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Silver nanoparticles for detection of methimazole by surface-enhanced Raman spectroscopy

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ABSTRACT

An efficient method was developed for quantitative detection of methimazole using surface enhanced Raman spectroscopy (SERS). Silver nanoparticles (AgNPs) were prepared by a reduction method and designed as SERS substrates for the detection of methimazole, which is of medicinal importance. The morphology and the structure of the nanoparticles were characterized using a transmission electron microscope, a UV–vis spectroscopy, a Fourier transformed infrared spectroscopy and a Raman spectroscopy. The average size of the AgNPs was 60 nm. The UV–vis spectrum showed a characteristic maximum absorbance at around 420 nm for AgNPs. The adsorption behavior of methimazole on the AgNPs substrates was investigated by SERS and density functional theory (DFT) calculations. SERS experimental and theoretical results imply that a chemical interaction is considered between the NPs and methimazole. SERS experiments indicated an enhancement in the bands, which was utilized to develop a linear correlation between the methimazole concentrations and SERS signal intensity.

1. Introduction

Methimazole (MTZ), known as 1-methylimidazole-2-thiol, is used in thyroid hormone biosynthesis by preventing the organification of iodide in the thyroid [1]. MTZ as an antithyroid drug is used for the treatment of hyperthyroidism, and in Graves' disease [2]. MTZ is one of the azole derivatives that extensively used in the field of inhibition of metals from corrosion [3], Fig. 1. Due to its presence in a wide range of pharmaceutical formulations and body fluids, the determination of MTZ is a significant area of interest. MTZ has been investigated by various methods including; electrochemical techniques, high-performance liquid chromatography, gas chromatography, fluorescence probe method, infrared and Raman spectroscopies [4,5]. However, these techniques required additional derivatization procedure and more time-consuming [6].

Surface Enhanced Raman Scattering (SERS), an advanced method of Raman technique, has become a center of interest for molecular characterization. SERS is a promising alternative method for the analysis of the biological and pharmaceutical compounds, due to its high-sensitivity, and non-destructive nature [7]. Spectral intensities in SERS are enhanced by a high factor, for example, 10^8–10^{10} can be obtained for target molecules adsorbed on the substrate surface compared to traditional Raman spectroscopy [8]. This enhancement is arising from the two main factors, electromagnetic and chemical charge transfer enhancements [9–11].

Several studies were reported for the investigation of pharmaceutical compounds in aqueous solution, using metal nanoparticles [12–14]. Due to attractive physicochemical properties, surface plasmon resonance, silver, and gold nanoparticles have been used as substrates for the structural investigation of some drugs such as mefenorex, pentylenetetrazole, L-amphetamine, pemoline, MTZ and cyclodextrin [15,16]. The molecular properties of the MTZ have been reported using FTIR, Raman, and SERS [17,18]. However, up to the best of our knowledge, there is no studies reported a quantitative method for the determination of MTZ by SERS.

The aim and motivation of this work was to develop a sensitive method without the need for sample preparation for the detection of methimazole in medical formulations using SERS with substrates of silver nanoparticles (AgNPs). DFT calculations were carried out for the bands assignment. The developed method was evaluated for the determination of MTZ in pharmaceutical forms.

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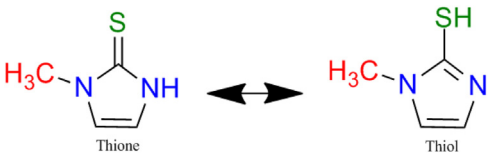

Fig. 1. Structures of Methimazole Forms.

2. Experimental

2.1. Chemicals and materials

Methimazole, 1-Methyl-2-imidazolethiol, analytical standard, ≥99% purity, the CAS number 60560, were purchased from Sigma-Aldrich. Trisodium citrate dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$, 98%) **(cat number is S-279, product number 78479**) was purchased from Fisher Scientific Company in U.S.A. Silver nitrate ($AgNO_3$, 99.8%), product number 30087, was purchased from BDH-Chemicals Ltd Poole England. Potassium bromide (KBr, ≥99%) was purchased from Sigma-Aldrich and used for making KBr pellets with silver nanoparticles for obtaining IR spectrum. Solutions were prepared with ultrapure water obtained from a water purification system (Ultra Clear™ Lab Water Systems, Siemens Water Technologies USA).

2.2. Synthesis

AgNPs were prepared by the following procedure. First, a solution of 0.1 M silver nitrate was prepared by dissolving $AgNO_3$ in 250 ml of deionized water, followed by heating the solution at 90 °C. Then, 10 ml of 0.5% solution of trisodium citrate dihydrate was added at a rate 1 drop/sec to the solution under stirring. After adding 5 ml, the solution color turned yellow. The solution was kept under boiling for one hour, the color of the solution changed to greenish yellow.

2.3. Characterization

The nanomaterials were characterized by various methods including; TEM technique to determine the particle size, morphology, and particle distributions of nanomaterials. The TEM images were taken using the JEM −2100F Field Emission Electron Microscope, JEOL- USA, at 200 kV acceleration voltage. The UV–vis spectra of the NPs were recorded on a genesis 10S UV–vis spectrophotometer (Thermo Scientific), using standard quartz cuvette at room temperature between 200 and 700 nm ranges. The colloid samples were prepared by dilution the stock solution 4x with distilled water.

2.4. Surface-enhanced Raman spectroscopy (SERS)

The SERS spectra of MTZ were obtained by using Raman spectroscopy system Lab Ram HP Evolution Raman spectrometer equipped with an internal He-Ne 17 mW laser at a 633 nm excitation wavelength. The laser was used on 10% power at the sample. SERS samples were prepared by using a 3: 1 volume ratio of the MTZ solutions to the colloid. A 10x objective was used for focusing the laser beam to the solution. The data acquisition time was 30 s with one accumulation for collection each SERS spectra. A cuvette with dimensions of 1 cm radius, 2 cm height was used as a sample cell for the Raman spectra. The SERS spectra were obtained in the range from 400 to 2000 cm^{-1}. The solid sample was prepared by adding a small amount of the MTZ solid on a glass slide for obtaining the spectrum using laser λ 633 nm, the acquisition time of 30 sec and objective 10x.

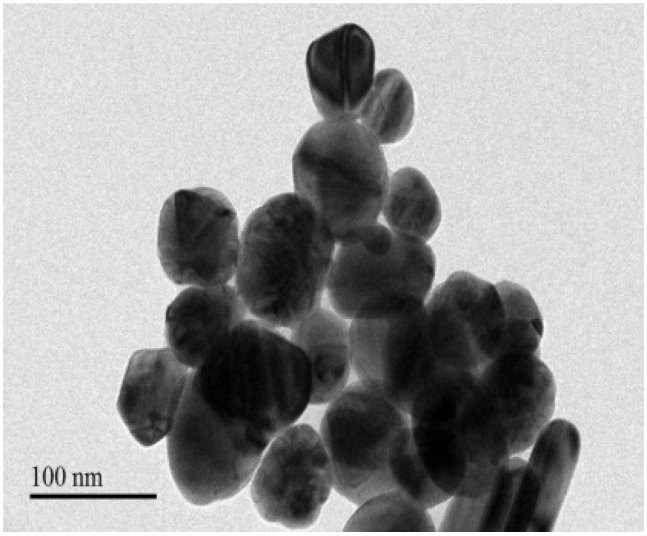

Fig. 2. The typical TEM images of AgNPs.

2.5. Computational details

The ab initio and DFT calculations were employed to assign the bands used for the detection of MTZ compound. The GAUSSIAN 09 program running on an IBM RS/6000 model S85 Unix server was used to carry out the DFT/B3LYP calculations. The 6–311++G (d, p) triple basis set was employed to optimize the structure of the compound. The Gauss −View program was used to collect the vibrational assignment, and Raman line activity of MTZ compound.

3. Results and dissections

3.1. Characterization

Fig. 2 shows the TEM image of AgNPs, which indicates uniform shape and well-dispersed particles with the average size of about ~60 nm as estimated by TEM scale. The Ultraviolet −visible (UV–vis) absorption spectrum AgNPs are shown in Fig. 3. The absorption characteristic maximum of AgNPs showed surface plasmon resonance band at 421 nm. The Raman spectra of the nanoparticles were given in Fig. 4. In the case of silver, no clear Raman bands were observed in the 200 cm^{-1} to 3000 cm^{-1} range of the spectra. However, it can be observed the spectra show a weak broadband 1380–1420 cm^{-1} and a very small peak at 926 cm^{-1} in silver.

3.2. Vibrational assignments

3.2.1. Vibrational assignment theoretically by DFT

The calculated wavenumbers were scaled using the scaling factor 0.961 for frequency region ≥2000 cm^{-1}, and scaling factor 0.985 for frequency region >2000 cm^{-1} [19–21]. The calculated CH stretching vibrational modes for MTZ is assigned at 3162, 3142, 3022, 2998, 2929 cm^{-1} which is corresponding to ν (C7-H), ν (C6-H), ν (C5-H11), ν (C5-H12), and ν (C5-H13). The NH stretching vibrational mode can be assigned at 3531 cm^{-1} in theoretical spectra. The band at 1588 cm^{-1} is corresponding to C=C stretching vibration mode. The C—S stretching vibrational modes were predicted to have four vibrational frequencies, at 1473, 1459, 1415 and at 1159 cm^{-1}. The peak at 238 cm^{-1} is attributed to C—S wag mode. The N-H in plane bending was assigned at three different frequencies. The NH (CH) mode (out the plane, and in plane) vibration was predicted at three different frequencies, the ring bend (in plane) was predicted three different vibrations, and at one