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Electrochemical behavior of N-methyl-N′-carboxydecyl-4,4′-bipyridinium probed by surface-enhanced Raman spectroscopy

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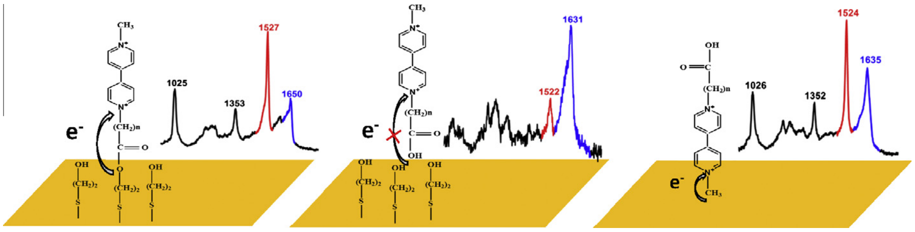
HIGHLIGHTS

- The electrochemical redox process of molecules was spectrally resolved.
- The different interaction modes between molecule and substrate were spectrally distinguished.
- Relative Raman intensity and frequency shift are sensitive to interfacial interaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Interfacial structure determines the activity and selectivity of a sensor and plays important roles in interfacial electrochemistry, electroanalysis, biosensing, etc. In situ electrochemical Raman spectroscopy appears to be a powerful tool to probe the electrochemical interface and surface process by providing the molecular fingerprint information. Herein, the electrochemical behaviors of N-methyl-N′-carboxydecyl-4,4′-bipyridinium (derivatives of methyl viologens, MV^{2+}) with different alkyl chain lengths ($n = 2$ and 10) on roughened Au electrodes were systematically investigated by the electrochemical surface-enhanced Raman spectroscopy (SERS). Three systems with different interfacial structures were constructed. One is to anchor the MV^{2+} molecules via esterification with the 2-mercaptoethanol molecule pre-assembled on the Au surface. The second system is similar to the first one but without esterification. The third system is the direct adsorption of MV^{2+} molecules on the bare roughened Au surfaces. The three systems gave different spectral response upon the change of the electrode potential. A drastically increased relative Raman intensity of 19a/8a modes of the MV^{2+} molecules was observed at negative potentials. The phenomenon is attributed to the formation of the reduced form of MV^{2+} molecules, which produces resonant Raman effect to enhanced the signal of 19a mode. The third system showed the highest electrochemical reduction activity towards the reduction of MV^{2+} molecules, followed by the first and second systems. The result indicates that the interfacial structure can sensitively influence electrochemical activity of the electrode.

Introduction

Interfacial structure determines the activity and selectivity of a sensor and plays important roles in interfacial electrochemistry, electroanalysis, biosensing, etc. [1–4]. Self-assembled monolayer (SAM) method appears to be a very convenient, flexible, simple but important approach to adjust the chemical and physical properties of the surface (including metals, metal oxides and semiconductors) [5–16]. SAM was initially discovered for surfactant and then alkanethiolates on metal surfaces, and has attracted great attention for several decades. Due to the strong interaction between thiol and gold, the SAMs of alkanethiolates on gold surfaces is the mostly studied system [7,15,17–24], which can be stable in the aqueous solution for several weeks.

SAMs with ω-functional groups, such as –OH or –COOH, provides reliable model systems for the investigation of interfacial chemistry

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related to wettability [25], friction [26], adhesion [27], and corrosion [28]. However, further modification of ω-functional groups are demanded for the application in the molecular device, biology and biochemistry [7,29]. A great amount of functional compounds have been anchored on Au surfaces through traditional organic reactions, such as esterification, acylation, and nucleophilic substitution (or addition) [30–35], to achieve different functions. For example, molecular switches can be obtained by immobilizing molecules with a high electrochemical activity on the surface [30] and the potential dependent orientation [32] and distance dependent electron transfer [32] have been analyzed by controlling the molecular length between substrate and functional target molecule.

To achieve the practical applications of SAMs, it is crucial to understand the interfacial properties, such as surface morphology, surface hydrophobicity/hydrophilicity, interfacial electron transfer rate, optical properties, surface orientation and structure. For these purpose, various surface analytical techniques have been involved, including SPM [16,20–22], contact angle goniometry [17,21,23,32], electrochemistry [32–35], ellipsometry [17,23,36], SPR [37], EELS [38], Infrared [39], Raman [40] and SFG [41]. Raman spectroscopy, especially surface-enhanced Raman spectroscopy (SERS), outstands itself by providing fingerprinted surface structural information for surface species on coinage and transition metal surfaces [42–45]. Recently, SERS has been developed to investigate thiol SAMs on roughened Au surfaces under different conditions: alkyl chain length, terminal group, and electrode potential [40,46–50].

Viologens have been widely applied to characterize the interfacial structure of SAMs on the electrode surface, due to the well-defined oxidation/reduction process [32,51]. Viologens also shows very characteristic Raman signature that allows the identification of its states on the surface [52]. Therefore, in this paper, we used viologens as a Raman probe to investigate the effect of the interfacial structure on the electrochemical process by SERS. We systematically studied the potential dependent electrochemical behavior of methyl viologen derivative N-methyl-N′-carboxydecyl-4,4′-bipyridinium (MV^{2+}) either anchored via esterification, spaced by thiol SAMs, or directly adsorbed on a roughened Au electrode. Different interfacial electrochemical processes and surface orientations of molecules could be clearly distinguished with the rich information provided by SER spectra.

Experimental

N-methyl-N′-carboxydecyl-4,4′-bipyridinium ($HOOC(CH_2)_nC_4H_4N_2C_4H_4N_2CH_3$) ($n = 2$, 10) was synthesized following the protocol described in Ref. [35]. For simplification, we named these two molecules as $MV2^{2+}$ and $MV10^{2+}$, respectively, or MV^{2+} for both. 2-mercaptoethanol and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) were purchased from Aldrich and used without further purification.

A polycrystalline Au rod (diameter 2 mm) was used as the working electrode. The counter and reference electrodes were a platinum ring and a saturated calomel electrode (SCE), respectively. All solutions were prepared with analytical grade reagents and Milli-Q water.

The SERS-active Au electrode was achieved following the method described in Ref. [53]. After rinsed with water, it was immersed in 0.1 M 2-mercaptoethanol for 6 h, then washed with water thoroughly to remove the physisorbed molecules. The Au electrode covered with the SAM of 2-mercaptoethanol was incubated in 0.1 M phosphate buffer (pH = 7) containing 1 mM $MV2^{2+}$ (or $MV10^{2+}$) with equal molar EDC for overnight, then rinsed with a large amount of water and mounted to a spectroelectrochemical cell filled with 0.1 M phosphate buffer solution (pH = 7) as the electrolyte.

Raman spectra were obtained using a confocal microprobe Raman system (LabRam I, Jobin Yvon, France). The excitation line was 632.8 nm from a He–Ne laser. A 50× long working distance (8 mm) objective was used.

Results and discussion

SAMs of MV^{2+} molecules anchored on a roughened Au electrode via esterification or direct adsorption

Fig. 1 shows the cyclic voltammogram of $MV10^{2+}$-anchored Au electrode in 0.1 M phosphate buffer solution (pH 7.0). A 500 mV/s scan rate was selected to achieve a curve with better identification of the redox peak compared with that obtained at a lower scan rate. The Au surface was functionalized with 2-mercaptoethanol SAMs first, which was then esterificated with $MV10^{2+}$. The redox peaks of viologen clearly appear at ca. −0.6 V, similar to the case reported on a smooth Au surface [32,35,51,54]. Whereas, the oxidation peak is weaker but broader than the reduction one in comparison with the nearly symmetric redox pair on the smooth surface. The different reversibility of the redox process might be ascribed to the highly heterogeneous morphology of a rough surface, resulting in a different spatial accessibility to the redox center.

Potential dependent SER spectra of $MV10^{2+}$ on the Au electrode and the normal Raman spectrum of the $MV10^{2+}$ solid are given in Fig. 2a. The SER spectra are much different from that obtained on a roughened Au electrode modified with thiol only (see Fig. S1), indicating the successful esterification of MV molecules on the Au surface. The tentative assignments of SERS peaks and normal Raman peaks are given in Table 1 according to previous experimental and theoretical investigations of viologen group [55–58]. With the negative shift of the potential from 0.3 V to −0.5 V, the SERS signal keeps increasing. But, the intensity increases drastically when the potential was further negatively moved to −0.7 V. The SERS signal is then decreased at more negative potentials (not shown), due to the interference of the hydrogen evolution in the interface.

The SER spectra and normal Raman spectrum of $MV2^{2+}$, a viologen with shorter chain, were shown in Fig. 2b and the related Raman peak assignment is also given in Table 1. Similar potential dependent behavior was observed for $MV2^{2+}$. However, the absolute SERS intensity (at −0.7 V) of $MV2^{2+}$ is about five folds stronger than that of $MV10^{2+}$. This phenomenon can be understood by a weaker EM enhancement for $MV10^{2+}$ molecule, because a longer

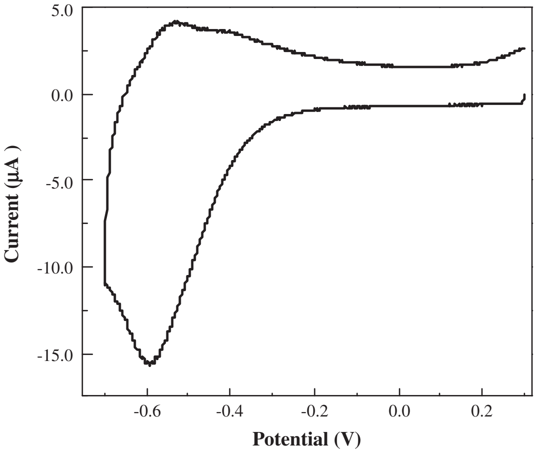

Fig. 1. Cyclic voltammogram of $MV10^{2+}$-functionalized Au electrode in 0.1 M phosphate buffer solution (pH 7.0). Scan rate is 500 mV s^{-1}.