

In situ Raman spectroelectrochemistry of azobenzene monolayers on glassy carbon

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Abstract In situ Raman spectra of chemisorbed azobenzene (AB) monolayers on glassy carbon (GC) electrodes were observed under potentiostatic conditions in acetonitrile (ACN) with tetrabutyl-ammonium tetrafluoroborate (TBA-BF₄). The Raman intensities of these spectra were high below -1000 mV, and this is attributed to the change in absorbance of AB on GC. In this paper, we describe chemisorbed AB molecules on GC electrode surfaces under potentiostatic conditions.

Keywords IR spectroscopy/Raman spectroscopy · Electroanalytical methods · Nanoparticles/nanotechnology

Introduction

Raman spectroscopy in conjunction with electrochemistry, known as in situ Raman spectroelectrochemistry, has been widely used in research for the characterization of materials, especially electrochemically active materials [1–9]. Our group has successfully used this technique for the identification of electrochemical reactions on anode and cathode materials in lithium ion batteries, and near the interface between the electrode surface and electrolyte solution in

batteries, fuel cells and molecular electronic devices [2–9]. This combination of high-resolution Raman spectroscopy and electrochemistry has proven to be advantageous in the study of reactions in the interfacial reaction field between an electrode and electrolyte solution.

Surface-enhanced Raman spectroscopy (SERS) has been used extensively since 1974 to study the microscopic features of surfaces [10]. If an electrode supports SERS by electromagnetic field (EM) and charge transfer (CT) mechanisms, then the Raman intensity of molecules adsorbed on the electrode surface is enhanced by a factor of 10⁵–10⁶ compared with that for free molecules when the SERS effect is applied [1, 10]. Unfortunately, since carbon does not support an EM mechanism, obtaining a Raman spectrum from a carbon adsorbate is not easy, especially under electrochemical conditions, because a CT contribution is required in order to acquire the surface Raman spectra [11, 12]. We have previously reported 4-nitroazobenzene (NAB) chemisorbed on a glassy carbon (GC) electrode surface under potentiostatic conditions using very sensitive spectrometers incorporating CCD detectors [6]. The in situ Raman spectra were consistent with the formation of a quinoid structure containing a C=C double bond between NAB and the graphitic surface. Electron transfer and spectral changes occurred over a wider potential range than expected for a conventional Nernstian equilibrium, but did not appear to be broadened by slow electron transfer kinetics. The results implied a coupling between the graphitic π system and the NAB orbitals. Rather than a discrete electron transfer to a free molecule, the electron transfer to chemisorbed NAB is more gradual, and presumably driven by the electric field at the electrode and solution interface.

In this paper, we present in situ Raman spectra for azobenzene (AB) chemisorbed on a GC electrode surface

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under potentiostatic conditions in acetonitrile (ACN) containing 1 M tetrabutyl-ammonium tetrafluoroborate (TBA-BF₄). The results reveal the change in the electronic structure of AB from the change in the in situ Raman spectra under electrochemical conditions.

Experimental

A special electrochemical cell made of Pyrex glass with a sapphire window was constructed for simultaneous electrochemical and Raman measurements. A 6×4×1.5 mm³ substrate for the working electrode was made of GC (GC-20, Tokai Carbon Co., Ltd., Tokyo, Japan). The effective area of the GC in contact with the electrolyte was 24 mm². In order to obtain a specular electrode surface, the GC was successively polished with 1.0 μm, 0.3 μm and 0.05 μm alumina slurries, and then rinsed with Millipore water.

A schematic of the NAB and AB derivatization procedure is shown in Fig. 1 [6, 13, 14]. NAB and AB were chemisorbed onto GC as the NAB diazonium salt (NABDS) and the AB diazonium salt (ABDS) formed by electrochemical reduction in ACN containing 1 M TBA-BF₄. The derivatization scan was one cycle of the cyclic voltammogram (CV; 200 mV/s) between +400 mV and -1800 mV, so as to avoid multilayer formation.

The potential of the derivatized GC electrode against an Ag/Ag⁺ electrode in ACN containing 1 M TBA-BF₄ was controlled with a conventional potentiostat, and all potential values quoted in this paper use the same reference. A platinum wire was used as the counter electrode. To avoid degradation of the electrolyte solution (1 M TBA-BF₄ in ACN) due to oxygen in air, all electrochemical experiments were performed in an Ar or N₂ atmosphere.

The 514.5 nm line of an argon ion laser (10 mW) was focused at the sample on the modified GC electrode [6]. Scattered light was collected and then dispersed by a high-throughput spectrometer. The Raman spectrum was taken with a highly sensitive CCD detector or an intensified diode

array detector between 500 cm⁻¹ and 2400 cm⁻¹ in one measurement at the various electrode potentials. The data accumulation time for one spectrum was 1000 s or less.

Results and discussion

Diazonium salt in ACN is electrochemically reduced on the GC electrode surface, as shown in Fig. 1. After electrochemical reduction of the diazonium salt, AB chemisorbs on the GC electrode surface. The CV curve was recorded at a scan rate of 200 mV/s for the GC electrode immersed in ACN containing 1 mM ABDS and 1 M TBA-BF₄, and is shown in Fig. 2. To avoid multilayer formation of AB, the derivatization CV scan consisted of one cycle. The current response due to the ABDS molecules was observed at approximately 0 V. The CV curve for ABDS salt is almost consistent with that measured in our previous experiments. After the derivatization of AB molecules on the GC surface, the electrode (AB-GC electrode) was subjected to in situ Raman measurements.

Figure 3 shows a CV recorded at a scan rate of 200 mV/s for the AB-GC electrode immersed in ACN containing 1 M TBA-BF₄. In our previous paper, we measured cyclic voltammograms for surface NAB monolayers on GC in ACN [6], and a current response was observed at approximately +1000 mV. AB may also be reduced below -1000 mV. However, no significant current response was observed for the AB-GC electrode in Fig. 3. In the potential range between +400 mV and -1800 mV, the structure of the NAB molecules on GC changes with an electronic structural change to a methide structure [6]. In spite of the lack of a current response, we expect that structural or

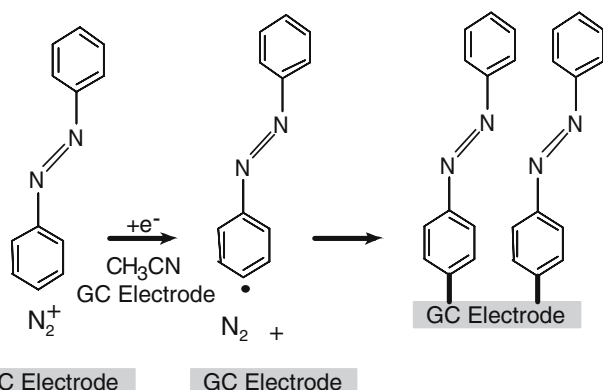


Fig. 1 Schematic of the AB derivatization procedure

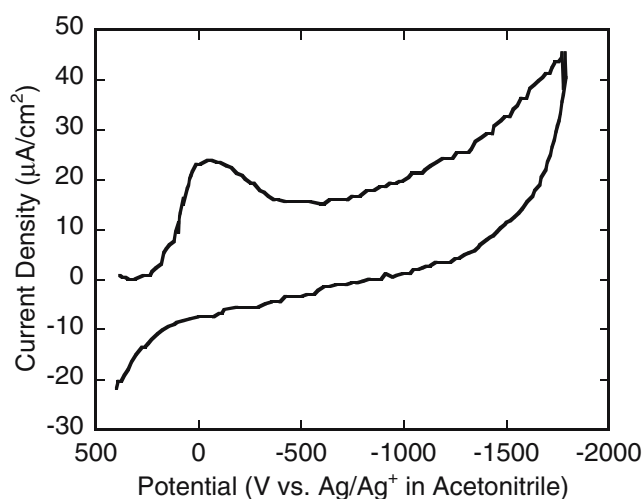


Fig. 2 Cyclic voltammogram for ABDS reduction on a GC electrode immersed in ACN containing 1 M TBA-BF₄, recorded at a scan rate of 200 mV/s

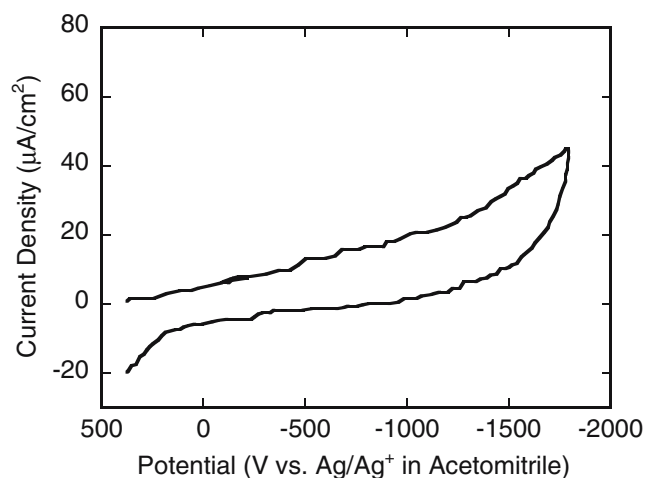


Fig. 3 Cyclic voltammogram for the AB-GC electrode immersed in ACN containing 1 M TBA-BF₄, recorded at a scan rate of 200 mV/s

electronic changes will occur in molecules on GC electrodes in AB-GC systems at various potentials.

In order to assign Raman lines to the AB molecules, Fig. 4 compares the relationship between 1 mM NABDS and ABDS contained in the electrolyte solution of ACN containing 1 M TBA-BF₄. A strong background due to fluorescence from NAB and AB molecules was observed in the raw spectra. The visible background was subtracted from the Raman spectra obtained as shown in Fig. 4. The actual background in NABDS was stronger than that observed for ABDS. The two Raman spectra include Raman lines attributed to the vibrations of both NABDS and ABDS molecules. The significant difference between the two Raman spectra is the Raman line for phenyl-NO₂ at 1107 cm⁻¹, which was not observed for ABDS. Therefore, these spectra are attributed to NABDS and ABDS molecules [6, 11, 12, 15].

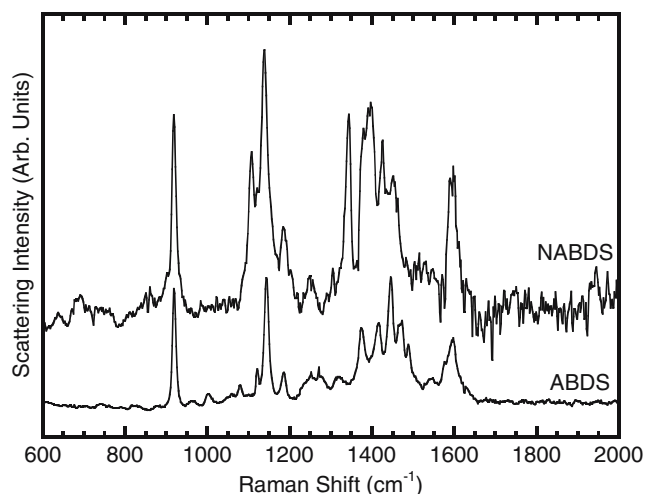


Fig. 4 In situ Raman spectra for NABDS and ABDS in ACN containing 1 M TBA-BF₄

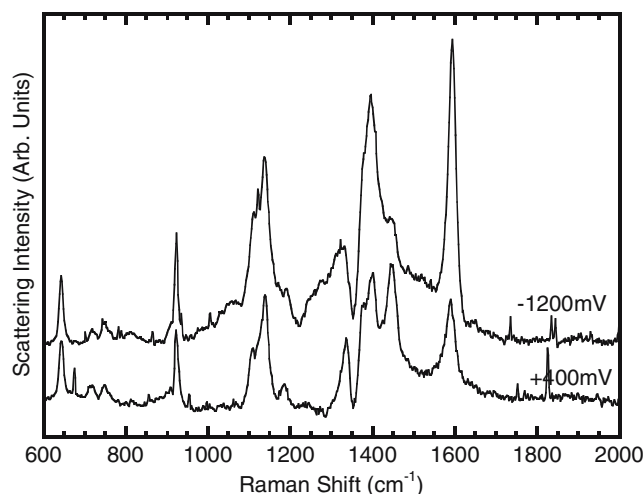


Fig. 5 In situ Raman spectra for NAB on GC in ACN containing TBA-BF₄ at +400 mV and -1200 mV

Raman spectral changes for NAB molecules on GC at both +400 mV and -1200 mV are shown in Fig. 5. The Raman spectra in Fig. 5 have had the Raman lines for ACN and GC subtracted from the raw spectra. Since ACN and GC have strong Raman intensities, we subtracted ACN and GC lines. In particular, several Raman lines at -1200 mV (Fig. 5), 1108.8 cm⁻¹ (phenyl-NO₂ stretch), 1138 cm⁻¹ (phenyl-NN), 1397.5 cm⁻¹ (N=N stretch) and 1592.6 cm⁻¹ (C=C stretch) are clearly more intense than the Raman lines at +400 mV [6, 11, 12, 15]. These lines are attributed to reduced NAB (methide) at -1200 mV [6].

Figure 6 shows in situ Raman spectra for AB on GC in ACN containing 1 M TBA-BF₄ at +400 mV and -1200 mV. The Raman intensity for AB on GC is weaker than that for NAB. In spite of a frequency shift, the Raman spectrum for AB on GC at +400 mV is similar to that for ABDS in ACN. The Raman intensities for several modes are increased at

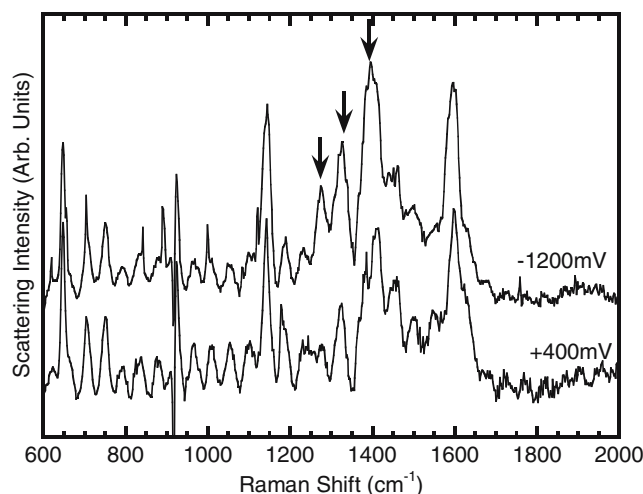


Fig. 6 In situ Raman spectra for AB on GC in ACN containing TBA-BF₄ at +400 mV and -1200 mV

–1200 mV. In fact, the Raman intensities for N=N stretching modes at 1277 cm^{-1} , 1379 cm^{-1} and 1399 cm^{-1} at +1200 mV are higher than those at +400 mV [6, 11, 12].

Chemisorbed NAB was previously reported to have a stronger Raman intensity, associated with resonance enhancement, than that for free NAB [6]. Since we have already observed increasing Raman intensities for monolayers of NAB and AB on GC at +400 mV, the resonance effect was expected in this experiment. On the other hand, we have previously proposed that a NAB molecule on GC changes into the NAB anion or methide below –1000 mV [6]. These changes accompany bonding structural rearrangements in the NAB molecule along with a decrease in valence value. The rearrangements might cause changes in the absorption of NAB molecules on GC. For the case of AB, absorption effects due to bonding structural rearrangements might also be expected. As a result, the Raman intensities for NAB and AB molecules on GC are more intense, due to a stronger resonance effect between the surface species and GC with the change in the potential. Unfortunately, a change in absorbance may not distinguish NAB/reduced NAB and AB/reduced AB on GC, because GC has low reflectance in reflection absorbance spectroscopy. Based on a comparison of the Raman spectra for NAB and AB at –1200 mV, the NAB spectrum is clearer than that for AB at –1200 mV. A possible explanation for this difference could be the difference in the polarizations of the NAB and AB molecular structures. Further work is required to obtain a more definite clarification of the dynamic behavior of electrochemical reactions with electron transfer.

Conclusion

An AB monolayer was electrochemically reduced at –1200 mV. At this potential, the Raman intensities for

reduced AB were increased. The reason for the increase in the Raman intensity is the change in absorbance for reduced AB. A likely explanation for this is the resonance enhancement of the electrochemically reduced AB-GC. The experimental results suggest that spectroelectrochemistry is a valid technique for electrochemical microanalysis of a GC–electrolyte interface.

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