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Rapid and Highly Efficient Detection of Ultra-low Concentration of Penicillin G by Gold Nanoparticles/Porous Silicon SERS Active Substrate

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ABSTRACT

A new method for the detection of ultra-low concentration of penicillin G (PG) antibiotic was innovated using gold nanoparticles/porous silicon (AuNPs/PSi) SERS active substrate. PSi was employed as a template and a reducing agent to deposited aggregated AuNPs with a high density of hot spot regions. A highly enhancement performance and reproducible AuNPs/PSi SERS substrate was fabricated. The AuNPs/PSi SERS substrate was investigated for detection PG drug at different concentrations ranging from 10^{-3} to 10^{-9} M. The results showed that the proposed AuNPs/PSi SERS substrate provide an efficient way for detection the lowest concentration of PG. The adsorption process of the PG drug on the surface of the AuNPs/PSi was investigated, it was found that PG was close to the surface of AuNPs/PSi through the carboxylate group. The enhancement factor (EF) of 5×10^7 and a 4.5% relative standard deviation of reproducibility were obtained at an ultra-low PG concentration of 10^{-9} M. The influence of the pH value on the EF for PG antibiotic under acidic and alkaline conditions (EF_{pH}) was studied, it was shown that the highest EF_{pH} with efficient activity toward PG was obtained at pH = 5.

1. Introduction

Penicillin antibiotic plays an efficient role in prevention and treatment of infectious diseases in human and animals [1,2]. However, the presence of residues of these antibiotic drugs in water is a universal environmental problem [3]. The existence of abuse and irregularity during the antibiotics use causes accumulation of the antibiotic vestiges in animal food [4] and environment [3,5]. There are many factors for the presence of the antibiotic drugs in the sewage, such as most of these antibiotics are excreted by the humans or animals without undergoing metabolism, extensive veterinary use, and the disposal of the unused drugs in the sewage [3]. Thus, the antibiotic drugs can be entered into the environment by many pathways, such as infiltration of the human and animal sewage, leakage from landfills and wastewater from treatment plants as well as farming sewage discharging into the environment before going through the wastewater treatment systems [5]. It is well known that the drugs aren't efficiently eliminated by the conventional wastewater treatments [3]. This brings several harms to both humans and animals due to the frequent occurrence of antibiotics resistance of certain bacteria [3–5]. Since the contaminant can bioaccumulate in aquatic life [3], the detection of the antibiotics is very important in order to prevent the entering of antibiotics into drinking water sources [3,5].

Several ways are used to detect the penicillin drugs, such as performance liquid chromatography, microbiological method, capillary electrophoresis and others [4]. However, practically, these common methods have some shortcomings involving complex sample preparation, professional technical personal and time-consuming procedure [1]. Thus, it is significant to develop a sensitive, low-cost, simple, rapid monitoring and reliable methods for monitoring the traces of antibiotics.

Surface-enhanced Raman scattering (SERS) with metallic nanoparticles is widely used as analytical tool for the molecular detection of explosive, environmental pollutants, drugs and pesticide [6,7]. Most of the studies have used gold or silver colloids to prepare SERS substrate, for example Jiang et al. [4] used assembled silver nanoparticles deposited on a glass substrate to prepare SERS substrates for detecting Penicillin antibiotic. They obtained that the benzylpenicillin sodium (NaBb) is close to the surface of Ag through the carboxylate group, and the detection limit of NaBb can be reduced to 1×10^{-7} mol/L. Pinheiro et al. [3] fabricated new magnetic-plasmonic SERS substrates using magnetic Fe_3O_4 nanosorbents, and they showed that the magnetic-plasmonic nanosorbents are promising systems for PG detection using the SERS effect.

To detect the ultra-low concentration of PG, a high peak of SERS is required. Several factors are contributed to the intensity of Raman signal, like density of hot spots and localized surface plasmon (LSP) [6,8]. These

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factors can be satisfied by employing porous silicon (PSi) as a template for gold nanoparticles (AuNPs) or silver nanoparticles (AgNPs) to prepare AuNPs/PSi or AgNPs/PSi SERS active substrate, since it can increase the density of the hot spots by controlling of the PSi morphology, i.e. by increasing of metal nanoparticles nucleation sites. This leads to aggregated metal nanoparticles, resulting in an increase in the number of the hot spots and consequently obtaining a highly enhancement factor (EF) [7–9].

In this work, a new generation of high efficient with high reproducibility AuNPs/PSi SERS active substrate has been innovated for detecting the ultra-low PG antibiotic concentrations ranging from 10^{-3} to 10^{-9} M.

2. Experimental Section

2.1. Materials

Chloroauric acid ($HAuCl_4$, 99.9%), PG ($C_{16}H_{17}N_2NaO_4S$, 96%) and ethanol (C_2H_5OH, 99.98%) were brought from Sigma-Aldrich, Germany. Hydrofluoric acid (HF, 40%) was obtained from HIMEDIA, India.

2.2. Porous Silicon Substrate Preparation

PSi substrates were prepared at room temperature by photoelectrochemical etching using CW diode laser of 630 nm wavelength and laser intensity of 30 mW/cm^2. A single-side polished (100) n-type silicon wafer with a resistivity of 10 Ω·cm was diced 1.5 × 1.5 cm^2 square, cleaned in a (1:10) mixture of HF and ethanol for 10 min for removing the native oxide layer found on the surface of silicon wafer and then washed with ethanol. The etching process was carried out using Teflon cell and counter electrodes; platinum ring is used as cathode electrode, and silicon wafer acts as anode electrode, as shown in Fig. 1. PSi substrate was prepared at etching time of 8 min, 20 mA/cm^2 current density, etching electrolyte solution composed of a mixture of HF/ethanol = 1:1 and illuminated area of the silicon surface of 0.66 cm^2.

2.3. Preparation of Gold Nanoparticles/Porous Silicon SERS Active Substrate

8×10^{-3} g of $HAuCl_4$ was dissolved in a mixture of HF and deionized water with volume of about 22 mL, resulting in the 10^{-3} M of $HAuCl_4$ diluted in 3 M of HF. The PSi substrates were immersed into the aqueous solution of $HAuCl_4$ and HF for 2 min at room temperature, and then the gold reduction process occurred according to the following equations [10]:

$$Si + 6HF \rightarrow H_2SiF_6 + 4H^+ + 4e^- \quad (1)$$

$$Au^{+3} + 3e^- \rightarrow Au \quad (2)$$

By these reactions, the gold nuclei formed on the PSi surface. And, because of the very fast gold growth rate, the Au aggregated on the surface of the PSi at very short dipping time.

3.563 g of PG sodium were dissolved in 100 mL pure water, resulting in the 0.1 M standard stock solution, this solution was successively diluted by the distilled water in order to prepare the aqueous solutions of PG with different concentrations of 1×10^{-2}, 1×10^{-3}, 1×10^{-5}, 1×10^{-7} and 1×10^{-9} M. And, the 0.01 M PG solution was adjusted to different pH values by NaOH or HCl. The prepared AuNPs/PSi immersed in the aqueous solution of PG with different concentrations and different pH values for 10 h at room temperature in order to investigate the AuNPs/PSi SERS active substrate.

2.4. Characterization

The morphology of the bare PSi and AuNPs deposited on the PSi was characterized using MIRA3 TESCAN field-emission scanning electron microscope (FE-SEM). The FE-SEM images of the samples were analyzed by using software program image J, version 7. Raman and SERS spectra were measured by APUS TESCAN Raman microscope, using 532 nm of DPSS ND:YAG (CW) laser for excitation, the laser excitation power and integration time were 10 mW and 3 s, respectively.

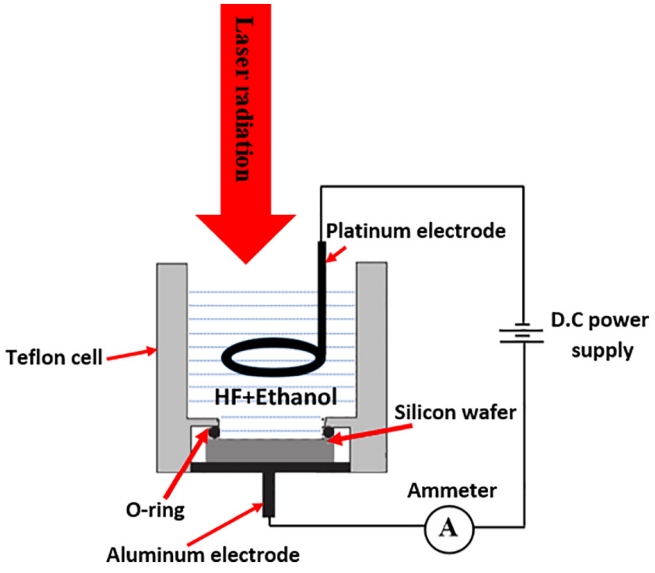

Fig. 1. Experimental setup of photoelectrochemical etching process.

3. Results and Discussion

3.1. Characterization of PSi Substrate

Fig. 2(a, b, c) shows the FE-SEM of the surface morphology of the PSi used as substrate for deposited AuNPs, cross-sectional FE-SEM image of PSi substrate and the statistical distribution of pore sizes of PSi substrate, respectively. The porosity and layer thickness of PSi substrate were determined as 55% and 2.5 μm, respectively. In the top view of the PSi substrate shown in Fig. 2(a), the macropores are in the form of quasi-ellipse, drop and quasi-spherical. These pores have sizes ranges from 0.75 μm to 3.25 μm, as shown in the Fig. 2(c). These different forms of pores are due to the silicon dissolution process as a result of absorption Gaussian shape of laser beam [11].

3.2. Characterization of AuNPs/PSi SERS Active Substrate

PSi acts as a source of gold nucleation sites required for the Au ions reduction process [10]. Surface morphology of the AuNPs deposited on the PSi substrate is demonstrated in Fig. 3(a, b), it presents that the growth of the AuNPs follows the morphology of the PSi. Fig. 3(a) views that the islands of AuNPs are formed, each island consists of aggregates of spherical AuNPs, and the average diameter of AuNPs ranges from 50 nm with a maximum percentage of 90.6% to 350 nm, as shown in Fig. 4a. The aggregates yield a dense of vacancies (nanogaps) among the pores (hot spots), the sizes of the nanogaps range from 5 nm to 85 nm and the peak nanogap size of 5 nm has a higher percentage of 41.4%, as shown in Fig. 4b. This morphology of the AuNPs is due to the randomly distribution of the density nucleation sites (Si—H bonds), since these sites are very necessary for metal ions reduction.

From the cross-sectional FE-SEM image of AuNPs/PSi SERS active substrate (Fig. 3b), it can be seen that the AuNPs covers the surface of the PSi, while the inner surface of pore walls is free of AuNPs, this is due to that the reduction of AuNPs on the surface of the PSi is very