

## The Charge Transfer Effect of SERS Induced by the Electrochemical Hydrogen Evolution Reaction

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**Detailed abstract:** As one of the important mechanisms of SERS, the charge transfer (CT) enhancement requires the strong interaction of the adsorbed species with the substrate in order to permit the transition of charge between the metal Fermi level (energy state) and the molecular orbital<sup>[1]</sup>. The high enhancement needs the match of the energy gap between the Fermi level (or surface state) and the orbital energy level of the adsorbed molecules with the energy of the incident light. The electrode Fermi level is usually adjusted by the applied potential to satisfy the CT resonance. For the electrochemical reaction process, the frontier orbital energy level of the reacting surface species should be greatly different from that of the adsorbed molecules. Thus, it is interesting to test the additional SERS enhancement induced by the electrochemical reaction.

In the present study, the influence of the electrochemical reaction on SERS intensity of thiourea (TU) and water adsorbed on silver electrode surfaces were investigated, respectively. The Raman experiments were performed on a confocal microprobe Raman system (LabRam I). The details of the Raman system and pretreatment of the Ag electrode can be found elsewhere<sup>[2]</sup>.

The SERS spectra of TU in pH 1 and 7 are showed in the Fig. 1 (a) and (b), respectively. The major bands of TU locate at  $\sim 710\text{ cm}^{-1}$  and  $\sim 1\,091\text{ cm}^{-1}$ . The strong  $933\text{ cm}^{-1}$  band is assigned to the symmetric stretching vibration of  $\text{ClO}_4^-$  as electrolyte anion, which coadsorbed on

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the surface. The electrochemical measurements indicate that TU can adsorb strongly at Ag electrode in a wide potential region from  $-0.2$  V to  $-1.5$  V (vs SCE). It is of interest that the SERS intensity reaches the maximum at different potential in acidic and neutral solutions. In the low pH solution, one can find that when the electrode potential shifted to  $-0.8$  V, all the band intensities increase remarkably. In the high pH solution (Fig. 1 (b)), at potentials positive of  $-1.0$  V only solution signal can be discerned. The intensity of the surface signals underwent a sharp increase at  $-1.2$  V. Interestingly, we found the maximum intensities in the two pH solutions have a certain relation with the occurrence of the electrochemical hydrogen evolution reaction (HER).

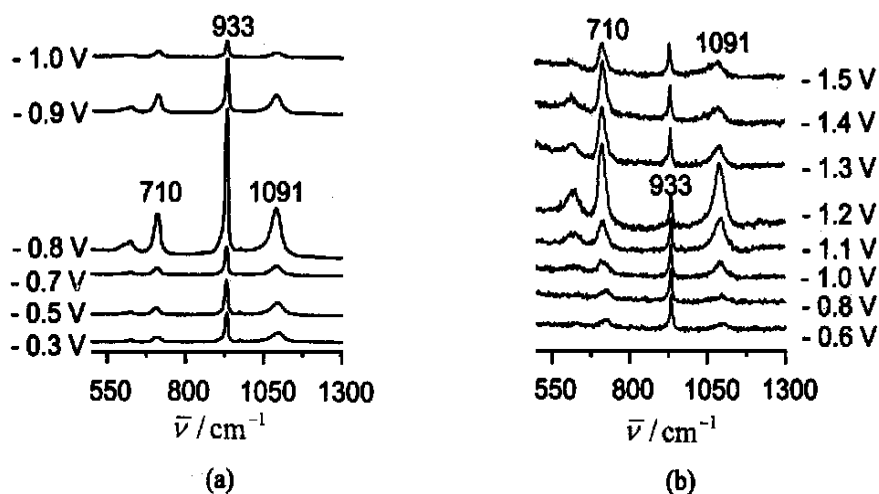


Fig. 1 SERS from the Ag electrode surfaces at different potentials in solution of  $0.1 \text{ mol} \cdot \text{L}^{-1}$  TU +  $0.1 \text{ mol} \cdot \text{L}^{-1}$   $\text{NaClO}_4$  with pH = 1 (a) and pH = 7 (b) respectively.

A systematic SERS experiments were performed in solutions with pH of 2.0, 2.5, 3.0, 3.5, 4.0 and 7.0 respectively. The profiles of the integrated band intensities ( $\sim 710 \text{ cm}^{-1}$ ) and the potentials are shown in Fig. 2. It can be found that the maxima of the intensities are located at  $-0.8$  V,  $-1.1$  V for pH 1.0 and 2.0 respectively and  $-1.2$  V for pH 2.5 ~ 7.0. Correspondingly, the current densities for each potential in different pH solution were presented in Fig. 3. From the two figures, it can be found that the potentials of the maximum intensity of SERS are right at the initial potentials of HER. It implies that there must have some relation between the HER and the additional enhancement of the SERS. A study on the SERS of water will be helpful for further understanding of this relation.

Fig. 4 shows the SERS of water from an Ag electrode in  $1.0 \text{ mol} \cdot \text{L}^{-1}$   $\text{Na}_2\text{SO}_4$  at different potentials. The broad band at  $1610 \text{ cm}^{-1}$  is assigned to the bending mode of water. It can be found that the band intensity increases with the negative movement of the potential. This can not

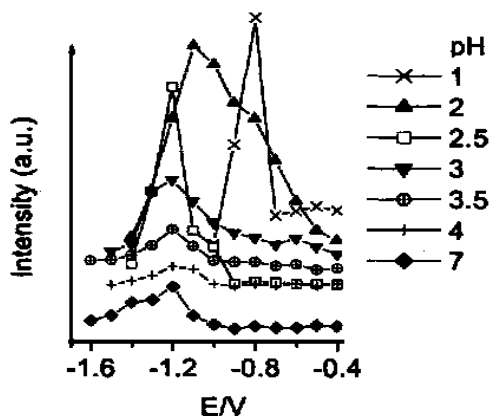


Fig. 2 The profile of integrated SERS intensities of the  $\sim 710 \text{ cm}^{-1}$  band versus electrode potentials

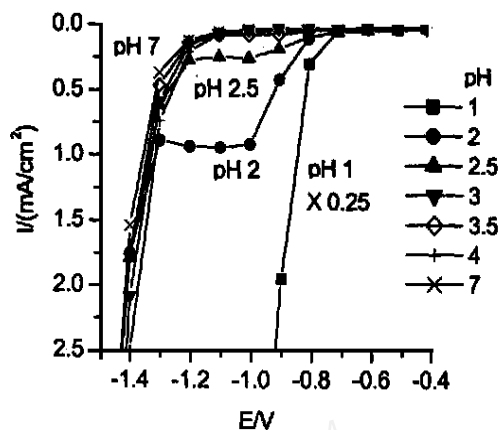


Fig. 3 The profile of the current density of HER versus potential in different pH

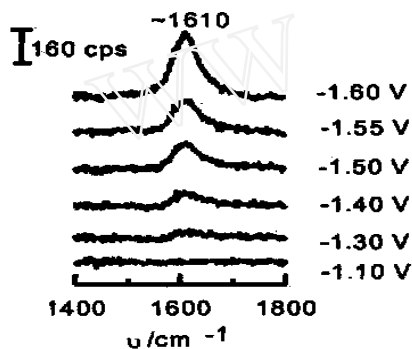


Fig. 4 SERS of water from Ag in  $1.0 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{SO}_4$  at different potentials

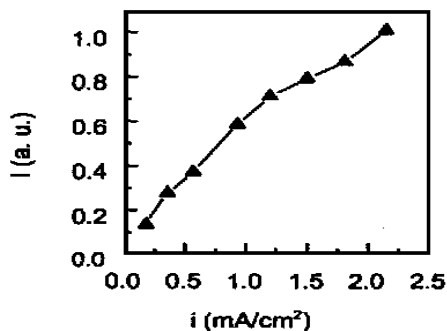


Fig. 5 Integrated SERS intensity ( $I$ ) of  $1610 \text{ cm}^{-1}$  band versus the current density of HER ( $i$ )

be explained in terms of the orientation change of the adsorbed water<sup>[3]</sup>. For SERS of water on Ag, the EM enhancement is about 2 to 4 orders<sup>[1]</sup>. While, the total enhancement can reach 4 to 7 orders in the present case, and thus, the CT effect may be involved<sup>[4]</sup>. However, water molecules can not effectively bond to the electrode due to a larger difference of these two energies<sup>[3]</sup>, which does not fulfill the conditions for the classic CT enhancement.

The Raman intensity of the  $1610 \text{ cm}^{-1}$  band and the corresponding current densities of HER are depicted in Fig. 5. The intensity almost increases linearly with the HER current. Hereby, one could assume that the additional enhancement is possibly related to the HER, during which the reaction intermediate with a matching energy level with the incident light was generated, thus the effective CT process could occur.

It may be reasonable to assume that the intermediate state generated during the HER could have the energy levels in resonance with the incident light to give the additional enhancement. Considering the extremely difficulty to in situ investigate surface reaction states, SERS may provide a new way to explore the intermediate energy levels during electrochemical reaction if we use the tunable laser to tune the incident photon energy to match the CT resonance. This study in turn will be helpful for further elucidating the SERS mechanism.

**Key words:** SERS, Thiourea, Water, Charge transfer effect

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# 电化学析氢反应诱导的电荷传递 SERS 效应

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**摘要:** 应用高灵敏度的共焦显微拉曼技术, 分别研究了水体系和不同 pH 值的硫脲体系中电化学反应与表面增强拉曼散射 (SERS) 效应之间的关系. 研究结果表明, 在电化学析氢反应电位区, 电荷转移增强机制起主要作用, 使表面物种的拉曼强度显著地增强.

**关键词:** 表面增强拉曼光谱; 硫脲; 水; 电荷转移效应