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Adsorption of N-(1-(2-bromophenyl)-2-(2-nitrophenyl)ethyl)-4-methylbenzenesulfonamide on silver nanoparticles: SERS investigation

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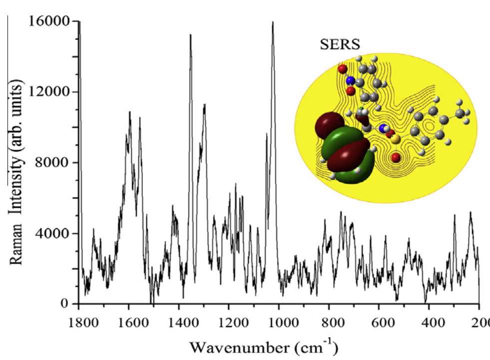
HIGHLIGHTS

- Silver nanoparticles were synthesized using combustion method.
- It is fcc crystalline structure with rod like shape.
- Spectral analysis reveals that BrS is adsorbed on the silver surface by tilted orientation.
- Theoretical calculations performed to study the vibrational features of BrS.

GRAPHICAL ABSTRACT



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ABSTRACT

SERS provides essential data regarding the interaction of molecules in drugs with DNA. In the present study silver nanoparticles were synthesized using a solution combustion method with urea as fuel. The prepared silver nanoparticles are rod like structure. Surface-enhanced Raman scattering (SERS) of N-(1-2-bromophenyl)-2-(2-nitrophenyl)ethyl)-4-methylbenzenesulfonamide (BrS) adsorbed on the silver nanoparticle was studied. The nRs and Raman spectral analysis reveal that the BrS adsorbed tilted orientation on the silver surface. Vibrational modes of nRs along with HF calculations are also performed to study the HOMO and LUMO behavior and vibrational features of BrS.

Introduction

SERS is the most sensitive techniques available to surface science. Its capability of delivering specific chemical identification

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and to couple this with a wide range of instruments, has led to its continuing use in both new and traditional areas of surface science. These are of prime importance to both fundamental research and to a range of industrial fields related to surface oxidation, adhesion, corrosion and catalytic processes and in advanced materials, biology and sensor research. This technique is applied in detection of DNA and RNA [1]. The surface enhancement is highly surface selective so the technique is sensitive to molecules adsorbed at, or very close to, the surface and it thus discriminates against molecules in the bulk solution. SERS gives information about the molecular structure of the adsorbate, its orientation at the surface [2,3] and the dependence of orientation and coverage of applied potential. The Raman cross section for water is low so that SERS can be easily used to study electrodes in aqueous solution.

The intensity enhancement of molecules adsorbed on the substrate mostly lies in the adsorption behavior of the molecules. One of the most important factors that could affect the molecules' adsorption behavior is the surfaces characteristic of the SERS-active substrates. Because of differences in the adsorption configuration the SERS spectra would have more or less differences in the same molecules adsorbed on different substrates [4,5]. Another important factor that could affect the molecules' adsorption behavior is the surface configuration of the molecules themselves. For allotropes, which are composed of the same elements, but whose configurations are not same, the adsorption behavior on the same substrate is not the same either.

Sulfonamides commonly named as Sulfa drugs are the medicines capable of controlling the bacterial infections [6]. The sulfonamide derivatives are known for their numerous pharmacological activities, antibacterial, antitumor, insulin-release stimulation and antithyroid properties. The phenolic azo- dyes derived from the sulfonamides have the therapeutic potentialities and special mode of action against the acute bacterial infections [7]. Some benzenesulfonamides are evaluated for their *in vitro* antitumor activity [8].

Benzenesulfonamide derivatives find wide applications in the synthesis of pharmaceutical products which have bactericidal properties and of various bioactive agents, artificial fibers, dyes, and plasticizers, and the synthesis of high molecular weight substances. Sulfonamides are chemotherapeutics most commonly used in veterinary practices because of their inexpensiveness and wide spectrum antimicrobial activity [9]. Sulfonamides represent one of the classical chemotypes associated with potent CA inhibition [10]. The chemistry of sulfonamides has been known as synthons in the preparation of various valuable biologically active compounds [11] used as an antibacterial [12], protease inhibitor [13], diuretic [14], antitumor [15], and hypoglycemic [16].

The present work deals with the orientation of BrS on the silver nanoparticles by Raman analysis of BrS and BrS on silver nanoparticles.

Experimental

Reagents

Silver nitrate, urea, DMF, 2-nitrobenzyl chloride, N-tosylimine, tetrakis(dimethylamino)ethylene were obtained from Sigma Aldrich chemicals and were used without further purifications. All glasswares were properly washed with distilled water and dried in hot air oven before use.

Preparation of silver nanoparticles

In the present work silver nanoparticles were prepared by a combustion method using urea as fuel as described in literature [17].

Synthesis of N-(1-(2-bromophenyl)-2-(2-nitrophenyl)ethyl)-4-methylbenzenesulfonamide

Into a two-necked flask equipped with a drying tube (silica gel) and a nitrogen inlet was added 15 mL of an anhydrous DMF solution of 2- nitrobenzyl chloride (0.5 g, 2.92 mmol) and N-tosylimine (3.21 mmol). The solution was cooled to −20 °C, maintained at this temperature for 30 min and then tetrakis(dimethylamino)ethylene (TDAE) (1 equiv.) was added dropwise (via a syringe). The solution was vigorously stirred at −20 °C for 1 h and then maintained at room temperature for 2 h. After this time, TLC analysis (CH_2Cl_2) clearly showed the total consumption of starting the product. The solution was filtered (to remove the octamethyl-oxamidinium dichloride) and hydrolyzed with H_2O (100 ml). The aqueous solution was extracted with chloroform (3 × 50 ml), the combined organic layers washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent, the white solid was recovered by diethyl ether and filtered yielding the bromo sulphonamide (BrS) (N-(1-(2-bromophenyl)-2-(2-nitrophenyl)ethyl)-4-methylbenzenesulfonamide) (Fig. 1).

Characterization techniques

The crystal structure and crystallite size of the sample were characterized by X-ray diffraction. The XRD patterns were collected from PANalytical X-ray diffractometer using Cu Ka radiation (k = 1.5406 Å) and the crystallite size was calculated at particular peaks with low and high intensity in the range 2θ ($20° \leqslant 2\theta \leqslant 80°$) as shown in Fig. 2. The field emission scanning electron microscopy analyzer (Advanced Micro Analysis solution AMETEK) was used (Fig. 3) for SEM analysis. Both Raman and SERS spectral measurements were obtained by a micro Raman system from Jobin Yvon Horiba LABRAM-HR with He—Ne 633 nm as excitation wavelength. The spectral resolution was 1 cm^{-1} and dispersive geometry was employed.

Results and discussion

XRD studies of silver nanoparticles

The XRD pattern of prepared Ag NPs was compared and interpreted with standard data (JCPDS ICDD 04-0783). In the XRD pattern (Fig. 2), four diffraction peaks were observed at 2θ = 38.88°, 44.15°, 64.31°, 77.27° which correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) Bragg's reflections of the face centered cubic (fcc) structure of metallic silver respectively. As per the Debye–Scherrer formula the calculated average particle size is found in the range of 67 nm.

SEM analysis of silver nanoparticles

SEM image of the prepared silver nanoparticles is shown in Fig. 3, which are rod like shape. Generally the size and the shape

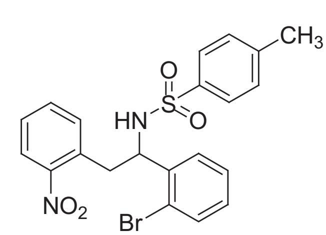

Fig. 1. Structure of N-(1-(2-bromophenyl)-2-(2-nitrophenyl)ethyl)-4-methylbenzenesulfonamide (BrS).