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Density functional theory and surface-enhanced Raman spectroscopy studies on endocrine-disrupting chemical, dimethyl phthalate

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ABSTRACT

A method to monitor endocrine-disrupting chemical contamination phthalate esters (PAEs) by surface-enhanced Raman scattering (SERS) spectroscopy has been investigated. The molecular structure and assignment of the vibrations of dimethyl phthalate (DMP), forming short chains in PAEs, has been studied by density functional theory (DFT) calculations. The structure of DMP with the dihedral angles of 1C-6C-11C-13O and 4C-5C-18C-20O being 133.78° and −24.00°, respectively, has the lowest energy. Theoretical vibrational frequencies using B3LYP/6-31 + G(d) (after scaling) show excellent agreement with the experimental normal Raman spectrum. In the region 200–1800 cm^{-1}, SERS spectra of DMP were measured using ordered gold nanosubstrates. All except the weak signals in the normal Raman spectrum of DMP were successfully enhanced. These results demonstrate that SERS technology could be developed as a rapid method for screening of DMP.

1. Introduction

Phthalate esters (PAEs) are a kind of endocrine-disrupting chemical which have toxic effects on estrogenic substances. PAEs are the dialkyl or alkyl aryl esters of phthalic acid, including an o-phenylene group and two carboxylate groups. PAEs have a wide range of applications and are constantly being released into the environment [1–7].

Currently, there are many techniques for the measurement of PAEs. Combined with some pretreatment techniques, detection limits for GC-MS [4], GC-FID [5–8], HPLC [3,9,10] for the determination of PAEs at the ppb level can be achieved. However, these methods involve time-consuming and labor-intensive procedures. It is of critical importance to develop simpler, quicker, cost-effective, as well as sensitive methods for screening large amounts of consumer plastic products for commonly used PAEs.

Surface-enhanced Raman scattering (SERS) spectroscopy, a novel and ultra-sensitive vibrational spectroscopic method, has developed greatly over recent years. The fingerprint-like Raman spectrum is able to provide overall and specific information on various chemical and biochemical components. However, signals from normal Raman spectroscopy are very weak because only one photon in a million will scatter inelastically (Raman shift). In SERS, when target molecules are attached to metallic nano-structures (typically Au, Ag, Cu, Pt, or Pd), Raman signals can be significantly enhanced millions of times in the highly localized optical fields of these structures due to “electromagnetic field enhancement” and “chemical or electronic enhancement” of the signals [11]. SERS is capable of providing significant enhancement of band intensities compared to normal Raman spectroscopy and has a great potential for rapid screening and detection of trace quantities of targets species.

In order to apply SERS to the screening of PAEs, there are two main problems to be solved, assignment of bands and enhancement of signals. Firstly, further studies concerning the assignment of specific vibrations to the Raman spectra of PAEs are still necessary. In previous papers, Fourier transform (FT) Raman spectroscopy was carried out on a range of 22 PAE plasticizers [12]. It was found that PAEs, as a group, can be identified by a set of six characteristic Raman bands (3074, 1726, 1600, 1580, 1040, and 652 cm^{-1}). Nyquist [13] had studied the characteristic bands of the o-phenylene group of PAEs. In his research, assignments were obtained indirectly by comparison with o-dichlorobenzene. In our research, assignment of the Raman spectrum of dimethyl phthalate (DMP), the PAE with the shortest chains, would be carried out using DFT calculations followed by a comparison with the

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experimental Raman spectrum. Secondly, our research aims to explore the use of SERS as a detection method for DMP. However, PAEs as esters are not easy to get close to surface of metallic nano-structures because that they are hydrophobic and do not form a strong bond to metallic nano-structures. We have investigated the potential for detection of DMP, forming short chains in PAEs, by SERS in this research.

The purpose of this paper is to report the assignment of DMP vibrations to the Raman spectrum and the results of SERS spectroscopy of DMP on the Au nano-substrate.

2. Materials and methods

2.1. Experimental

2.1.1. Sample and instrument

DMP (>99%, AR agent) and dichloromethane (CH_2Cl_2, > 99.5%, AR agent) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

A Raman confocal microscope LabRAM HR 800 (HORIBA Jobin Yvon Inc. France) was used for the normal Raman and SERS measurements.

2.1.2. Software and data analyzer

DFT calculations were performed with Gaussian 03 software [14]. The Omnic 6 Professional software suite (Thermo Electron Corporation, UK) was normally used to acquire, process, analyze and manage the FT-IR or Raman data and also analyze the theoretical and experimental spectral data. Sigmaplot for Windows v 11.0 (Systat Software Inc. California, USA) was used to create 3D graphs and to realize data visualization. OriginPro 8.1 (Originlab Inc. Northampton, USA) was used to pre-process the spectra, including smoothing and subtraction of baselines. VEDA 4 program [15] was used to analyze the PED (potential energy distribution) values.

2.1.3. SERS-active substrates

Gold SERS-active substrates (Klarite^{TM}, Renishaw Diagnostics Ltd. Hampshire, UK) were used in this study. Klarite^{TM} devices were fabricated on silicon wafers coated with 100 nm gold nanoparticles. A 6 mm × 10 mm chip consisted of a 4 mm × 4 mm patterned SERS-active area with inverted pyramidal subunits, with ~1.8 μm openings between the depressions and separated by ~0.4 μm bridges from each other (Fig. 1). The sharp edges of the pyramidal subunits, or “hot spots” of this gold metal surface can produce surface plasmon resonances induced by the incident excitation laser, generating an enormously enhanced electromagnetic field effect on signals generated within the highly localized optical fields originating in the metallic structures [16].

2.1.4. Normal Raman and SERS spectroscopy

Normal Raman and SERS spectroscopy of DMP were conducted using a Raman confocal microscope LabRAM HR 800. Normal Raman spectroscopy of DMP was obtained from a drop of sample in pure form on the metal plate. The method of detecting DMP by SERS is as follows. Two microliters of 10 ppm DMP dissolved in dichloromethane were dropped on to the gold SERS-active substrates and dried naturally in air (Fig. 1). When the analyte droplet was almost free of solvent, the Raman confocal microscope LabRAM HR 800 with a 785 nm laser as the excitation light source was used to obtain the SERS spectrum. A 50× objective was used with a $30 \times 30\,\mu m^2$ laser area, 15 mW laser power and an integration time of 20 s. The undamped power on the sample is about 6 mW, which is low enough to avoid heating the substrate.

2.2. Calculations

Most of the DFT calculations of the structure and vibration frequencies of DMP were performed in Gaussian 03 using the B3LYP and the 6-31G(d) and 6-31 + G(d) basis sets [17].

The conformer with C_{2v} symmetry of DMP was used as the input geometry for the Gaussian 03 process and the 6-31G(d) basis set to perform geometry optimization and calculate vibration frequencies. It yields an imaginary frequency, which means that there are some geometric distortions for which the energy is lower than for the current structure (indicating a more stable structure). Two methods were adopted to find the minimum energy structure at the 6-31G(d) basis level. One is to distort the molecule along the

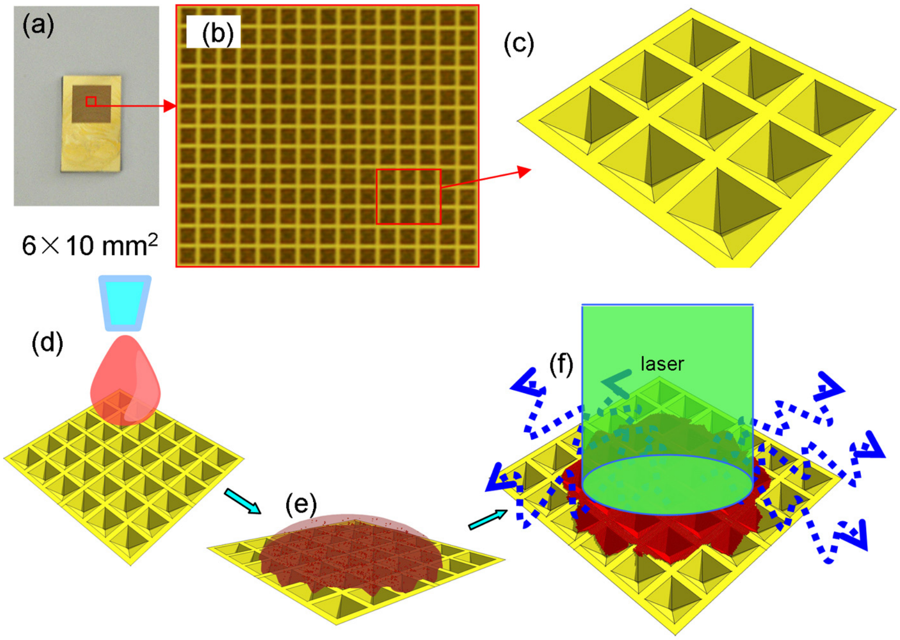

Fig. 1. The structure of the substrate and a schematic diagram of the detection of DMP by SERS: (a) photo, (b) optical image (×100 objective), and (c) 3D-sketch of ordered Au nano-substrate; (d–f) schematic diagrams of detection of DMP by SERS coupled with Au nano-substrate.