Plasmon-Enhanced Electronic and Vibrational Raman Scattering for Monitoring Interfacial Electrochemical Redox Processes

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Abstract: Nanolaminate nano-optoelectrodes can generate plasmon-enhanced electronic and vibrational Raman scattering signals to probe transition state dynamics during electrochemical redox reactions based on voltage-dependent spectroscopic signatures of interfacial electronic and molecular states at plasmonic hotspots.

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1. Summary

Understanding the mechanisms of electrochemical reactions requires studying transition states (TSs)—the short-lived, high-energy molecular configurations in the reaction pathway [1-2]. While conventional electrochemical surface-enhanced Raman spectroscopy (EC-SERS) primarily provides vibrational information [3], it suffers from limitations in hotspot reproducibility and often overlooks the electronic information associated with TSs.

This study introduces a novel *in situ* dual-channel EC-SERS strategy utilizing scalable nanolaminate nano-optoelectrode (NLNOE) devices [4]. These NLNOEs uniquely integrate plasmon-enhanced vibrational Raman scattering (PE-VRS) and plasmon-enhanced electronic Raman scattering (PE-ERS) to concurrently probe TS dynamics within electrically connected plasmonic nanocavities during electrochemical reactions. Using the AgCl(s) + e− ⇌ Ag(s) + Cl−(aq) redox system on Au/Ag NLNOEs, we demonstrate the capability of this dual-channel approach to capture distinct yet correlated PE-VRS and PE-ERS signatures of the (AgCl)* TS (**Figures 1**).

Our findings reveal a significant increase in PE-ERS signals during interfacial redox reactions concurrent with the emergence of (AgCl)* TSs, characterized by filled bonding and unoccupied antibonding orbitals with negligible energy gaps. Additionally, the observation of increased PE-VRS signals during the redox reaction reveals that the (AgCl)* TS with partial bonding can increase electron cloud distortion under laser excitation to elevate Raman cross-section and PE-VRS signals (**Figures 2**). To further explore the versatility and universality of our dual-channel EC-SERS methodology, we conducted *in situ* EC-SERS measurements with Au-sidewall-coated Au-Ag-Au NLNOE

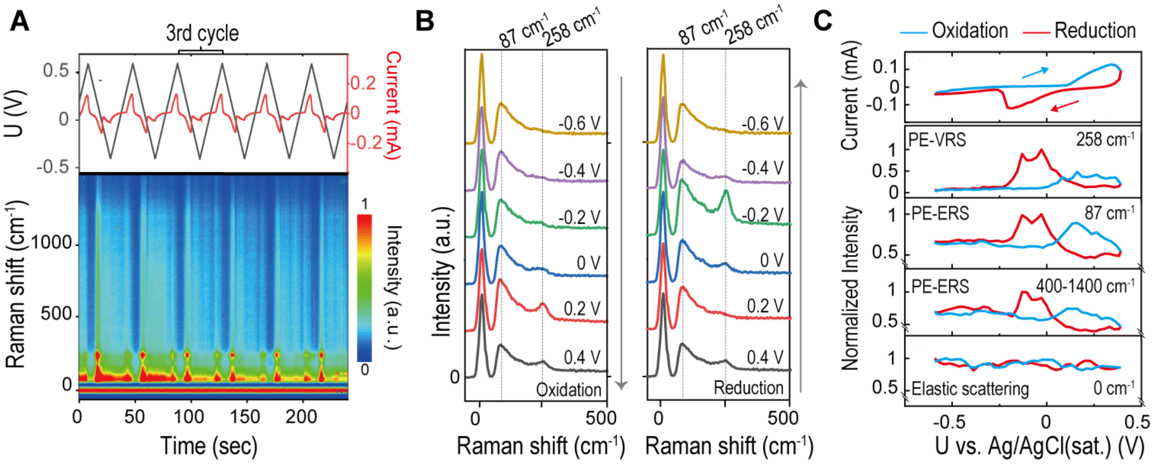

Figure 1: EC-SERS Measurement Insights of PE-ERS and PE-VRS Signals from Au/Ag NLNOEs under Electrode Potential Modulation during $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$ redox cycles. (A) Temporal current measurements (top) taken during CV from 0.4 to -0.6 V, alongside time-resolved EC-SERS spectra (bottom) under 785 nm laser excitation using NLNOEs in 1× PBS solution. (B) EC-SERS emission spectra from NLNOEs in 1× PBS under 785 nm laser excitation at potentials ranging from 0.4 to -0.6 V during a single redox cycle, showcasing oxidation (left) and reduction (right) phases. (C) Cyclic potential-dependent current (top) and normalized EC-SERS emission intensities (bottom) for critical spectral features: the PE-VRS peak at 258 cm^{-1} associated with the stretching vibration of Ag-Cl bonds, the PE-ERS pseudo-peak at 87 cm^{-1}, the broad continuum intensity of PE-ERS signals integrated from 400 cm^{-1} to 1400 cm^{-1}, and elastic scattering peak at 0 cm^{-1}.

devices under different chemical environments. By varying the electrolyte composition (1× PBS and 1× PBS-equivalent KH_2PO_4) while maintaining a constant total ion concentration, we modulated the relative concentrations of Cl^- ions, thereby influencing the competition between Ag/AgCl and Ag/AgH_2PO_4 redox reactions within the Ag nanolayers. Our results demonstrate the capability of the dual-channel EC-SERS approach to distinguish different interfacial redox reactions based on the distinct electronic and vibrational signatures associated with covalent and ionic bond characteristics. This expanded capability highlights the broad applicability of our methodology for investigating interfacial redox reactions in diverse electrochemical systems.

In summary, we have introduced a pioneering dual-channel EC-SERS methodology that synergistically combines PE-ERS and PE-VRS to capture both vibrational and electronic Raman information, providing unprecedented insights into interfacial transition state activities. This approach allows us to successfully probe the (AgCl)* TS activities during redox reactions within the plasmonic nanocavities of Au/Ag NLNOEs. By simultaneously monitoring both electronic and vibrational transitions, this dual-signal strategy offers a richer understanding of interfacial electronic states and significantly expands the scope of EC-SERS applications. Our novel NLNOE design strategically aligns electrochemical reaction sites with plasmonic nanogap hotspots, enabling efficient and accurate spectral measurements for reaction monitoring. The inherent versatility of the NLNOE platform, including the possibility of substituting the silver layer with other reactive materials, opens avenues for extensive exploration of various electrochemical reactions. The effectiveness of this method is demonstrated across different NLNOE nanostructures and chemical environments.

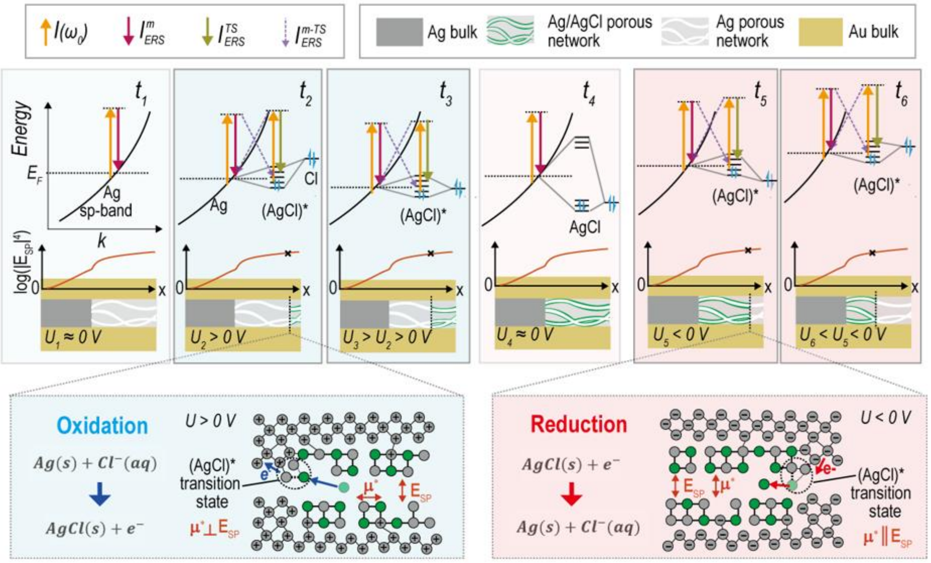

Figure 2: Diagram illustrating the interfacial electronic structures linked to Ag-Cl bond dynamics during the $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$ electrochemical redox reaction within Au/Ag/Au nanogap hotspots at the electrode-electrolyte interface. Microscopic illustration of changes between the steady-state covalent Ag-Cl bonds (or Ag and Cl elements) and the (AgCl)* transition state (TS) within the nanoporous Ag/AgCl network at six representative times.

2. References

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