

Surface-enhanced raman scattering (SERS) spectroscopy for trace level detection of chlorogenic acid

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ABSTRACT

Surface-enhanced Raman scattering (SERS) spectroscopy is one of the most sensitive tools for the detection of molecules adsorbed on nanometer-sized roughened metal surfaces. Additionally, SERS combines high sensitivity with the observation of vibrational spectra of the adsorbate, giving complete information on the molecular structure of the system under investigation. In this paper, good SERS substrates in the form of silver-coated films with an average size of ~16 nm particles were produced by reducing silver nitrate by neat formamide. SERS was then applied for the trace-level detection of chlorogenic acid (CGA) adsorbed over these silver-coated films. SERS spectra with good signal-to-noise (S/N) ratio, was achieved for the identification and characterization of CGA down to 10^{-9} M concentration. Copyright © 2013 VBRI press.

Keywords: Chlorogenic acid; surface-enhanced Raman scattering; trace-level detection; adsorption.



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Introduction

The identification of molecules in traces has become increasingly important in forensic and medical diagnostics. In this regard, Raman spectroscopy due to its ability to identify the molecular structure of materials under investigation has gained enormous interest. The only drawback with the Raman scattering technique is its inherent weakness that results in low sensitivity and hence, its inability to detect traces of materials. This limitation of the Raman technique has been overcome with the exploitation of the surface-enhanced Raman scattering (SERS) [1]. It has been observed that the Raman signal is strongly enhanced when the molecule under investigation is placed onto roughened metal surfaces or to nanometer-sized metallic colloidal particles [1,2].

SERS has thus, become an increasingly popular technique not only for studying the molecules or ions at trace concentrations but also in understanding its binding characteristics as well as estimating their possible orientations on the metal surfaces [3-16]. An important aspect of SERS is its potential for probing the interaction between various adsorbates and metallic surfaces. Recently, the potential of SERS has been actively explored for trace-level detection [17-21], and researchers are engaged in the development of stable nanostructures for the recognition of low concentration of adsorbates.

Chlorogenic acid (CGA as shown in **Fig. 1**) is an ester of caffeic acid and quinic acid and is known to be an antioxidant. It is an important plant metabolite and has wide anti-viral, anti-bacterial effects and might contribute to the prevention of cardiovascular diseases. Antioxidant activities of CGA are normally due to the presence of phenolic groups in addition to other hydroxyl groups. Since metallic silver is known to have bactericidal properties, synergistic effect might increase the efficiency of the drug when the antioxidant is adsorbed over metal surface. Hence, in this paper we also report the adsorption characteristics of CGA over silver surface. The SERS spectra of CGA were recorded with good signal-to-noise (S/N) ratio down to 10^{-9} M concentration. The results obtained show the groups involved in binding to the silver surface and in addition to chemical enhancement; electromagnetic enhancement mechanism also contributes to the SERS activity.

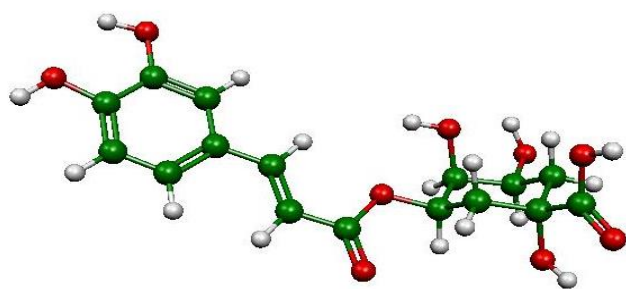


Fig. 1. Structure of chlorogenic acid (CGA) along with the atom numbering.

Experimental

Chlorogenic acid (CGA), formamide and AgNO_3 , used for the preparation of silver-coated films and Raman measurements were from Aldrich chemicals, Spectrochem, India, and S. D. fine chemicals, India, respectively and were used without further purification. For the preparation of silver-coated thin films, glass slides were taken and cleaned thoroughly with chromic acid, washed with Millipore water and then dried in oven. These glass slides were then dipped in 5×10^{-2} M solution of AgNO_3 in formamide for four hours. Formamide reduces Ag^+ ions to Ag^0 and the nanoparticles formed get deposited on the glass slides to form silver-coated films. Detailed method of preparation of the silver coated thin films and their characterization are reported elsewhere [22]. The silver-coated films were then dipped in the aqueous solutions of CGA for 15 mins. These films were then removed from the solution, washed with Millipore water, dried in air and characterized using UV-Visible absorption and atomic force microscopy (AFM). The UV-Visible absorption spectra were recorded for the silver-coated films with and without CGA using a Jasco V650 spectrophotometer. The surface morphology of the silver-coated films in non-contact mode was analyzed using AFM (model-SPM Solver P47). Raman and SERS spectra of CGA were recorded at room temperature using the 532 nm line, from a diode-pumped Nd^{3+} :YAG laser (SUWTECH laser, model G-SLM-020 from Shanghai Uniwave Technology Co. Ltd.). The laser power used to excite the Raman spectrum was 25 mW. The Raman scattered light was collected at the back-

scattered geometry and detected using a CCD based, home-built monochromator [23] together with a super notch filter, covering a spectral range of $150\text{-}1700\text{ cm}^{-1}$.

Results and discussion

Atomic force microscopy (AFM) analysis

AFM images of the silver-coated film and the CGA adsorbed film are shown in **Fig. 2(a)** and **(b)**, respectively. AFM results showed that silver particles were spherical in shape with the average size being ~ 16 nm. Moreover, there was no observable change in either the size or shape of the silver particles in CGA adsorbed film as shown in **Fig. 2(b)**.

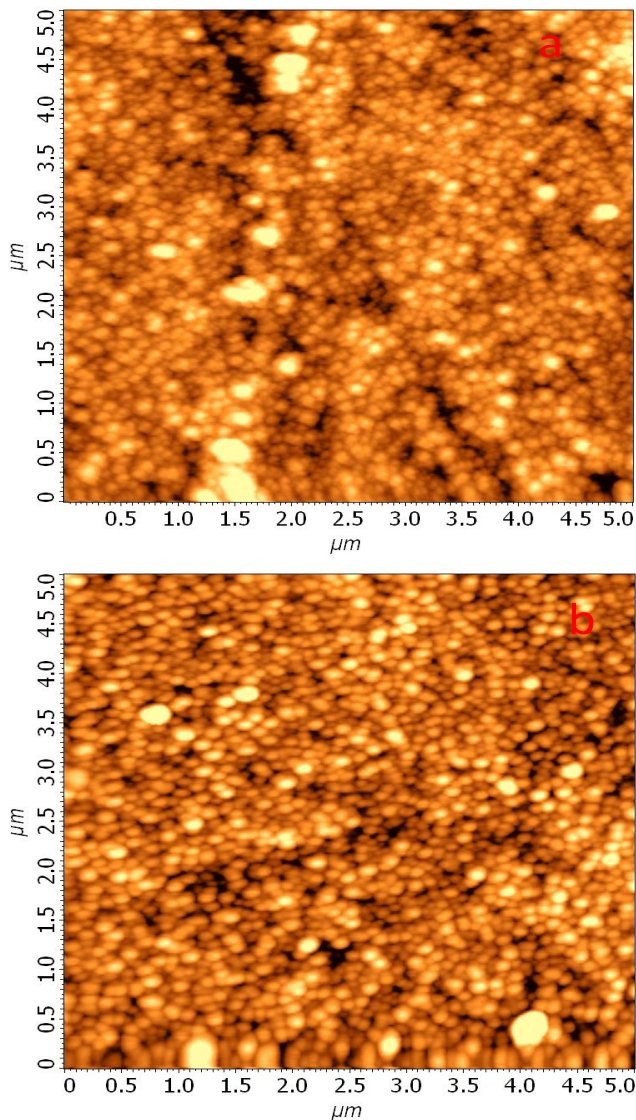


Fig. 2. AFM image ($5\mu\text{m} \times 5\mu\text{m}$) showing (a) silver-coated film and (b) CGA adsorbed silver film

UV-Vis absorption spectra of silver-coated films

The UV-Vis absorption spectrum of the silver-coated film is shown in **Fig. 3**. The figure shows the appearance of surface plasmon band at 396 nm. The absorption spectrum of the silver film with added CGA at concentration of 10^{-6} M showed changes with a slight red shift of the surface plasmon band along with the appearance of a shoulder

around 540 nm, which is attributed to a charge transfer/aggregate band [24, 25].

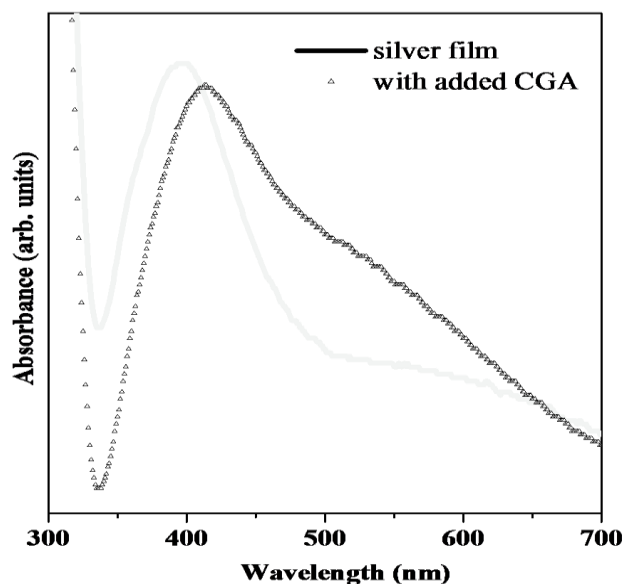


Fig. 3. UV-Vis absorption spectrum of silver-coated film and with added CGA.

Normal raman spectra of CGA and its vibrational assignments

The Raman spectrum of CGA in the solid state is shown in Fig. 4(a). The Raman vibrations observed in the solid state are tabulated in Table I. In the solid state, two strong bands are observed at 1605 and 1629 cm^{-1} assigned to phenyl ring stretch and C_1C_2 ethylenic stretch, respectively. Few medium intensity bands are observed at 1000, 1116, 1160, 1188, 1252, 1287, 1444 and 1474 cm^{-1} . Of these vibrations, 1000 and 1116 cm^{-1} are attributed to cyclohexane (cyc) ring bend and cyc CH, COH bend. 1160 cm^{-1} mode is assigned to phenyl ring bend while 1188 cm^{-1} mode corresponds to phenyl ring CH, COH bend. 1252 and 1287 cm^{-1} vibrations are attributed to C_6O_{13} stretch and cyc ring CH_2 twist, respectively. 1444 and 1474 cm^{-1} modes are assigned to phenyl ring stretching and C_9O_{23} stretching vibrations, respectively. Weak bands are observed at 723, 740, 770, 821, 858, 980, 1203, 1344, 1382, 1518 and 1688 cm^{-1} . Of these vibrations, the modes observed at 723, 740, 858, 980 and 1382 cm^{-1} correspond to cyc ring bend and cyc CH, COH bend while the vibrations at 770, 821, 1203 and 1344 cm^{-1} are attributed to phenyl ring bend. The 1518 cm^{-1} mode is assigned to phenyl ring stretch in combination with C_6O_{12} and ethylenic C_1C_2 stretches. The mode observed at 1688 cm^{-1} is assigned to cyclohexane ring $\text{C}_{24}=\text{O}_{26}$ stretch.

Surface-enhanced Raman scattering (SERS) spectra of CGA

The SERS spectrum of CGA (10^{-8} M) adsorbed on silver film is shown in Fig. 4(b). Significant changes are observed in the SERS spectrum with respect to the normal Raman spectrum in the solid state with selective enhancement of some of the Raman bands. The vibrational frequencies observed in the SERS spectrum along with their approximate assignments are listed in Table I.

Table I. Approximate assignments of normal Raman (solid) and SERS frequencies (in cm^{-1}) of CGA.

| Raman | SERS | Approximate assignments |
|--------|--------|--|
| 1688w | | $\text{C}_{24}=\text{O}_{26}$ str. |
| 1629s | 1640s | $\text{C}_1=\text{C}_2$ str.+ C_6O_{12} str.+ ph. ring str. |
| 1605s | 1577s | ph. ring str., $\text{C}_1=\text{C}_2$ str., C-ph. str. |
| | 1547s | C_6O_{12} str., ph. ring str., $\text{C}_1=\text{C}_2$ str., |
| 1518w | 1512s | ph. ring str., C_6O_{12} str., $\text{C}_1=\text{C}_2$ str. |
| 1474m | 1472s | C_9O_{23} str., C_8O_{22} str., ph. ring str. |
| 1444m | | ph. ring str., ph. CH, COH bend |
| | 1385s | CO_2 sym. str., cyc. CH, COH bend, |
| 1382w | | cyc. ring CH bend, $\text{C}_{24}\text{O}_{27}\text{H}_{42}$ bend |
| 1344w | 1349w | $\text{C}=\text{CH}$ bend, ph. ring bend |
| 1287m | 1283s | cyc. CH_2 twist, cyc. CH, COH bend |
| 1252m | 1246s | C_6O_{13} str., $\text{C}=\text{CH}$ bend, ph. ring bend |
| 1203sh | 1224sh | ph. ring CH, COH bend |
| 1188m | 1187m | ph. ring CH, COH bend, C-ph. str. |
| 1160m | 1166sh | ph. ring bend, ph. CH, COH bend |
| 1116m | 1116w | cyc. ring bend, cyc. CH, COH bend |
| 1000m | 1001w | cyc. ring bend, cyc. CH, COH bend, $\text{C}_{14}\text{O}_{13}$ str. |
| 980w | 968w | $\text{C}_{14}\text{O}_{13}$ str., cyc. ring breathing, cyc. CH, COH bend |
| | 944w | ph. ring bend, ph. CH, COH bend |
| | 918w | cyc. ring bend, cyc. CH, COH bend |
| 858w | 845w | cyc. ring bend, cyc. CH, COH bend |
| 821w | 796w | ph. ring bend |
| 770w | 764w | ph. ring breathing |
| 740w | | cyc ring bend, cyc. CH, COH bend |
| 723w | | |
| | 687w | CO_2 bend, cyc ring bend |
| | 641w | cyc. ring bend, cyc. CH_2 twist $\text{C}_6\text{O}_{12}\text{O}_{13}$ bend |
| | 620w | cyc. ring CH, COH bend |
| | 567w | CO_2 rock, cyc. CH, COH bend |
| | 449m | cyc. ring bend, ph. ring bend |
| | 418w | cyc. ring bend, cyc. CH, COH bend |
| | 348m | CO_2 twist, cyc CH, COH bend |
| | 237s | (Ag-O str) |

Abbreviations used: eth: ethylene; ph: phenyl ring; cyc: cyclohexane ring; s: strong, m: medium, w: weak; sh: shoulder, str.: stretch, oop: out-of-plane.

The SERS activity centers mainly on the vibrations in the region 1200–1700 cm^{-1} . The most significant feature in the SERS spectrum is the emergence of a very strong band at 1385 cm^{-1} assigned to the CO_2^- symmetric stretch. The enhancement in the intensity of the CO_2^- stretching vibration suggests that the CO_2^- group is involved in the interaction with the silver surface. Strong SERS bands are also observed at 1640, 1577, 1547, 1512, 1472, 1283 and 1246 cm^{-1} and are attributed to $\text{C}_1=\text{C}_2$ ethylenic stretch, phenyl ring stretch, C_6O_{12} stretch, phenyl ring stretch, C_9O_{23} stretch, cyc. CH_2 twist and C_6O_{13} stretch, respectively. Moderate intensity Raman peaks are observed at 1187, 449 and 348 cm^{-1} and are assigned to phenyl ring CH, COH bend, cyc ring bend and CO_2 twist, respectively. The SERS spectrum also shows weak bands at 1349, 1224,

1166, 1116, 1001, 968, 944, 918, 845, 796, 764, 687, 641, 620, 567 and 418 cm^{-1} . Of these modes, 1349 is assigned to C=CH bend. The vibrations at 1224 and 1166 cm^{-1} modes are attributed to phenyl ring CH, COH bend and phenyl ring bend. The modes at 1116, 1001, 918, 845, 641 and 418 cm^{-1} correspond to cyc ring bend in conjunction with cyc CH, COH bend. The bands observed at 944 and 796 cm^{-1} are attributed to phenyl ring bend. The Raman bands at 764, 687 and 567 correspond to phenyl ring breathing, CO₂ bend and CO₂ rock. The SERS spectrum also shows a strong band at 237 cm^{-1} assigned to Ag-O stretching vibration.

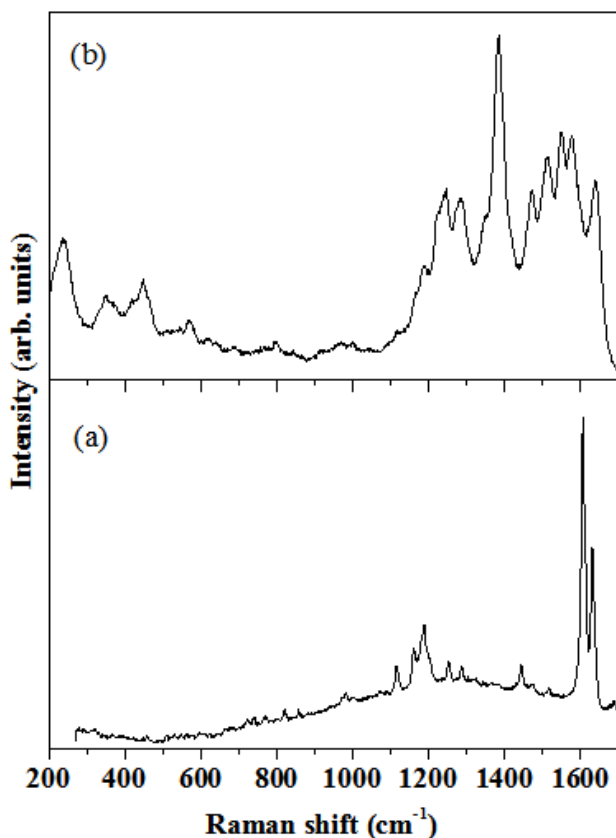


Fig. 4. (a) Normal Raman spectrum of solid CGA and (b) SERS spectrum of CGA

The comparison of the SERS and the normal Raman spectra of the solid below 1000 cm^{-1} provide some interesting details. In the SERS spectrum, several weak intensity Raman bands are observed, which are barely visible in the solid spectrum and are observed at 944, 918, 845, 687, 641, 620, 567, 449, 401 and 348 cm^{-1} . Of these modes, the 918, 845, 641, 449 and 418 cm^{-1} vibrations are assigned to cyclohexane ring bend. The modes at 944 (796) and 764 cm^{-1} are attributed to phenyl ring bend and ring breathing, respectively. The 687, 567 and 348 cm^{-1} modes are assigned to CO₂ bend, rock and twist, respectively. The appearance of an intense peak in the SERS spectrum at 237 cm^{-1} assigned to the Ag-O stretching vibration confirms that CGA is bound to the silver surface through the carboxylate group. The SERS spectra of CGA (at different concentrations) adsorbed on silver-coated films are shown in Fig. 5(a-e). The figure clearly shows enhanced sensitivity in Raman intensities at low (10^{-9} M) CGA

concentration. The silver-coated film dipped at 10^{-8} M CGA solution shows huge enhancement in Raman intensity in the region of 1200-1700 cm^{-1} as well as 150-500 cm^{-1} as compared to 10^{-6} and 10^{-7} M CGA.

The enhancement of SERS intensity on the silver-coated film may be attributed to two possible reasons. Firstly, due to the formation of nanoscale pores on the silver-coated film that may lead to huge enhancement in SERS intensity as has been reported earlier on silver-coated silicon nanopores and nanostructured gold film [26-28]. Secondly, the formation of silver nanoparticle aggregates on the silver-coated film might lead to enhancement in Raman intensity. In fact huge electromagnetic enhancement might occur between two or more aggregated silver nanoparticles (i.e. hot spots) leading to sharper and huge Raman bands as observed in the SERS spectra of CGA (10^{-8} M) adsorbed over silver-coated films. These results are corroborated by the SERS data of Musick et. al. [29]. Our SERS data demonstrate that the silver-coated films prepared using formamide as solvent as well as reducing agent provides good SERS substrates for various practical applications (*viz.* trace-level detection, sensors, etc.).

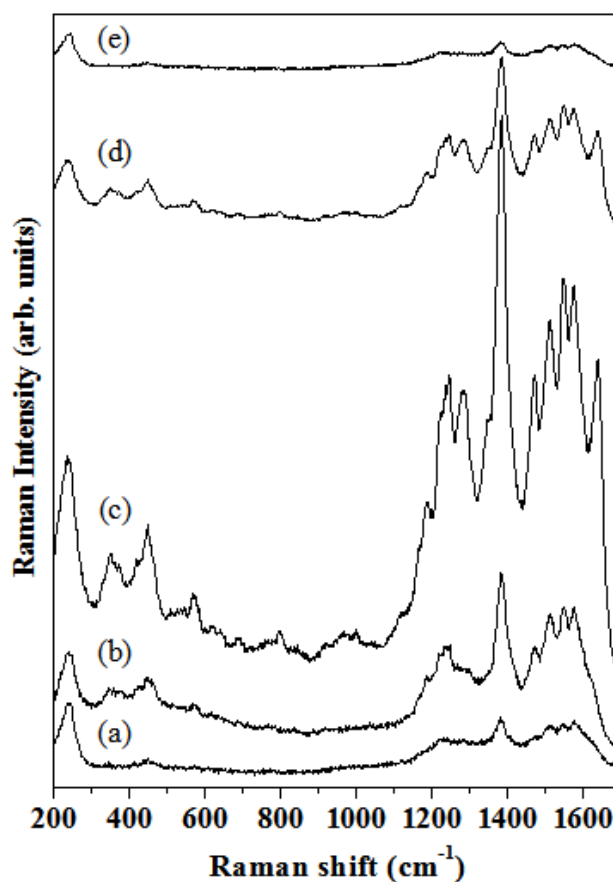


Fig. 5. Effect of concentration of CGA (adsorbed on silver film) on the SERS spectra, (a) 10^{-6} M, (b) 10^{-7} M, (c) 10^{-8} M, (d) 10^{-9} M and (e) 10^{-10} M

Binding of CGA with the silver surface

The interaction of the adsorbed CGA on the metal (silver) surface depends on the active sites of the molecule through which the binding takes place and can be estimated from the enhancement of the relevant Raman bands according to

the electromagnetic surface selection rules as predicted by Moskovits [30] and Creighton [31]. From our SERS spectra, it is observed that the silver-coated film dipped at 10^{-7} , 10^{-8} and 10^{-9} M CGA solution shows good Raman sensitivity and hence enhancement factors ($\sim 10^8$ - 10^9) for various Raman vibrations. The huge enhancement in the intensity of the CO_2^- symmetric stretching vibration at 1385 cm^{-1} observed in the SERS spectrum clearly suggests that the CO_2^- group is directly involved in the interaction with the silver surface. This is further supported with the appearance of a strong band at 237 cm^{-1} assigned to Ag-O stretching vibration. In addition, huge enhancement in various phenyl ring stretching and bending modes in the SERS spectrum suggest chemisorption of the CGA molecule to the silver surface directly through the carboxylate group. The observed enhancement in various Raman vibrations for traces of CGA ($\sim 10^{-8}$, 10^{-9} M concentration) indicates the efficiency of the silver-coated film for SERS based applications. Moreover, it also infers that in addition to the chemical enhancement, electromagnetic enhancement plays an important role in determining the SERS activity.

Conclusion

The formation of good SERS substrates viz. silver-coated film over glass slides was achieved by the reduction of silver nitrate with neat formamide. SERS was then applied for the trace-level detection of CGA adsorbed over these silver-coated films. Good signal-to-noise (S/N) spectrum, was achieved for the identification and characterization of the vibrational structure of CGA in solid state and for traces of CGA (10^{-9} M) on silver surface. The interpretation of the observed features in the SERS spectrum in terms of the enhancements of the various vibrations and the application of 'surface selection rules' seems to strongly suggest that the interaction of CGA is primarily through the oxygen atom of the carboxylate group which indicated that CGA is chemisorbed to the silver surface through the oxygen atoms of the carboxylate group. The SERS study clearly shows that the phenolic groups of CGA are not involved in binding with the silver surface and hence, remain free, thereby retaining its anti-oxidant activity. Hence, adsorption of anti-oxidants viz. CGA over silver films might lead to an increase in its anti-oxidant activity. Moreover, the huge enhancement in the intensities of various in-plane Raman bands for traces of CGA inferred that in addition to chemical enhancement, electromagnetic enhancement mechanism also contributes to the SERS activity.

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