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Full Length Research Paper

Study of electron transfer process of TCNQ under external electric field

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A series of electron transfer process of 7,7,8,8-tetracyanoquinodimethane (TCNQ) under external electric field was observed according to the ultraviolet-visible and Fourier transformed Raman spectra of TCNQ obtained with the self-made biservice electrochemistrical thin film cell for ultra-violet/Raman spectrometer in the present work. The concrete process refers to TCNQ turned into TCNQ$^-$, then into TCNQ^{2-} as well as the process of TCNQ^{2-} being oxidated into dicyano-p-toluoyl cyanide (DCTC$^-$) in the presence of oxygen under external electric field. The behaviors of some characteristic peaks, such as the one around 400 nm of TCNQ, around 700 to 900 nm of TCNQ$^-$ and around 330 and 488 nm of TCNQ^{2-} at different circumstances were found according to the aforementioned spectra. Meanwhile, the interpretation of these peaks was presented in this study. This paper is valuable in pharmacokinetics, biomembrane and chemical sensor, etc.

Key words: Electron transfer, TCNQ, spectra, electric field.

INTRODUCTION

7,7,8,8-tetracyanoquinodimethane (TCNQ, whose molecular formula is $C_{12}H_4N_4$) can form various thin films of complexes with perfect photoelectric properties by combining them with different kinds of metals or compounds. Therefore, it is well focused owing to its wide potential prospect in application (Ho and Liao, 2003). The investigation of electron transfer process in liquid especially the electrochemistry has been widely focused because much difficult issue in physical chemistry, such as the utility of pharmacokinetics, biomembrane and chemical sensor, etc., had been solved by means of electrochemistry method (Zhang et al., 2002; Qu et al., 2010). Due to its unusual electron transfer properties, some investigations of TCNQ were undertaken (Kamitsos and Risen, 1983; Gu et al., 1994; Gorishnyi et al., 2011; Choi et al., 2002). These investigations focused mainly on electrical conductivity properties of the coordination compounds coordinated from TCNQ and metallic ion, the properties of TCNQ$^-$ and TCNQ^{2-} formed from TCNQ as well as the various photoelectric properties of the TCN Q coordination compounds thin film (Mochida et al., 2003; Duyne et al., 1979; Wan et al., 2000; Oyamada et al., 2003). Majority of investigations on TCNQ were taken under some microenvironment, such as various solutions and under various external fields. So far, the investigation of electron transfer process of TCNQ in liquid by means of electrochemistrical method has not been reported. In this article, we focused the effect of some micro-environments on TCNQ especially external electric field. Accordingly, detailed electron transfer process of TCNQ under external electric field was investigated according to the UV-Vis spectrum and Fourier transformed Raman spectrum of TCNQ. Accordingly, some laws were obtained experimentally.

This article aims at investigating the behaviors of electron transfer process of TCNQ under external electric field according to the spectra of TCNQ, TCNQ$^-$ and TCNQ^{2-}, and discussing the mechanism of the behaviors.

MATERIALS AND METHODS

Some of the instruments used in this study are TU-1901 ultraviolet visible optical absorption spectrometer made in Beijing Puxi Tongyong, and RFS100/S Fourier transformed Raman spectrometer.

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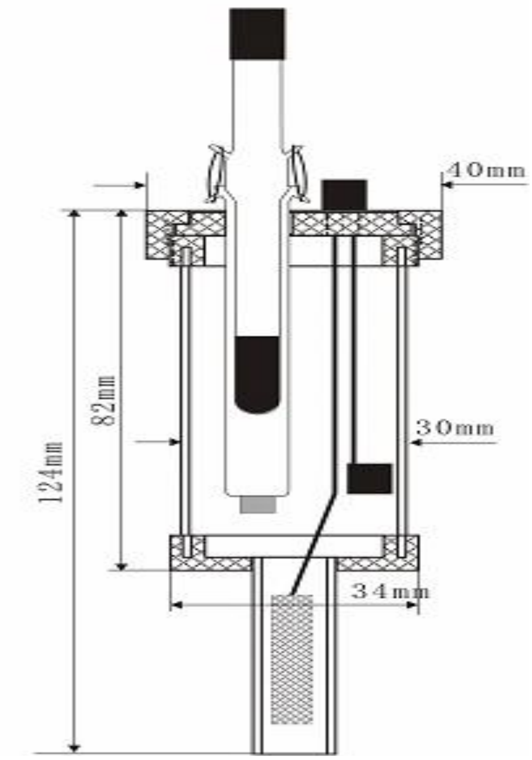


Figure 1. Self-made thin cell.

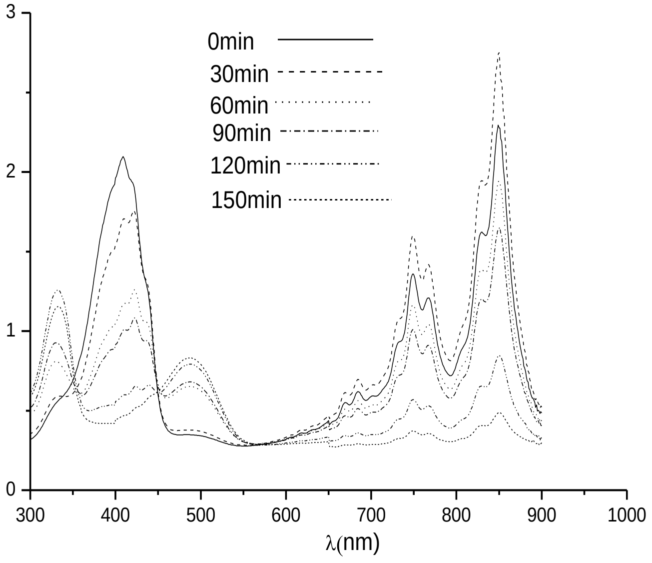


Figure 2. UV-Vis spectra of TCNQ in DMF at different electrical running time.

Besides, a self-made ultra-violet/Raman biservice electrochemistrical thin film cell was devised in our laboratory (Figure 1), which is practically used in investigating microenvironment effect on TCNQ. In the cell, platinum net was chosen as the working electrode, platinic slice was chosen as the pair-electrode and saturated calomel electrode was chosen as reference electrode. Meanwhile, saturated NaCl solution was chosen as the salt bridge to keep the concentration of Cl^- stable. Impedance effect and edge effect are also taken into account.

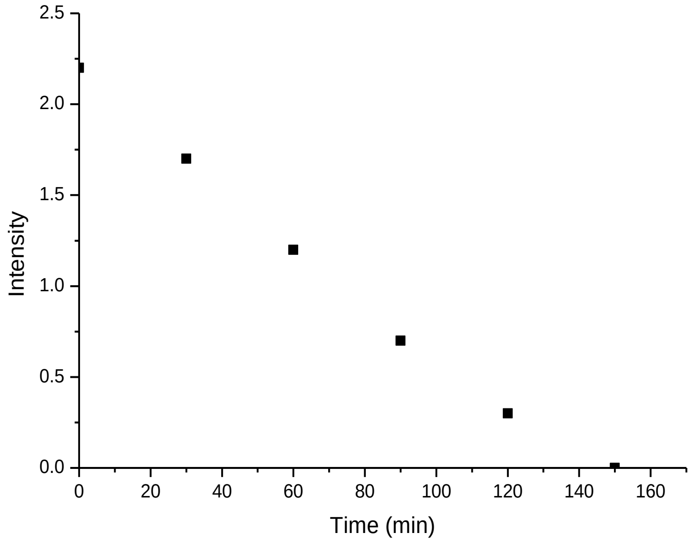


Figure 3. Tendency of UV-Vis absorption peak of TCNQ in DMF with electrical running time at 400 nm.

All samples are analytical reagents: liquid N, N-dimethyl formamide and liquid chloroform with their purity being all over 99.5% was chosen; TCNQ was purchased from Fluka Company, and its purity is over 98%; NaCl whose purity is over 99.8% was chosen.

TCNQ was dissolved into N,N-dimethylformamide (DMF), and then the solution of TCNQ in DMF was confected at the concentration of 10^{-4} mol/L with a little chloroform dissolved in the solution as supporting electrolyte. Also, 10 ml saturated NaCl solution was confected and then put into the thin film cell. The UV-Vis absorption spectra of the samples were measured using the TU-1901 ultraviolet visible optical absorption spectrometer.

In the same way, the solution of TCNQ in DMF with concentration of 10^{-3} mol/L with a little chloroform dissolved in the solution as supporting electrolyte was also confected. 10 ml saturated NaCl solution was also confected and then was put into thin film cell. The Fourier transformed Raman spectra TCNQ in DMF were measured using the RFS100/S Fourier transformed Raman spectrometer. All measurements were taken at room temperature and under ambient pressure.

RESULTS AND DISCUSSION

We measured the UV-Vis absorption and Raman spectra of TCNQ in DMF under external electricity. Figure 2 shows the variation of UV-Vis absorption spectra of TCNQ in DMF with electrical running time. Figure 3 indicates the tendency of UV-Vis spectra of TCNQ in DMF at 400 nm with electricity time. Figure 4 indicates the tendency of UV-Vis absorption peak intensity of $TCNQ^-$ in DMF with electricity time at the range of 700 to 900 nm.

The following behaviors can be easily found in Figure 3, which have not been reported before. Firstly, the UV-

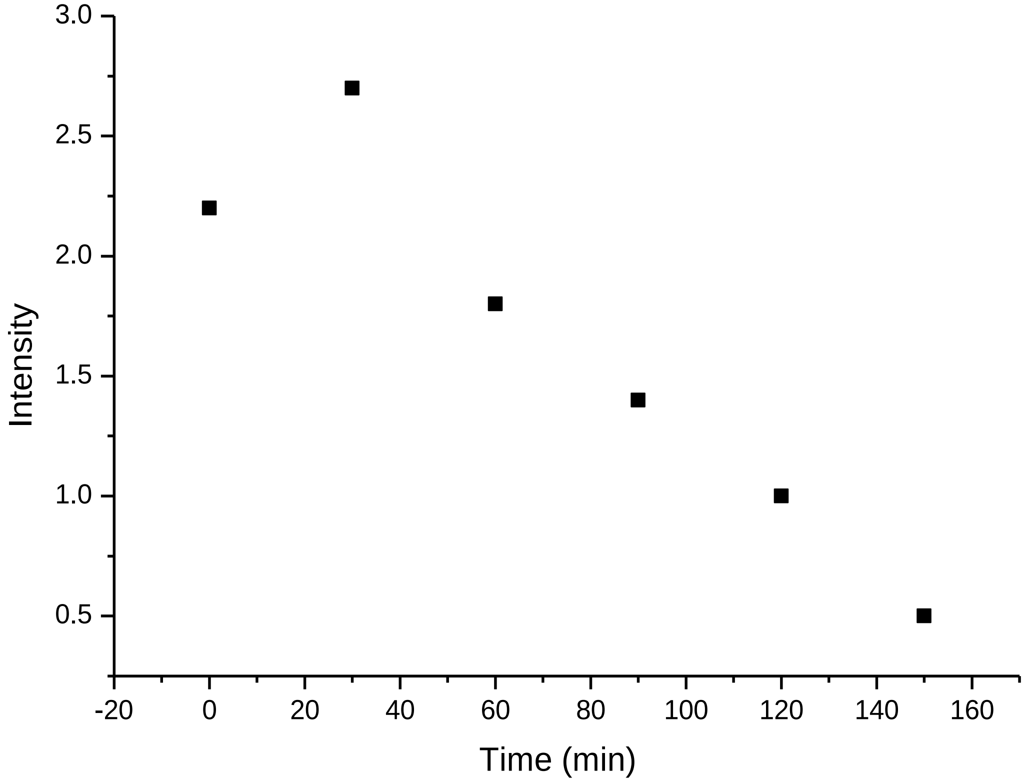


Figure 4. Intensity tendency of UV-Vis absorption peak of TCNQ- in DMF with electrical running time within 700 and 900 nm.

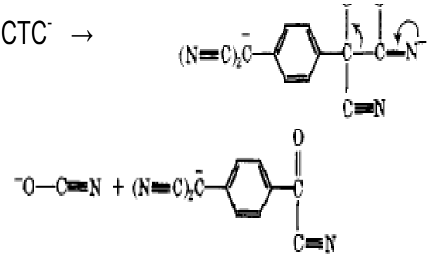
Vis absorption peak intensity at 400 nm which is of π→π* transition decreased with increasing the electrical running time, and even disappeared afterwards. Secondly, the intensity of the continuous absorption band of 700 to 900 nm appeared differently with increasing electrical running time. Concretely, it increased at first and then decreased gradually with increasing electrical running time. Thirdly, with the increase of electrical running time, that is, the increase of the electric charge quantity, the absorption peak intensity at 330 nm increased gradually. Fourthly, at the apparent increase of the peak intensity at 330 nm, the peak intensity at 488 nm increased gradually afterwards. Finally, during the electrical running time, the absorption peak intensities of 330 and 488 nm are both weaker than that of 400 nm.

The interpretation for the phenomena mentioned earlier mainly embodies as follows. Being a good electron acceptor, TCNQ can easily turn into univalence anion $TCNQ^-$ after accepting an electron. Then, it can turn further into bivalence anion $TCNQ^{2-}$ after accepting another electron due to the symmetric structure of the two sides of the benzene ring in it. The univalence anion $TCNQ^-$ and the bivalence anion $TCNQ^{2-}$ of TCNQ are all stable without oxygen. Nevertheless, $TCNQ^{2-}$ does not keep stable in the presence of oxygen, namely, it can be oxidated into new compound, dicyano-p-toluoyl cyanide ($DCTC^-$), while the content of $TCNQ^{2-}$ increased (Duyne et al., 1979). The reaction formula is related as follows:

$$TCNQ + e \rightarrow TCNQ^- \qquad (1)$$

$$TCNQ^- + e \rightarrow TCNQ^{2-} \qquad (2)$$

$TCNQ^{2-} + O_2 \rightarrow DCTC^- \rightarrow$



(3)

As mentioned earlier, the phenomenon that the absorption peak intensity of TCNQ at 400 nm actually decreased with increasing electrical running time and even disappeared just implied the variation law of TCNQ content in the electrode vessel because the band around 400 nm is the characteristic peak of TCNQ, then its behavior did reflect the variation law of TCNQ content. Similarly, the variation law of the band range of 700 to 900 nm indicated that the $TCNQ^-$ content in the electrode vessel substantially varied as the same behavior the band range of 700 to 900 nm behaved, because the continuous absorption band of 700 to 900 nm is just the characteristic peak of $TCNQ^-$. Concretely, when being powered at the beginning, TCNQ accepted an electron

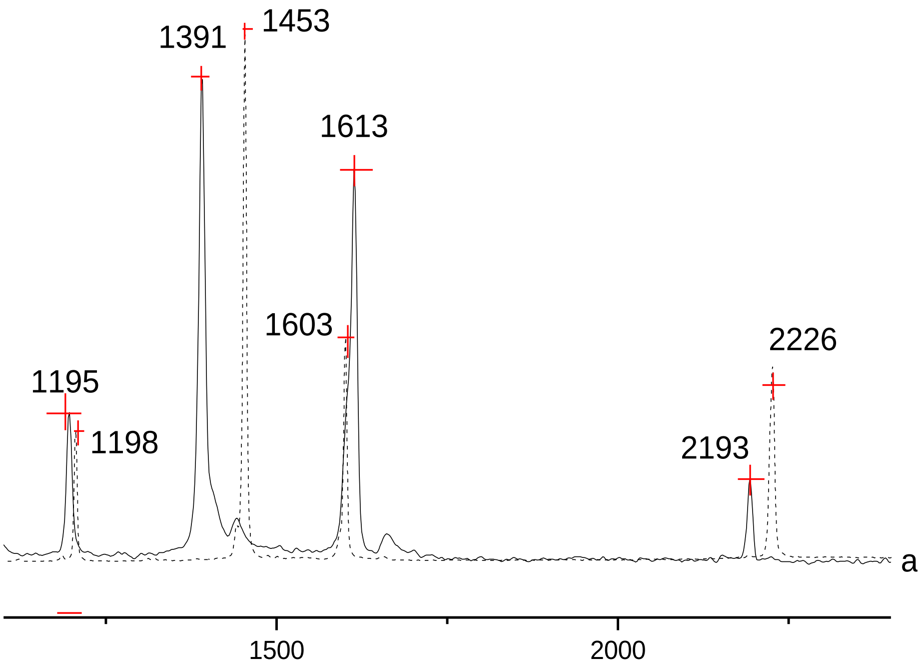


Figure 5. Raman Spectra of TCNQ in DMF solution under electricity (dotted line) and without electricity (solid line).

Table 1. Raman shift of TCNQ into TCNQ$^-$ (cm^{-1}).

Characteristic peak	TCNQ	TCNQ$^-$	$\Delta\upsilon$
υ_2	2226	2193	33
υ_3	1603	1613	10
υ_4	1453	1391	62
υ_5	1198	1195	3

and then turned into TCNQ$^-$, which means the TCNQ content decreased while the TCNQ$^-$ content increased. With increasing electrical time, TCNQ$^-$ accepted another electron and then turned into TCNQ^{2-}, and then the TCNQ$^-$ content decreased while the TCNQ^{2-} content increased, which can also be testified according to the behavior of the peak at 330 nm since the band around 330 nm is the characteristic peak of TCNQ^{2-}. Meanwhile, that the intensity of the absorption band at 488 nm increased gradually indicates that TCNQ^{2-} was oxidated gradually into a new compound DCTC$^-$ in the presence of oxygen because the band of 488 nm is the characteristic peak of DCTC$^-$.

Figure 5 shows the comparison between the two Fourier transformed Raman spectra of TCNQ in DMF solution both in electric filed and without electricity. The wavenumber shifts of some principal characteristic peaks of TCNQ and TCNQ$^-$ according to Figure 5 are listed in Table 1, where $\Delta\upsilon$ denotes the wavenumber shift of TCNQ into TCNQ$^-$. It is easily found in Figure 5 also in Table 1 that every band shifted significantly when the solution was being electrified. Compared with the behavior, the Fourier transformed Raman spectra of TCNQ appeared before being electrified, the one of that being electrified behaved quite differently as follows which have not been reported before in the existing references: (1) the characteristic peak located at 1453 cm^{-1} originally shifted to 1391 cm^{-1}; (2) the characteristic peak located at 1603 cm^{-1} originally shifted to 1613 cm^{-1}; (3) the characteristic peak located at 2226 cm^{-1} originally shifted to 2193 cm^{-1}; (4) the characteristic peak located at 1198 cm^{-1} originally shifted to 1195 cm^{-1}.

In this study, the aforementioned phenomena have not been reported. The interpretation for the Fourier transformed Raman shift mentioned is as follows. Firstly, the characteristic peak of 1453 cm^{-1} is of the C=C bond ring stretching vibration mode v_4. Then, the bond order of TCNQ changed 0.145 when TCNQ turned into TCNQ$^-$ after it had accepted an electron. Meanwhile, the vibration band shifted 62 cm^{-1} towards lower wave number at 1391 cm^{-1} which is the characteristic band of TCNQ$^-$. Secondly, the characteristic peak of 1603 cm^{-1} is assigned to the C=C stretching vibration mode v_3. The bond order of TCNQ here changed 0.053 after it accepted an electron. Accordingly, the band shifted 10 cm^{-1} to the wave number of 1613 cm^{-1} which is the characteristic band of TCNQ$^-$. Thirdly, the same behavior occurred to the v_2 band 2226 cm^{-1} which is assigned to the C≡N stretching vibration mode whose band order changed 0.044 with the band shifted to a lower wave number at 2193 cm^{-1} which is the characteristic band of TCNQ^{-}. Fourthly, as for v_5, the band 1198 cm^{-1}, that is, the characteristic band of C-H bending vibration mode, when TCNQ accepted an electron and turned into TCNQ^{-}, it only shifted slightly, that is, it only shifted 3 cm^{-1} to the band of 1195 cm^{-1} which is the characteristic band of TCNQ^{-}, owing to no change in bond order (Oyamada et al., 2003; Duyne et al., 1979).

Conclusions

A series of electron transfer process of TCNQ occurred in external electricity, which embodies mainly in the following properties of both UV-Vis absorption spectra and Fourier transformed Raman spectra were obtained. Concretely, with increasing electric quantity, that is, with increasing electrical running time: (1) the intensity of the absorption peak around 400 nm decreased gradually and even disappeared; (2) the one around 330 nm increased gradually; (3) the one around 488 nm behaved as the one of 330 nm; (4) the one in the range of 700-900 nm behaved quite differently, it increased at the beginning, then decreased; (5) different Raman shifts of some bands in Fourier transformed Raman spectra were observed after electricity than those without electricity.

The interpretation of these properties is that TCNQ turned into TCNQ^{-} at first and then into TCNQ^{2-} in the external electrical field. Further, TCNQ^{2-} was oxidized into DCTC^{-} with the presence of oxygen. The Fourier transformed Raman spectral band shift of some groups in electrical field indicated that TCNQ did turn into TCNQ^{-}.

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