Probing Electric Field Distributions in the Double Layer of a Single-Crystal Electrode with Angstrom Spatial Resolution using Raman Spectroscopy

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ABSTRACT: The electrical double layer (EDL) is the extremely important interfacial region involved in many electrochemical reactions, and it is the subject of significant study in electrochemistry and surface science. However, the direct measurement of interfacial electric fields in the EDL is challenging. In this work, both electrochemical resonant Raman spectroscopy and theoretical calculations were used to study electric field distributions in the EDL of an atomically flat single-crystal Au(111) electrode with self-assembled monolayer molecular films. This was achieved using a series of redox-active molecules containing the 4,4′-bipyridinium moiety as a Raman marker that were located at different precisely controlled distances away from the electrode surface. It was found that the electric field and the dipole moment of the probe molecule both directly affected its Raman signal intensity, which in turn could be used to map the electric field distribution at the interface. Also, by variation of the electrolyte anion concentration, the Raman intensity was found to decrease when the electric field strength increased. Moreover, the distance between adjacent Raman markers was ∼2.1 Å. Thus, angstrom-level spatial resolution in the mapping of electric field distributions at the electrode−electrolyte interface was realized. These results directly evidence the EDL structure, bridging the gap between the theoretical and experimental understandings of the interface.

Many significant electrochemical reactions happen in the electrical double layer (EDL),1−6 at the electrode−electrolyte interface. The most commonly used model of the electrochemical interface was modified by Bockris et al. on the basis of the Gouy−Chapman−Stern model.7−9 The EDL contains two regions: the Stern layer and the diffuse layer. Starting at the electrode surface and moving out into the bulk electrolyte, the electric potential first decreases linearly (Stern layer) and then exponentially (diffuse layer). The EDL structure influences the electric potential distribution within these layers, which can affect the electrochemical reaction mechanisms and rates. Hence, elucidating EDL structures and electric field distributions is an important but challenging fundamental endeavor.

Recently, techniques such as cyclic voltammetry and infrared, Raman, and X-ray absorption spectroscopies have been applied to study interfacial layers and the EDL structure.10−19 For example, Gooding et al.12 used cyclic voltammograms (CVs) of self-assembled monolayers (SAMs) of ferrocene on electrode surfaces to measure the formal potential of surface ferrocene. They then calculated the interfacial potential distribution of the electrical double layer using the method proposed by Smith and White.15 Harris et al. used surface-enhanced Raman spectroscopy to measure the Stark tuning rates of nitrile-terminated SAMs to predict interfacial electric fields.11 Despite these significant advances, those techniques rely upon SAMs with unstable thicknesses and roughened Ag electrode surfaces, which structurally vary and thus cannot accurately measure electric fields with angstrom resolution.

In the present work, electrochemical resonant Raman spectroscopy was used to measure the electric field distribution within the double layer at the electrode−electrolyte interface of an atomically flat single-crystal Au(111) electrode coated with different viologen-based SAMs (Figure 1a). To maintain uniform SAM thicknesses, seven different viologen molecules with different alkyl chain lengths but a total length of 16 carbon atoms (Figure 1b) were synthesized and used to construct the SAMs. The seven viologen molecules are labeled HS-nV(16 − n). From the mercapto surface anchoring group, the alkyl chain lengths (n and 16 − n) were varied to change the position of the 4,4′-bipyridinium group (V), used as a Raman marker, within the overall molecule. Thus, the distance between the Raman marker and the electrode surface could be precisely controlled and changed. By variation of the distance of the marker group from the surface and measurement of changes in its Raman signal intensity, the changes in the electric field distribution within the double layer were observed with angstrom spatial resolution. By measurement and

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Of the three states, the V⁺ oxidation states are presented in Figures 1d and S2. **simulation of the signal intensities of the Raman marker at different electrolyte concentrations, the effect of changes in the double layer electric field distributions could be effectively imaged, providing important information about the EDL structure.**

The redox-active viologen moiety has three distinct oxidation states and two successive one-electron redox processes: V⁺ and V++ (Figure 1c). Current work also used to calculate the SAM surface coverage (Table S1), corresponding to a surface coverage of (3.5 × 10⁻⁸ mol/cm²), which is consistent with literature reports. However, it is significantly lower than the surface coverage of densely packed alkanethiol SAMs (~8 × 10⁻¹⁰ mol/cm²). Therefore, electrolyte ions will likely be able to penetrate into the SAMs and form ion pairs with viologen moieties, thereby influencing electric fields in the double layer. The ion-pair concentration will differ with changes in surface coverage, which can change the nature of the double layer.

The experimental/calculated Raman spectra of different viologen oxidation states are presented in Figures 1d and S2. Of the three states, the V** radical cation, unlike the other two states, is stable and can produce strong resonant Raman spectra under 638 nm laser illumination. Figure 2a shows the resonant Raman spectra of the seven viologen SAMs on Au(111). All of the spectra have been normalized to the surface coverage. In all of the spectra, four characteristic Raman bands attributed to V** are visible at 1028, 1359, 1529, and 1656 cm⁻¹. The strongest V** band at 1529 cm⁻¹ is assigned to in-plane C−C stretching and C−H bending in the 4,4'-bipyridinium group. Differences in the normalized Raman intensities of the 1529 cm⁻¹ band of the respective SAMs can be used to study the electric field distribution at different positions in the double layer. Figure 2b (black line) shows the normalized Raman intensity of the 1529 cm⁻¹ peak as a function of the alkyl chain length n. The normalized Raman intensity first increases then decreases as n increases, reaching a maximum at HS-6V10. Additionally, the formal oxidation potentials of the viologen molecules (Figure 1c) are included in Figure 2b (red dotted line). With increasing distance from the electrode surface, the potential drops sharply and then slowly, and the change in oxidation potential is roughly consistent with the Raman intensity result that the turning point occurred at HS-6V10. On the basis of the literature, changes in oxidation potential due to the changing distance of the redox-active viologen marker group from the electrode surface may be related to the EDL structure. The Raman intensity of the 1529 cm⁻¹ peak is also affected by the electric fields in the double layer and increases sharply when V** moves out of the Stern layer. However, it does not continue to rise and begins to decrease. Intrinsically structural properties and ion-pair formation may contribute to this decrease in Raman intensity. In Figures 2c,d, S3, and S4, the intrinsic Raman intensities of the seven HS-nV(16 − n)** molecules are fundamentally the same, while their dipole moments are different because of the different charge distributions, which influence the Raman intensity in the electrochemical environment.

Because of the hydrophobic nature of V**, polarizing the electrode surface will result in the formation of an ion-pair layer between V** and the electrolyte anion, producing an induced electric field in the SAMs. As discussed previously, the ion penetration into the SAMs is dependent on the surface coverage and anion concentration in the electrolyte, while the Raman intensity of V** spectral bands is influenced by the induced electric field. For these reasons, the Raman intensities for all of the molecules were calculated under exposure to different electric dipole fields at −0.7 V vs SCE (Tables S2–S8). Clear Raman intensity changes occur as a result of
changes in the electric dipole field, and the degree of change differs among the molecules, suggesting that the sequence of Raman intensity for the seven molecules would be changed in different induced electric fields.

To verify the accuracy of the above results, the concentration of ion pairs was adjusted by varying the NaClO₄ electrolyte concentration to study the effect of the induced electric field on the spectral band intensities of the Raman markers in the different SAMs. In Figure 3a, the electric Raman intensity of the 1529 cm⁻¹ viologen molecule (HS-6V10) on the Au(111) electrode. The shows a maximum Raman intensity shift to HS-8V8 upon increasing the electrolyte concentration induces stronger dependence of the 1529 cm⁻¹ peak for the seven molecules exposed to 0 au and −0.010 au dipole electric fields. Intensities are given relative to 8V8. (d) Concentration dependence of the 1529 cm⁻¹ intensities for HS-6V10 in NaClO₄, NaF, and NaBr.

The largest contribution to our understanding of the electric double layer. The largest distribution of V⁺ is equal for sites of HS-6V10 and HS-8V8. Figure 4b shows the effective potential of the Raman marker group without the induced electric field. The potential is steady near the Au(111) surface and then decreases, which conforms to the EDL theory. These results suggest that the Raman intensity is influenced by synergistic effects involving the applied potential and induced electric field dictated by the electrolyte concentration. The Raman intensity of one marker group provides unambiguous evidence regarding the interaction between the applied potential and the induced electric field and maps the nₑ distribution in the double layer.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c05162.

Experimental and Computational Section, schematic illustration of the spectroelectrochemical cell, Raman spectra of HS-6V10 in different states, dipole vectors of seven molecules, Raman spectra of seven molecules in NaF, Raman spectra of HS-6V10 and HS-12V4 in different concentrations of NaClO4, Raman spectra and CVs of HS-6V10 at different concentrations of NaF and NaBr (PDF)

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Notes
The authors declare no competing financial interest.

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