

分类号\_\_\_\_\_

密级\_\_\_\_\_

U D C\_\_\_\_\_

编号\_\_\_\_\_

厦 门 大 学  
博 士 后 研 究 工 作 报 告

壳层隔绝纳米粒子增强拉曼光谱及其电化学应用

Rajapandiyan Panneerselvam

工作完成日期 2014年9月—2016年6月

报告提交日期 2016年7月

厦 门 大 学 （福建）

2016年7月

# 壳层隔绝纳米粒子增强拉曼光谱 及其电化学应用

## Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy and Its Applications in Electrochemistry

博 士 后 姓 名 Rajapandiyan Panneerselvam

流动站（一级学科）名称 厦门大学化学

专 业（二级学科）名称 物理化学

研究工作起始时间 2014年9月14日

研究工作期满时间 2016年9月14日

厦门大学人事部（福建）

2016年7月

# 厦门大学博士后研究工作报告

## 著作权使用声明

本人完全了解厦门大学有关保留、使用博士后研究工作报告的规定。厦门大学有权保留并向国家主管部门或其指定机构送交该报告的纸质版和电子版，有权将该报告用于非赢利目的的少量复制并允许该报告进入学校图书馆被查阅，有权将该报告的内容编入有关数据库进行检索，有权将博士后研究工作报告的标题和摘要汇编出版。保密的博士后研究工作报告在解密后适用本规定。

本研究报告属于： 1、保密（ ）， 2、不保密（ √ ）

纸本在 年解密后适用本授权书；

电子版在 年解密后适用本授权书。

（请在以上相应括号内打“√”）

作者签名： 日期： 年 月 日

导师签名： 日期： 年 月 日

## Abstract

Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) attracted significant attention by eliminating the material and morphology generality problems of SERS. For the past few years, SHINERS has been extensively employed in many fields such as electrochemistry, food science, and material science. This report compiles our research works in the past two years (2014-2016). First, I clearly introduce the development of SHINERS technique, from Raman spectroscopy to SERS and TERS, and finally SHINERS. The basic concepts and principles of these techniques will be discussed. Obviously, the synthesis of shell-isolated nanoparticles (SHINs) is the most important thing for SHINERS experiments, so this report also explains the preparation procedure and characterization methods. Compared with the contact mode SERS and other Raman methods, the shell-isolated mode possesses several advantages to obtain Raman signals from a wide range of surfaces/morphologies. An unequalled application of SHINERS over other spectroscopic techniques is its applicability on single-crystal surfaces in electrochemistry field. So this report mainly highlights some important applications of SHINERS on metal single crystal surfaces in the past two years. By using EC-SHINERS method, we studied the adsorption behaviour of pyridine and DNA bases on Au (*hkl*) electrodes surfaces, and obtained the direct spectral evidences for the molecular orientation on the single crystal surfaces under different potentials. Then, the report explains an example for in situ investigation of chemical reactions on a single crystal surface. By obtaining the directly spectral proof of the intermediates during the surface reaction, the mechanism of an electro-oxidation process on gold single crystal surfaces is better understood. Last, the report discusses the application of SHINERS and shell-isolated mode in other plasmon-enhanced spectroscopies such as surface-enhanced fluorescence, tip-enhanced Raman spectroscopy, and its application on nanocatalytic reactions by monitoring the photocatalytic reaction pathway of PATP to DMAB. Finally, this report presents the outlook for future developments in SHINERS field.

**Keywords:** Au@SiO<sub>2</sub>, SHINERS, electrochemistry, single crystal electrodes.

## 内 容 摘 要

壳层隔绝纳米粒子增强拉曼光谱 (SHINERS) 的发明突破了表面增强拉曼散射光谱 (SERS) 在形貌普适性以及基底普适性的问题, 受到了人们的极大的关注。在过去的几年间, SHINERS 技术已被广泛应用于各个领域, 特别是在电化学领域的应用尤为突出。本报告主要辑录在过去的两年中 (2014-2016) 我们关于 SHINERS 技术的研究工作。首先本文清晰的介绍了 SHINERS 技术的发展过程, 从最初的常规拉曼光谱到后来的 SERS 以及针尖增强拉曼散射光谱 (TERS), 进而到最新的 SHINERS 技术的出现, 并对其中与各项技术相关的基本概念、原理进行了详细介绍。在进行 SHINERS 试验的时候, SHINs (Au@SiO<sub>2</sub>) 纳米粒子的合成毋庸置疑是最为重要的部分, 所以我们具体介绍了常规 SHINs 粒子的合成方法。相较于常规拉曼方法而言, SHINERS 技术一个很明显的优势是其能被方便的应用于单晶界面电化学过程的监测研究。所以在之后的应用中, 本文就最近两年已发表的相关论文进行介绍。在应用这部分内容中, 本文首先介绍利用原位 EC-SHINERS 方法监测金单晶界面吡啶分子的电化学吸附行为。发现在不同电位区间, 吡啶分子在单晶界面具有不同的吸附构型, 同时 DNA 分子在金单晶界面的吸附以及相应的电化学行为也得到相应的研究。界面反应, 特别是固/液界面反应在物理、化学、表面科学等领域普遍存在。固/液界面上电荷迁移、小分子吸附以及表面结构等的监测研究是进一步了解电催化反应和界面反应机理的关键。所以我们利用 EC-SHINERS 方法原位研究了金单晶电极表面的电氧化过程。详细考察了不同晶面结构、pH 值以及阴离子对于金单晶表面的电氧化过程的影响, 得到电氧化过程中间物种 OH 的直接光谱证据, 为理解金电极表面电催化机理提供了有益的帮助。我们也把 SHINERS 技术以及壳层隔绝的模式扩展到银纳米粒子以及银针尖上, 并取得新的进展。最后我们对 SHINERS 技术的发展进行了简要的总结及展望。

**关键词:** Au@SiO<sub>2</sub>, SHINERS, 电化学, 单晶电极

# 目 录

Abstract.....	I
内 容 摘 要.....	II
符 号 表.....	IV
1 Introduction.....	1
2 Experimental procedure.....	4
2.1 Preparation of shell-isolated nanoparticles.....	4
2.2. Instruments.....	5
3 Results and Discussion.....	6
3.1 SHINERS Study of Pyridine Adsorption on Au ( <i>hkl</i> ) Electrodes Surfaces.....	6
3.2 In Situ Investigation of Electrooxidation Processes at Au( <i>hkl</i> ) Single Crystal Surfaces.....	8
3.3 “Smart” Ag Nanostructures for Plasmon-Enhanced Spectroscopies.....	10
3.4 Shell-isolated nanoparticle-enhanced Raman spectroscopy study of the adsorption behaviour of DNA bases on Au(111) electrode surfaces.....	12
4 Summary and Outlook.....	13
Acknowledgements.....	14
References.....	15
Personal Curriculum Vitae.....	18
List of Publication.....	28
Permanent Address.....	31

## 符 号 表

<b>SERS</b>	Surface-enhanced Raman spectroscopy
<b>SHINERS</b>	Shell-isolated nanoparticle-enhanced Raman spectroscopy
<b>TERS</b>	Tip-enhanced Raman spectroscopy
<b>SPR</b>	Surface plasmon resonance
<b>Electromagnetic enhancement</b>	EM enhancement
<b>Chemical enhancement</b>	CM enhancement
<b>SHINs</b>	Shell-isolated nanoparticles
<b>SITERS</b>	Shell-isolated tip-enhanced Raman spectroscopy
<b>SHINEF</b>	Shell-isolated nanoparticle-enhanced fluorescence
<b>EC-SHINERS</b>	Electrochemical SHINERS
<b>Au@SiO<sub>2</sub> NPs</b>	Silica coated gold nanoparticles
<b>PICT</b>	Photo-induced charge transfer mechanism
<b>SEM</b>	Scanning electron microscope
<b>TEM</b>	Transmission electron microscope

## 1 Introduction

In 1928, the Raman scattering effect was discovered by the Indian physicist C. V. Raman, since then Raman spectroscopy obtained a great attention from the entire scientific community.<sup>1</sup> Raman spectroscopy can offer much more information about the structure and properties of the surface species or interface elements from electrodes while maintaining the capability of offering real-time information in a non-invasive manner.<sup>2</sup> In 1974, through electrochemical roughening method, Fleischmann et al. obtained unusually intense Raman spectra of pyridine adsorbed on roughened silver surface.<sup>3</sup> At first, they thought that the unexpected high quality Raman spectrum was obtained because of the high electrode surface area after oxidation-reduction cycling. In 1977, after carefully checking the experimental and theoretical calculations, Van Duyne and Creighton explained that the enhanced Raman signals was due to an enhancement ( $10^5$ - $10^6$ ) in Raman cross-section of pyridine molecules.<sup>4,4b</sup> Later, the effect was called as surface-enhanced Raman scattering (SERS) effect. It is widely accepted that there are two mechanisms contribute to the SERS enhancement namely: an electromagnetic enhancement mechanism (EM) and a chemical enhancement mechanism (CM). However, electromagnetic enhancement plays a major role when compared to chemical enhancement. The chemical enhancement is due to the chemisorption interaction and the photon-driven charge transfer between adsorbed molecules and metal nanostructures.<sup>5,6</sup>

The electromagnetic field enhancement is originated from surface plasmon resonance (SPR) of metal nanostructures. Surface plasmons resonance is a collective oscillation of the surface conduction electrons in metal nanostructures.<sup>7</sup> When an electromagnetic radiation with the same frequency is interacting with the metal nanostructures, the electric field of the radiation excites the conduction electrons into collective oscillation. The enhanced electromagnetic field, existing in a tiny volume around the metallic surfaces, enhances the Raman cross section of molecules located in the vicinity of the nanostructured surfaces.

Generally, SERS effect is associated with the following features: 1) only a certain metals, such as Ag, Au, and Cu exhibit strong SERS enhancement effect;<sup>8</sup> 2) the



strength of SERS effect not only depends on the metal itself, but also depends on the size, shape, and nanogap dimension of the nanostructures;<sup>9</sup> 3) SERS technique provides ultra-sensitive detection by measuring the first layer molecules on the metal surface; 4) SERS and normal Raman spectroscopy exhibit different selection rules in terms of relative intensity and frequency of the same vibrational bands; 5) SERS enhancement factors vary among different probe molecules due to the distinct properties of molecules or ions adsorption on the metal surfaces.

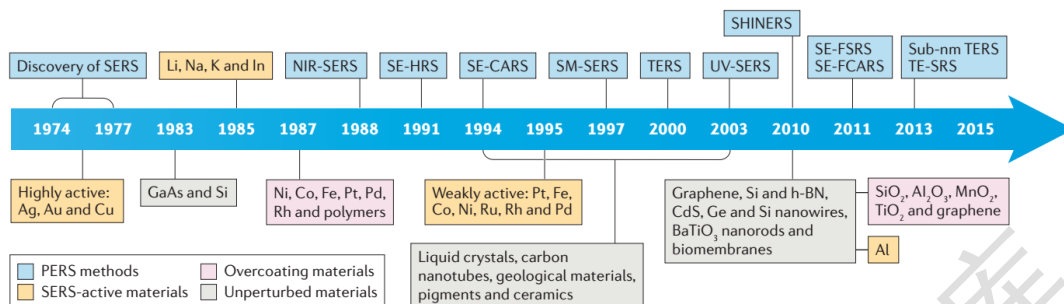
To obtain huge SERS enhancement, several researchers employ noble metals such as Au, Ag, or Cu metal nanostructures for SERS studies. Though, several material such as transition metals, metal oxide, graphene can enhance the Raman signals, the enhancement obtained from these materials are significantly lower than the noble metals.<sup>10</sup> Thus the lack of SERS substrate material has greatly restricted the number of specific applications of SERS. In order to expand the SERS effect to other materials or surfaces, a “borrowing” strategy was proposed during the 1980s. The “borrowing” strategy mainly include two different pathways: either by coating SERS-active metals on non-SERS-active substrates or by coating non-SERS-active materials over SERS-active substrates surface. This “borrowing” strategy employ the long-range effect of the electromagnetic field which generated by SERS-active materials, including Ag or Au, to increase the Raman signal of probe molecules adsorbed on the non-SERS-active substrates. Several researchers have obtained SERS signals from some transition metals (e.g. Pt, Pd, Rh, etc.) by coating ultrathin shells of these transition metals on Au or Ag NPs or other relevant nanostructured surfaces.<sup>11</sup>

To apply SERS in other fields, it is necessary to analyse the working modes of SERS in all kinds of SERS measurements. Generally, SERS working modes can be classified into two types, namely contact mode, and non-contact mode. In contact mode, the noble metal nanoparticles not only act as signal amplifiers, but also act as a host to accommodate probe molecules. In non-contact mode, the metal nanoparticles are separated from the surface of interest/probe molecules. Thus, non-contact mode is a key step forward to extend the applications of SERS in other fields where molecules will be adsorbed on any substrate/any morphology.

In 2000, the invention of tip-enhanced Raman spectroscopy (TERS) is a major

breakthrough in Raman spectroscopy field because it solved a few problems associated with contact mode SERS.<sup>12,13,14,15</sup> Interestingly, TERS technique merges Raman spectroscopy with scanning probe microscopy (SPM) to provide chemical information with high spatial information.<sup>16</sup> In TERS, a sharp plasmonic gold or silver tip generates a well-defined hot spot on the target surface under a suitable excitation wavelength. However, TERS tip is prone to contamination and sensitivity problems under electrochemical conditions. Particularly when single crystal electrodes are used, one has to employ a higher numerical aperture objective in a side-illumination mode with a shorter working distance. When the electrolyte layer becomes thicker, it is very difficult to obtain a good focus. Therefore, EC-TERS needs a special set up to obtain Raman signals under electrochemical conditions.<sup>17</sup>

In 2010, our group developed a novel “shell-isolated mode” overcome the issues associated with material and morphology problems of SERS.<sup>18</sup> In SHINERS, the TERS tip concept was substituted by a layer of Au-core SiO<sub>2</sub>-shell nanoparticles (Au@SiO<sub>2</sub> NPs or SHINs). In this case, each gold nanoparticle core of SHINs can act as a single TERS tip, which means several SHINs are excited in one micron-sized laser spot simultaneously. Notably, SHINERS technique employs shell-isolated mode which is different from contact mode and non-contact mode. The SERS-active Au NPs core of SHINs act as “signal amplifiers” which can increase the Raman signals of probe molecules around or adsorbed on the target surface. The outer ultrathin yet pinhole-free silica shells (2-5 nm) can effectively protect the core Au NPs from the outer chemical environment, and preclude the Au NPs contact with the surface species/probe molecules. As a result, this technique can provide the original information about the target systems. We named this technique as “shell-isolated nanoparticle-enhanced Raman spectroscopy” or “SHINERS.” Importantly, SHINERS does not suffer from material or morphology generality problems, because SHINs can be employed to examine any target surface with diverse compositions and morphologies, and the SHINERS technique has already been used to investigate a number of challenging systems.<sup>19</sup>



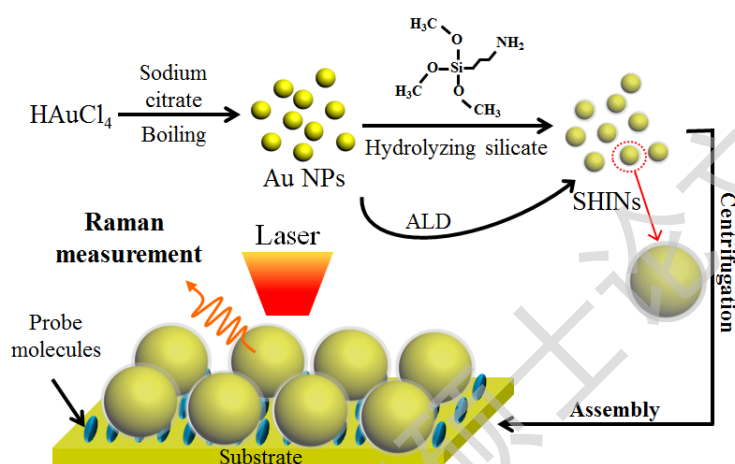
**Figure 1. Key developments in plasmon-enhanced Raman spectroscopy.** NIR-SERS, near-infrared surface-enhanced Raman spectroscopy; PERS, plasmon-enhanced Raman spectroscopy; SE-CARS, surface-enhanced coherent anti-Stokes Raman spectroscopy; SE-FCARS, surface-enhanced femtosecond coherent anti-Stokes Raman spectroscopy; SE-FSRS, surface-enhanced femtosecond stimulated Raman spectroscopy; SE-HRS, surface-enhanced hyper-Raman spectroscopy; SHINERS; shell-isolated nanoparticle-enhanced Raman spectroscopy; SM-SERS, single-molecule surface-enhanced Raman spectroscopy; sub-nm TERS, tip-enhanced Raman spectroscopy with sub-nanometre resolution; TE-SRS, tip-enhanced stimulated Raman spectroscopy; UV-SERS, ultraviolet SERS. Reproduced from the literature.<sup>20</sup>

## 2 Experimental procedure

### 2.1 Preparation of shell-isolated nanoparticles

Here, we describe the detailed experimental procedure of SHINs using 55 nm Au@SiO<sub>2</sub> as an example. The Au NPs (55 nm) were synthesized by classical Frens procedure. In detail, 200 mL 0.01% HAuCl<sub>4</sub> solution was stirred in a round-bottom flask under heating conditions, after boiling, 1.4 mL 1% sodium citrate solution was added and continued the reaction for 1 h, then cooled down at room temperature.<sup>18</sup> The SHINs were prepared as following: added 30 mL Au NPs solution into a 100 mL round-bottom flask for stirring at room temperature and then dropped 400  $\mu$ L 1 mM APTMS solution. After 15 min stirring, 3 mL 0.54 % Na<sub>2</sub>SiO<sub>3</sub> solution (pH  $\approx$  10.3) was added into the above solution. 3 minutes later, the mixed solution was transferred to a 90  $^{\circ}$ C bath and stirred for some time. Through controlling the reaction time, pH

values, temperature and gold nanoparticles concentration, the SiO<sub>2</sub> shell could be tuned with different thicknesses. After certain heating time, the hot solution should be quickly cooled down and then centrifuged for several times. At last, the concentrated SHINs was diluted with pure water to certain volume for further electrochemical or Raman measurements. It is worthy to mention that the SHINs can easily form a submonolayer on a target surface almost without obvious aggregates. Importantly, to get reproducible Raman signals and high enhancement, one should make sure that the target surface should be covered with an appropriate amount of SHINs.



**Figure 2.** General overview of SHIN synthesis.

For pinhole tests, the procedure is as follows: first, 10 $\mu$ L SHINs solution was deposited (with pinhole and centrifuged) on a Si wafer and dried for a certain time; then 20  $\mu$ L of 10 mM pyridine solution was deposited on the SHINs and covered with a thin quartz window. Finally, the sample was subjected to Raman measurements.<sup>18</sup>

## 2.2. Instruments

Scanning electron microscope (SEM) images were recorded with a HITACHI S-4800, transmission electron microscope (TEM) images were recorded with a JEM 2100. CVs were recorded with a CHI-630E potentiostat. All the electrochemical measurements were carried out using a standard glass three room cell. A saturated calomel electrode (SCE) and a Pt wire served as reference and counter electrodes, respectively. In the case of EC-SHINERS measurements, the electrode potential was

controlled with an Autolab PGSTAT30 (Metrohm). The EC-SHINERS measurements were carried out with a confocal Raman system Xplora (Jobin-Yvon Horiba). The excitation wavelength was 638 nm. The microscope objective was 50 × magnification with a numerical aperture of 0.55. All the EC-SHINERS measurements were carried out using a teflon three electrode cell. SCE and Pt wire were used as reference and counter electrodes, respectively. All potentials given were referred to the SCE potential scale. For more details, please refer the respective research article.<sup>21,17,22,23</sup>

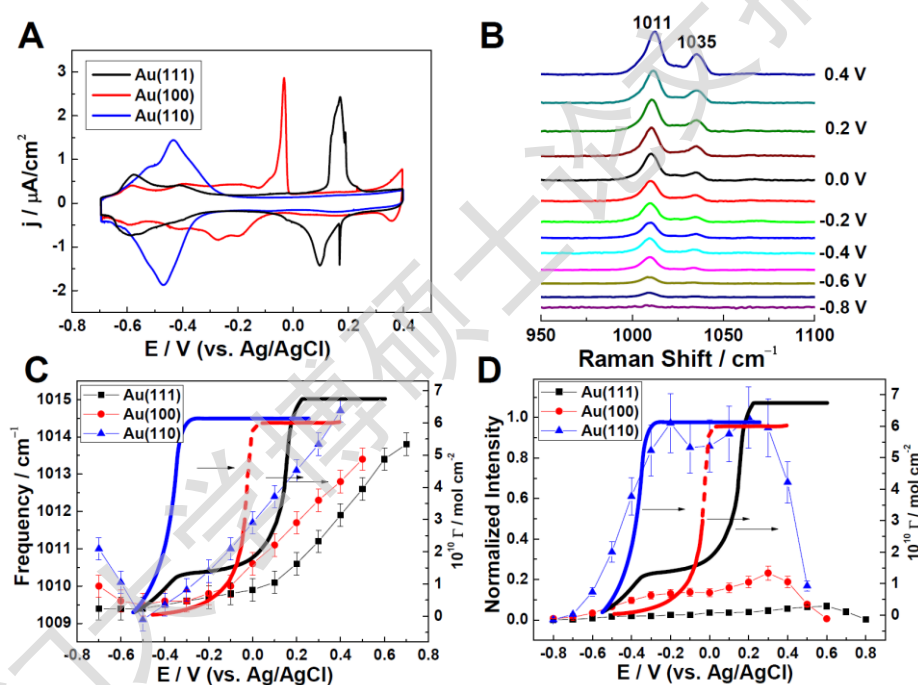
### 3 Results and Discussion

#### 3.1 SHINERS Study of Pyridine Adsorption on Au (*hkl*) Electrodes Surfaces

Pyridine (Py) is a standard probe molecule that can be used to understand the coordination and orientation behaviour of chemical molecules at metal interfaces. Our group utilized EC-SHINERS method to examine the electrochemical adsorption behavior of Py on Au(*hkl*) single crystal surfaces in 0.1 M NaClO<sub>4</sub> solution.<sup>22</sup> Different factors, such as the crystallographic orientation, Py concentration and applied potential were examined systematically. **Figure 3A** shows the CVs of 1 mM Py on three basic low-index Au(*hkl*) single crystal electrodes in 0.1 M NaClO<sub>4</sub> solution. **Figure 3B** shows the typical EC-SHINERS spectra of Py on the Au(111) surface from -0.8 V to 0.4 V potential range. The peak at 1011 cm<sup>-1</sup> was attributed to the Py  $\nu_1$  ring breathing mode, and the peak at 1035 cm<sup>-1</sup> was attributed to the Py  $\nu_{12}$  symmetric triangular ring deformation mode.

Generally, the Raman peak of a probe molecule is associated with adsorption configuration and surface coverage rate. By using  $\nu_1$  mode of Py on Au(111) as an example, we found that the Raman frequency and intensity of  $\nu_1$  mode around 1011cm<sup>-1</sup> increases with the increasing potential (**Figure 3 B**), but the enhancement factor is not same in different potential regions as shown in **Figure 3C-D**. At low potential region (  $E < 0.1$  V), the Raman frequency of  $\nu_1$  mode increased little, but when  $E > 0.1$ V, the frequency of  $\nu_1$  mode undergoes obvious change and the Stark tuning rate is about 5.6 cm<sup>-1</sup>/V, which indicates the adsorption configuration or orientation of Py is different compared to the negative potential region. When Py molecules were flat-adsorbed on the electrode surface, there was a weak binding

interaction between  $\pi$ -orbital electrons and the electrode surface, thus, the relevant Raman signal was weak; When Py molecules were vertically adsorbed on the electrode surface, there was a strong interaction between the nitrogen atom lone pair of electrons and the electrode surface, so the relevant Raman signal was strong. From the potential-Raman frequency relationship and potential-Raman intensity relationship results we can conclude that Py flat-adsorbed on the Au(111) electrode surface when  $E < 0.1$  V, and vertically adsorbed on the Au(111) electrode surface when  $E \geq 0.1$  V, which was in good agreement with the reported articles that Py forms a full monolayer on Au(111) at higher potentials.



**Figure 3.** (A) CVs of Au(*hkl*) electrodes in 0.1 M NaClO<sub>4</sub> solution containing 1 mM Py. (B) SHINER spectra of Py molecules on Au(111). The relationship of Raman frequency (C) and normalized Raman intensity (D) with potentials for the  $\nu_1$  mode, and accompanied with surface concentration isotherms (bold curves). Reproduced with permission.<sup>22</sup> Copyright 2015, American Chemical Society.

Additionally, we found that the orientation of Py on Au(100) and Au(110) surface would be changed from flat-adsorbed to vertically adsorbed following the potential

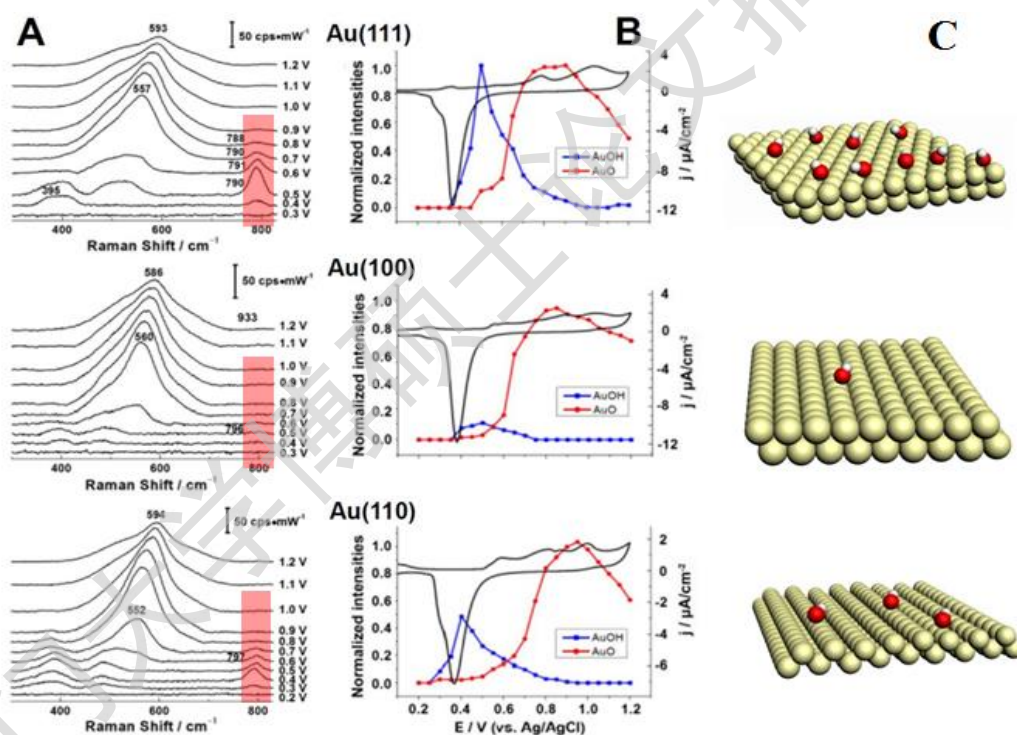
increase too. The potentials of Py monolayer completion decreasing in the order of Au(111) > Au(100) > Au(110) on three basic-index gold single crystal surfaces, this trend is same as the potential of zero charge ( $E_{PZC}$ ) order obtained without Py. It means that the electrode surface charge plays an important role during the adsorption process. But the Raman peak intensity of  $\nu_1$  mode for adsorbed Py molecules on three basic-index Au(*hkl*) electrode surfaces increasing as the order of Au(111) < Au(100) << Au(110) (**Figure 3D**). Thus, EC-SHINERS can be used to investigate the adsorption behaviour of probe molecules on Au single crystal electrodes at electrochemical interfaces.

### 3.2 In Situ Investigation of Electrooxidation Processes at Au(*hkl*) Single Crystal Surfaces

In electrocatalytic processes, the formation of oxide greatly affects the performance of a catalyst and also the reaction mechanism. Therefore, it is imperative to understand the electrocatalytic process to fabricate or design efficient new catalysts. However, the conventional analytical techniques are not able to detect the key intermediates because of the complexity in in situ studies. Most of the reaction mechanisms were deduced based on the electrochemical techniques and combined with the theoretical calculations, but it was still a challenge to prove these results by direct in situ Raman spectra.

To solve this issue, in situ EC-SHINERS technique provides a novel way to real-time investigate the electrocatalytic reaction pathways at well-defined noble metal single crystal surfaces. Our group employed in situ EC-SHINERS method to investigate the electrooxidation processes at Au(*hkl*) single crystal surfaces, and provided spectral evidence for the electrooxidation intermediates.<sup>21</sup> As shown in **Figure 4**, there is no obvious Raman peak in the range of 300-800  $\text{cm}^{-1}$  during the positive scan until 0.4 V on Au(111) single crystal electrode surface. There was a Raman peak around 790  $\text{cm}^{-1}$  following the potential increased to 0.4 V, and its intensity reached maximum at 0.5 V, then decreased and almost disappeared at 0.9 V. According to the references and the DFT calculation results, we considered the peak at 790  $\text{cm}^{-1}$  belonged to the gold-hydroxide bending mode  $\delta_{\text{AuOH}}$  of the adsorption on top sites.

To confirm our conclusion, a deuterium isotopic experiment was also carried out, and the results shown that the bending mode of AuOH at  $790\text{ cm}^{-1}$  shifts toward the lower wavenumber  $694\text{ cm}^{-1}$  in deuterated water, which clearly confirms that the band around  $790\text{ cm}^{-1}$  was assigned to the gold-hydroxide bending mode  $\delta_{\text{AuOH}}$ . We also found that there was a broad band at  $360\text{--}420\text{ cm}^{-1}$ , when the potential reached to  $0.3\text{ V}$ , the band blue-shifted about  $20\text{ cm}^{-1}$  in heavy water experiment, which is also in agreement with the previous references. When the potential was at  $0.7\text{ V}$ , there was another board band at  $567\text{ cm}^{-1}$ , it shifted to  $593\text{ cm}^{-1}$  following the potential increased, which is attributed to Au-O stretching.



**Figure 4.** (A) The SHINERS spectra of electrooxidation at Au(111), Au(100) and Au(110) electrode surfaces in  $0.1\text{ M NaClO}_4$  (pH is  $\sim 9$ ); (B) Normalized SHINERS intensities of the stretching mode of AuO and the bending mode of AuOH at different potentials. CV of Au(111) electrode in  $0.1\text{ M NaClO}_4$  is presented (pH is  $\sim 9$ , scan rate is  $2\text{ mV/s}$ ); (C) Schematic diagram of OH species on three low index Au(*hkl*) surfaces. Reproduced with permission. Copyright 2015, American Chemical Society.



Degree papers are in the “[Xiamen University Electronic Theses and Dissertations Database](#)”.

Fulltexts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to [etd@xmu.edu.cn](mailto:etd@xmu.edu.cn) for delivery details.