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Detection of 6-Mercaptopurine by silver nanowires-coated silicon wafer based on surface-enhanced Raman scattering spectroscopy

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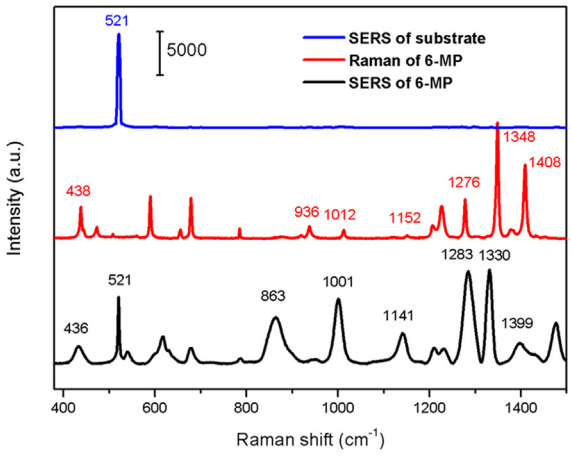
HIGHLIGHTS

- The silver nanowires-coated silicon wafer (AgNWs-Si) was served as SERS substrate for detecting 6-Mercaptopurine (6-MP).
- The prepared AgNWs were characterized by TEM image, UV–vis spectroscopy and X-ray diffraction.
- With the 521 cm^{-1} band of silicon as internal standard, band intensity ratio of 6-MP to silicon, that is I_{1001}/I_{521}, can be used for quantification.
- The detection limit (S/N = 3) is 0.012 $\mu mol\,L^{-1}$ and the linear concentration range is 0.05–3.8 $\mu mol\,L^{-1}$.

GRAPHICAL ABSTRACT



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ABSTRACT

The silver nanowires (AgNWs) were prepared through the method of polyol. The prepared AgNWs were characterized by TEM image, UV–vis spectroscopy and X-ray diffraction (XRD). AgNWs were assembled onto silicon wafer through entropy-driven self-assembly method. The 521 cm^{-1} band of silicon was used as internal standard band. The SERS performance of AgNWs-Si substrate was characterized by using R6G as the probe molecule, and the SERS substrate is employed to detect 6-MP. The linear concentration range of 6-MP is 0.05–3.8 $\mu molL^{-1}$ and the corresponding correlation coefficient is 0.994. The method is satisfactory for detecting 6-MP in two kinds of commercial tablets.

1. Introduction

In recent years, surface enhanced Raman scattering spectroscopy (SERS) is a new and burgeoning analytical method. SERS could provide vibrational spectroscopic fingerprints of chemical and biological materials. SERS is a powerful method for trace detection [1–4], because it can realize fast and nondestructive detection under mild testing conditions with high sensitivity, good selectivity and perfect resolution. SERS has been widely applied in many fields [5–9]. In the aspect of quantitative analysis, SERS shows great potentials. However, it is significant to choose an excellent SERS

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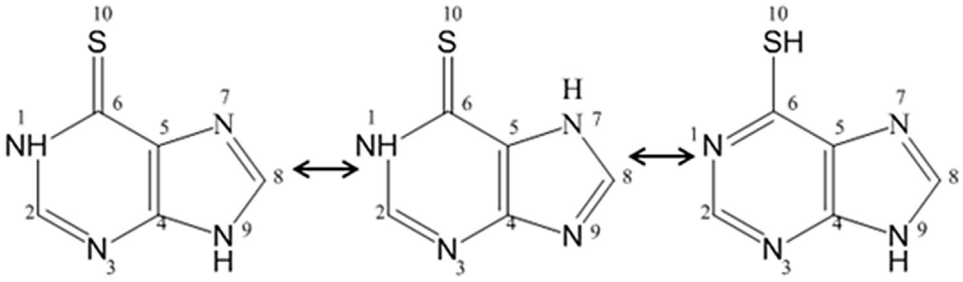

Fig. 1. Structure of 6-Mercaptopurine tautomers studied.

active substrate with a large of uniform and stable "hot" spots to achieve a better SERS performance.

Currently, uniformly oriented SERS active structures have attracted widespread attention for their high enhancement and directional characteristics. Compared with other metal nanostructures, silver nanowires (AgNWs) have great potential applications as probe and device because of their unique optical, electrical and thermal properties [10]. AgNWs could be a better model for studying the dependence of photon-plasmon interactionand electromagnetic scattering properties [11,12]. In addition, the resonance frequencies could be changed by adjusting the length or diameter of AgNWs. Therefore, AgNWs may be an ideal SERS substrate for high aspect ratio, high crystalinity and large surface area [13].

However, like most metal nanoparticles, AgNWs are prone to be uncontrollably and randomly aggregated in solution phase, yielding relatively unstable and irreproducible SERS signals. An entropy-driven assembly strategy was employed to construct uniform and highly ordered silver nanowires-coated silicon wafer (AgNWs-Si) with high activity, stability, and reproducibility as SERS substrate. Entropy is a driving force to prevent aggregation of AgNWs and promote ordering arrangement. Such an ordering occurs only when the concentration of AgNWs suspension is above a critical value to maximize the entropy of the self-patterned structure by minimizing the excluded volume per AgNWs in the arrays [14].

6-Mercaptopurine (6-MP), one of purine derivatives, is characterized with polymorphism of its molecular structure. The biological and pharmacological properties vary with different isomers [15]. According to the experimental and theoretical results, inaqueous solution 6-MP is largely present as Thion N9H, Thion N7H and Thiol N9H (see Fig. 1). Other isomers are difficult to observe due to their low concentrations [16]. 6-MP can be used to interfere with purine metabolism, prevent the synthesis of DNA, thereby inhibit proliferation of tumor cells [17]. 6-MP is mainly used in the treatment of lymphoblastic leukaemia [18,19].

With the increasingly taking of 6-MP, the detection of 6-MP is of great significance for clinical applications. Some methods have been reported for the detection of 6-MP, including high-performance liquid chromatography (HPLC) [20–23], reversed phase high performance liquid chromatography (RP-HPLC) [24], electrochemistry [25], voltammetry [26], spectrophotometry [27,28] and the desorption of electrochemical reduction [29]. However, all these methods show their limitations and demerits, including complicate separation process, frequent calibration, complex sample preparations and high costs. Therefore, it is necessary to develop a simple, sensitive, stable and reliable method for the detection of 6-MP.

In this work, AgNWs were prepared through the method of polyol. The AgNWs-Si substrate was prepared through the entropy-driven self-assembly technique. Azo dye R6G was used as probe molecule in order to assess SERS performance of the AgNWs-Si substrate. For the purpose of accurate quantification, silicon wafer was employed as internal standard for its distinct Raman peak at 521 cm^{-1} [30] and the band intensity ratio of the 6-MP to silicon was used for quantitative analysis. According to the experimental results, the proposed method has some advantages in simplicity, sensitivity and stability and has applied to the analysis of real tablets successfully.

2. Experimental

2.1. Chemicals

Silver nitrate ($AgNO_3$, 99.85%), anhydrous ethylene alcohol (EG), poly (vinylpyrrolidone) (PVP, Mw = 360,000), ferric chloride ($FeCl_3$), acetone (C_3H_6O) and anhydrous ethyl alcohol were purchased from Beijing Ding Guo Biotech. Co., Ltd., China. 6-Mercaptopurine was purchased from Aladdin. Britton–Robinson buffer containing 0.04 mol L^{-1} H_3BO_3, 0.04 mol L^{-1} H_3PO_4 and 0.04 mol L^{-1} CH_3COOH was adjusted to the desired pH with 0.2 mol L^{-1} NaOH. The buffer was used to control the acidity of the sample solution. All glassware was cleaned with freshly prepared aqua regia (HCl/HNO_3, 3/1, v/v) and rinsed thoroughly with ultrapure water prior to use. All chemicals are analytical grade and used without further purification.

2.2. Instruments

The UV–vis absorption spectrum was measured by a Shimadzu UV-3600 spectrometer. The TEM image was obtained with a JEM-2100F Transmission electron microscope operating at an acceleratingvoltage of 80 kV. The surface morphology was recorded on a JEOL JSM-6700 field-emission scanning electron microscope (FE-SEM) operated at 3.0 kV. X-ray diffraction (XRD) was recorded on Siemens D5005. Normal Raman and SERS measurements were performed with a Jobin Yvon/Horiba LabRam Aramis Raman spectrometer with a 633 nm excitation source and the Raman band of a silicon wafer at 521 cm^{-1} was used to calibrate the spectrometer. The typical exposure time for each measurement in this study was 10 s with one time accumulation.

2.3. Preparation of AgNWs

The preparation of AgNWs was carried out according to the reported procedures [31]. Fig. 2 shows the schematic illustration of the preparation of AgNWs. Briefly, 0.2 g of PVP was first added to 25 mL of EG and completely dissolved using magnetic stirring at room temperature. Afterwards, 0.25 g of $AgNO_3$ was added to the PVP solution. Complete dissolution was required to obtain a transparent and uniform solution. Finally, 3.5 g of a $FeCl_3$ salt solution (600 mM in EG) was dumped into the mixture and stirred for one or two minutes. The mixture was then immediately transferred into a reactor preheated at 130 °C to grow AgNWs for 5 h until the reaction