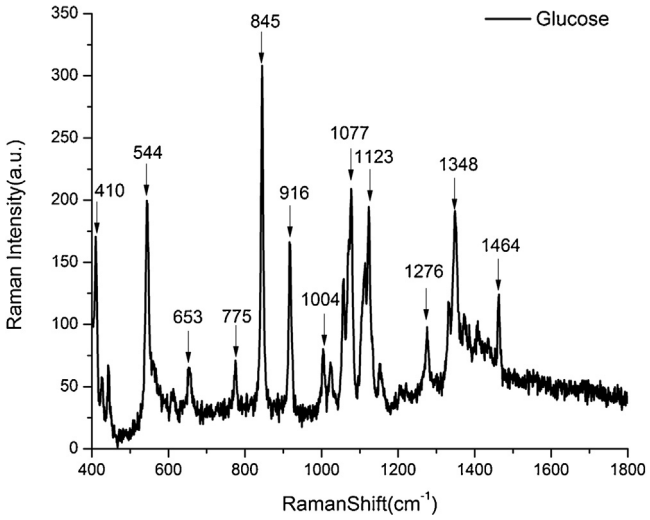

Fig. 1. Raman spectrum of D-glucose in the crystalline state.

The synthesis method of GO-AuNR hybrid substrate was similar to the previous process [8]. Firstly, the SiO_2/Si substrate was washed clean under ultrasonication in acetone, ethanol and ultrapure water in turn. Secondly, aqueous AuNRs with a volume of 50 μL was then deposited on the surface of the substrate. At last, the AuNRs substrate was incubated in aqueous graphene oxide dispersion for 8 h. The interaction between GO and AuNRs was induced by the electrostatic force. Because the surface is absorbed by CTAB, AuNRs have lots of sites with positive charges. Meanwhile, because the surface of GO is highly oxygenated and has negative charged carboxyl group, GO exhibits negative charges. Therefore, GO could be absorbed on the surface of AuNRs substrate via electrostatic interaction.

For the measurements of SERS substrates, liquid glucose with various concentrations was prepared and the total concentrations were 10^{-4} M, 10^{-3} M, 10^{-2} M, 10^{-1} M, 1 M respectively. The samples with the same volume of 20 μL were dropped onto the SERS substrates respectively.

3. Results and discussion

3.1. Design strategy for a glucose sensor

The SERS spectrum of D-glucose in the crystalline state is shown in Fig. 1. The wavenumber range has been shown between 400 and 1800 cm^{-1}, containing the available majority of vibrational information. The vibrational bands correspond closely to the report of Soderholm et al. [27]. The wavenumber regions of 1200 cm^{-1}–1500 cm^{-1} have been identified for deformational vibrations of HCH and CH_2OH functionalities. The wavenumber regions of 950 cm^{-1}–1200 cm^{-1} are assigned to the C—O stretching region (with some contribution of C—C stretching modes). The wavenumber regions of 700 cm^{-1}–950 $cm^{-1}$are assigned to side-group deformational vibrations (such as COH, CCH and OCH) containing "fingerprint" or anomeric bands (also C—C contribution). The wavenumber region below 700 cm^{-1} involves skeletal region containing exocyclic (500 cm^{-1}–700 cm^{-1}) and endocyclic (below 500 cm^{-1}) deformations [22,28]. This analysis of band assignments is instructive for our purpose.

The initial measurement protocol for the Raman spectra of liquid glucose was to add the glucose analyte to the SERS-based substrates fabricated by pure AuNRs and GO-AuNRs hybrids respectively. However, none of inherent Raman peaks of glucose could be found out in the spectra. Indeed, the normal Raman scattering cross