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Ag/SiO_2 surface-enhanced Raman scattering substrate detection in plasticizer

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Abstract

In this study, we demonstrated a simple process to fabricate a high-performance surface-enhanced Raman scattering (SERS) substrate. We deposited the self-assembling monodispersive SiO_2 spheres on the silicon wafer, and Ag film was coated on it to obtain the Ag/SiO_2 SERS substrate. The Ag/SiO_2 SERS substrates were applied to detect the three kinds of plasticizer with different concentration, including DEHP (bis(2-ethylhexyl)phthalate), BBP (benzyl butyl phthalate) and DBP (dibutyl phthalate). The enhancement of SERS behavior caused by surface plasmon resonance can be observed using the Ag/SiO_2 SERS substrates. Especially, the DEHP concertation can be detected at 40 ppm. The developed Ag/SiO_2 SERS substrates with low cost, high sensitivity, and quick response displays a potential for the design and fabrication of functional sensors to identify the harmful plasticizers which plastic products release in daily life.

1. Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy has widely utilized to detect the chemical, drugs or contaminations.[1,2] Since the technique for fabrication of nanoscale materials dramatically advanced in last two decade, the periodic metallic structure can be fabricated simply by chemical synthesis or physical process in appropriate condition. The thing has been applied in SERS spectroscopy to extend the applications of SERS spectroscopy since the intensity of SERS signal depends on the feature of nanostructure, including shape, size and distribution. [3,4] Thus, the SERS signals will be enhanced by a strong electromagnetic field owing to localized surface plasmon resonances combined with the vibration intensities of the substances near the metal nanostructures. The limitation of its detection can be increased as well.

The plasticizer is an additive and generally used to improve the flexibility, plasticity or viscosity of the polymer. The phthalate ester, such as dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and bis(2-ethylhexyl) phthalate (DEHP) are the most common employed. However, these plasticizers might release from plastic product due to an unstable temperature in use, long-term usage and critical situation of pH value. Once plasticizers were touched and further absorb by human body, some of them are usually endocrine disruptors and directly affect our health as well as cause severe diseases like cancer. Thus, the detection of plasticizers in our daily life should be considered.

In this study, we propose a fast-detection and high-sensitive SERS substrate built by a monolayer of silver-coated SiO_2 sphere on silicon wafer. The as-prepared SERS substrate was applied to enhance the intensity of Raman scattering signal of plasticizers, involving DEHP (bis(2-ethylhexyl)phthalate), BBP (benzyl butyl phthalate) and DBP (dibutyl phthalate). The spectroscopic behavior and enhancement of Raman scattering signal have been studied systemically.

2. Experimental Section

According to our previous work [5], we adopted the sol-gel method to synthesized amorphous monodispersive SiO_2 spheres. Tetraethylorthosilicate (TEOS, Acros, 98%) was dissolved in in ethanol, then stirred at 30 °C for 30 min. The TEOS solution was mixed with 20 mL of ammonia solution (28-30 wt% solution of NH_3 in H_2O), and reacted for 2 h. Finally, the 380 nm SiO_2 spheres was obtained. To isolate the SiO_2 sphere from solution, the SiO_2 colloid solution was centrifuged and washed with ethanol. After three times of washing procedure, the SiO_2 spheres were dried at 100 °C for 12 h.

The 2.0 wt% 380 nm SiO_2 spheres were dispersed uniformly in 95 % ethanol aqueous by ultrasonic treatment. The monolayer structure consisted of amorphous monodispersive spherical silica particles was established on the silicon wafer by a spin coating method to prepare the SiO_2 sphere array substrate, and it was dried at 80 °C for 24.0 h. Then, a 150 nm silver layer was deposited on the SiO_2 sphere array substrate by a thermal evaporator. Finally, the Ag-coated SiO_2 (Ag/SiO_2) SERS substrate was obtained.

The plasticizers were detected in this study, including BBP (99.9%), DBP (99.9%), and DEHP (99.9%). All the plasticizers mention above with different concentration were spin coated on Ag/SiO_2 SERS substrate at 5000 rpm. To measure the enhancement of signal in Raman scattering spectra, these SERS substrates with/without plasticizers were placed on the piezoelectric stage of the micro-Raman spectrometer (WiTec, Alpha300S) and excited by a 632.8 nm He-Ne laser (25mW).

3. Results and Discussion

The SERS substrate consisted of Ag-coated SiO_2 spheres on silicon wafer was obtain after the process parameter optimization. The array of 380nm SiO_2 spheres was coated at spin rate of 2000 rpm. The thickness of Ag monolayer which deposited by thermal evaporation is 150 nm. The chemical structures of three kinds of plasticizer are shown in **Figure 1 (a-c)**. Raman spectra of BBP, DBP, and DEHP are shown in **Figure 1 (d-e)**. The compounds show the similar Raman spectra due to the main structure containing phthalate and C=O bonding.

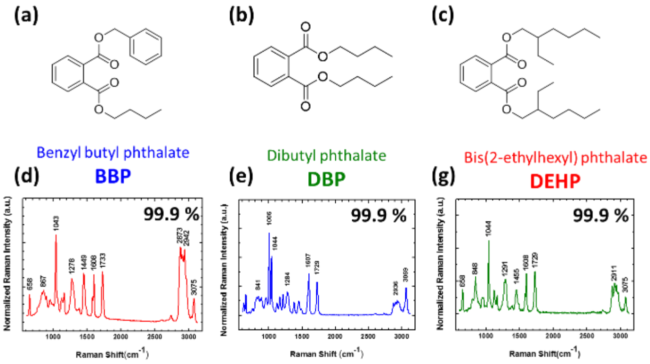

Fig. 1 Chemical structures and Raman spectra of **(a,d)** BBP, **(b,e)** DBP, and **(c,g)** DEHP.

To discuss the enhancement of SERS signal of plasticizers, we chose the characteristic peak located at 1043 cm^{-1} which indicates the aromatic ring breathing mode to define the enhancement factor (***EF***) by following formula: $EF = I_{SERS\ Substrate}/I_{Glass\ Slide}$.[5] The ***EF*** value and corresponding Raman spectra of DEHP on different substrate are shown in **Figure 2(a-c)**. The ***EF*** value of Ag/SiO_2 SERS substrate can achieve to ~2×10^4 fold. We further find out the relation between DEHP concentrations and Raman intensity as shown in **Figure 2(d)**. As the concentration below 1000 ppm, the enhancement of Raman intensity at 1043 cm^{-1} versus concentration belong to a linear trend. While concentration is higher than 1000 ppm, it becomes an exponential trend.

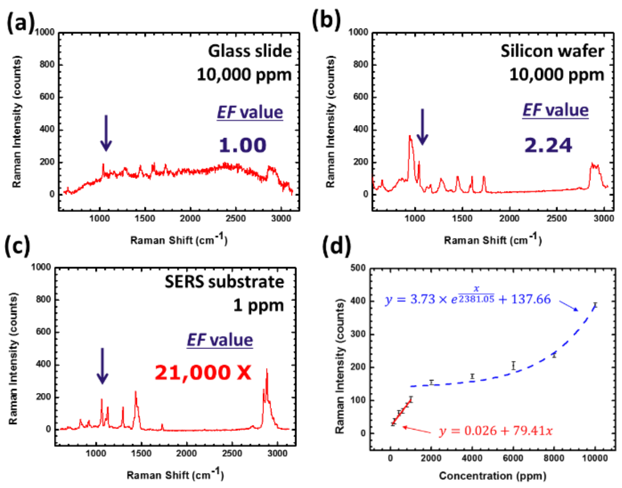

Fig. 2 Raman spectra of DEHP for enhancement factor on different substrates.

In order to obtain the detection limit of DEHP on SERS substrate, Raman spectra of DEHP with different concentration were measured as shown in **Figure 3**. The signal of C=O bonding at 1703 cm^{-1} was chosen for identifying the existence of DEHP. These spectra indicated that the intensity of DEHP signal decreased as concentration was diluted. However, DEHP at 40 ppm was able to be detected. It seems to prove that the detection limit for DEHP using our SERS substrate can reach 40 ppm for DEHP.

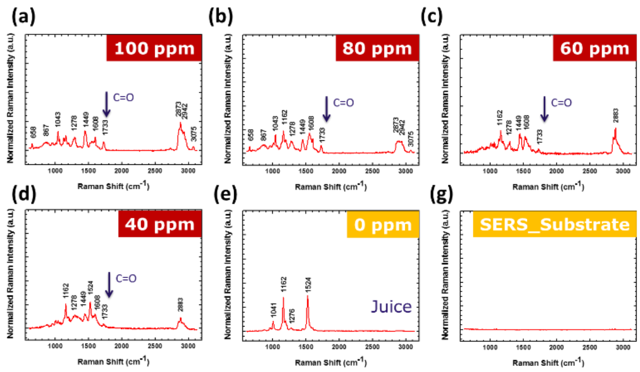

Fig. 3 Raman spectra of DEHP with different concentration.

4. Conclusions

The Ag-coated SiO_2 sphere on silicon SERS substrate is fabricated by a spin coating method followed by thermal evaporation process. A 2×10^4 fold enhancement of Raman spectra is observed in this substrate prepared with 380 nm SiO_2 spheres self-assembled on a silicon wafer and coated with a 150 nm Ag layer. Also, the detection limit of DEHP on the developed Ag/SiO_2 SERS substrate can reach 40 ppm.

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