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Rectifying effect of heterojunction fabricated in freestanding thin film of polyaniline containing azobenzene side-chain*

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An innovative heterojunction is fabricated between two sides of a freestanding thin film of HCl-doped polyaniline (PANI) derivative containing azobenzene side-chain, which is synthesized through an N-alkyl-substituted reaction. Of the film, the side with being irradiated by UV light during preparation is represented as 'A side'; the other side without being irradiated is represented as 'N side'. The electrical properties of the heterojunction are measured and the rectifying effect is observed in the current–voltage characteristic curves with the values of rectifying ratio (γ) being 20 at ± 0.06 V at $T = 77$ K and 4 at ± 0.02 V at $T = 300$ K separately.

Keywords: polyaniline, rectifying effect, azobenzene, heterojunction
PACC: 7340E, 7340L, 7360R

1. Introduction

Azobenzene-containing functionalized polymers have attracted considerable attention due to their many interesting effects, such as photoinduced isomerization, photoinduced gyrotropy, and photoinduced anisotropy. Accordingly, they may be candidate materials in optical switching, optical storage, holography, and light modulation applications.[1−3] One of the main properties to be exploited is the photoinduced reversible trans⇔cis isomerization of the azobenzene group as shown in Fig.1. The trans isomer can absorb the UV light and isomerize into the cis form. In the same way, the cis isomer can also turn back to trans isomer by absorbing visible light. This reverse process can also happen spontaneously through thermal isomerization progress.[4] It is reported that the dynamic process relies on the trans-cis-trans isomerization cycles that are usually accompanied with a structural change, as revealed by the changes of dipole moment and geometry.[5,6]

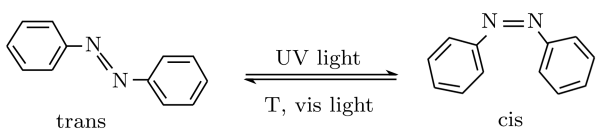


Fig.1. Reversible isomerization process of the azobenzene group.

Polyaniline (PANI) as one of widely studied conducting polymer[7,8] has excellent properties and potential applications in electronic and optical technologies and good environmental stability. It has been reported in Refs.[9, 10] that the trans–cis photoisomerization can take place in the sulfonic acid-doped PANI derivatives containing azobenzene group with being irradiated by UV light. In this paper, we report that we have successfully synthesized photoinduced PANI derivative, poly (aniline-co-N-propane [4-(4-nitrophenylazo)-phenyloxy] aniline) (denoted as PAPNPA), which can be cast into a freestanding film from its N-methyl-2-pyrrolidinone (NMP) solution. One side of the film was treated with UV light. As is well known, the heterojunction has been widely investigated due to many special features and applications in light-emitting diode, sense organs and solar cells.[11] However, what we have fabricated is a kind of novel heterojunction in a thin free-standing film, which is quite different from traditional one. The

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electric properties are measured at 77 and 300 K separately. We conclude that there are accumulated the positive charges on the 'A side', shown by analysing the obtained exceptional voltage–current curves. The rectifying effect of the heterojunction is also observed from the $I - V$ characteristic curves.

2. Experimental details

1-Bromo-3-(4-(4-nitrophenylazo)phenyloxy) propane (B3) was successfully synthesized by using the Williams etherfication method, more details can be found in Ref.[12]. The fully reduced leucoemeraldine (LEB) PANI powders were prepared by using a typical method.[10,13] A solution of methylsufinyl carbanion in dimethyl sulfoxide was prepared by using a method as described in Ref.[14]. The LEB powders were added into the sodium methylsufinyl carbanion solution at 60°C. A dark-yellow anion solution formed after a 4 h reaction. The solution was cooled down to 40°C, and B3 was added with vigorous stirring. The reaction was allowed to continue for another 24 h, and then the reacted mixture was poured into the distilled water, under vigorous stirring, to precipitate the copolymer. Finally, the precipitate was washed with distilled water, ethanol, acetone, then dried under reduced pressure for 48 h in sequence. The PAPNPA film with a thickness of about 5 μm can be obtained by casting its NMP solution onto a glass substrate. After drying at room temperature in air, 1.0 M/L HCl solution was dropped on the film, and then the film was dried by an ultraviolet lamp as shown in Fig.2(a). Therefore, HCl doped PAPNPA film was prepared and then detached from the glass substrate to form a free-standing film. For convenience, the side that was irradiated by UV light is represented as 'A side'; the other side without being irradiated by UV light is represented as 'N side'. The trans–cis isomerization of the azobenzene group takes place on the 'A side' upon the irradiation of the UV light, which is accompanied with a structural change.

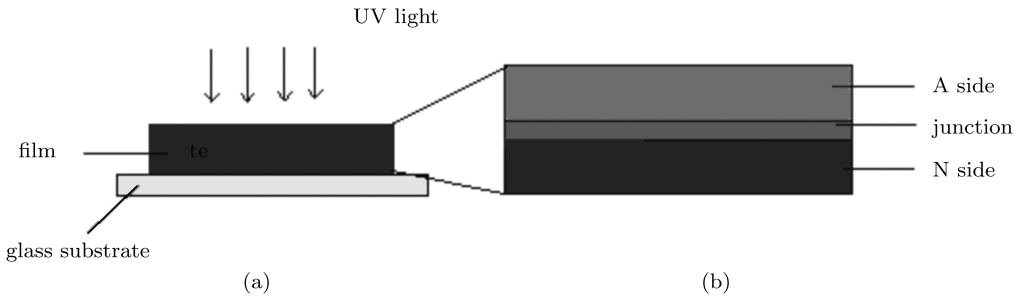


Fig.2. Schematic illustration of the preparation of HCl-doped freestanding PAPNPA film.

Here we note that the Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) spectra of the synthesized PAPNPA film indicate the presence of azobenzene groups in the resulting PANI derivative. Furthermore, the expected photo-induced isomerization of the azobenzene side-chain is also shown in the UV–vis spectrum as reported in our previous work.[13] In addition, Long *et al*[15] has found that the conductivity of the normal side ('N side') is about 1.2 S/cm, which is about 500 times larger than that of the 'A side'. Therefore, as shown in Fig.2(b), we suggest a possible heterojunction fabricated between the 'A side' and the 'N side' and the film is likely to show a rectifying effect in terms of previous work.

We fabricated electrodes with silver paste and gold wires to measure the electrical properties of the film that had a typical dimension of 1.5 mm × 1 mm × 5 μm. The voltage–current ($V - I$) curves were measured by a two-probe technique using a 220-programmable current source and a 181-nanovoltmeter (Keithley, USA), which were autocontrolled by a computer. The current increased from zero to a maximum value and immediately decreased to zero in two minutes, and the measurement was repeated.

3. Results and discussion

We measured the electric properties of the PAPNPA film at $T = 77$ and 300 K , with a supplied current flowing from 'A side' to 'N side' of the film as shown in Fig.3(a). The supplied current increased first

from zero to 10 nA and then reduced down to zero in two minutes and the measured $V-I$ curves are shown in Fig.3(b). A corresponding higher voltage was obtained at $T = 77$ K than at $T = 300$ K. Especially, the $V-I$ curve in an increasing current phase cannot be superposed on that in a reducing current phase either at $T = 77$ or at 300 K: the voltage still keeps increasing in the reducing current phase.

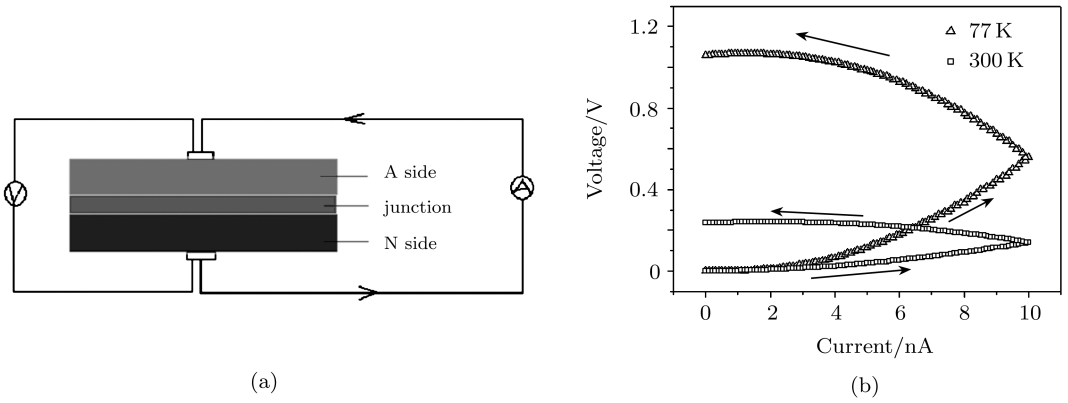


Fig.3. Schematic illustration of the supplied current flowing from 'A side' to 'N side' of the film (a), and the $V-I$ characteristic curves obtained at $T = 77$ K and 300 K separately.

On the other hand, we supplied a current flowing from 'N side' to 'A side' of the film separately at $T = 77$ K and at 300 K as shown in Fig.4(a). The supplied current first increased from zero to 10 nA and then reduced down to zero in two minutes. The $V-I$ curves measured at 77 and 300 K are plotted in Fig.4(b). These curves are shown to be absolutely different in shape from those in Fig.3(b). Figure 4(b) shows that as current increases from zero to 10 nA, the voltage first goes up to a peak value and then comes down; while the supplied current reduces from 10 nA to zero, the voltage keeps reducing down to zero and further to negative values. The fact that the branch of $V-I$ curve in the phase of increasing current cannot be superposed on that in the phase of reducing current is the same as that indicated in Fig.3(b).

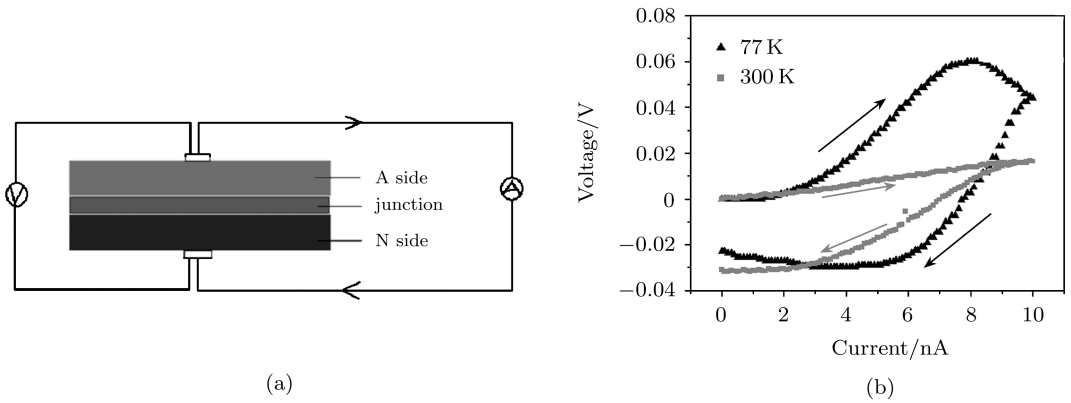


Fig.4. Schematic illustration of the supplied current flowing from 'N side' to 'A side' of the film (a), and the $V-I$ characteristic curves at $T = 77$ and 300 K.

According to the above analysis of the obtained $V-I$ curves, we propose that there appears a voltage due to positive charges possibly accumulated on the 'A side' during the supplied current flowing through the film. The obtained voltage can be described as $V_t = V_s + V_c$, where V_s represents the voltage arising from the supplied current and V_c represents the voltage originating from the accumulated charges. Thus, in Fig.3(a), when the supplied current flows from 'A side' to 'N side', both V_s and V_c are positive, and the latter keeps increasing with the accumulation of positive charges. However, when the supplied current flows from 'N side' to 'A side' (Fig.4), V_c is reversed, i.e. contrary to V_s in sign and keeps increasing with the accumulation of the positive charges on the 'A side'. So as shown in $V-I$ curves in Fig.4 (b), V_t

increases first with the increase of the V_s and then declines as the reverse voltage V_c increases. Here, we note that the accumulation of positive charges illustrated above is possibly attributed to the fabricated heterojunction in the film.

Supposing that a heterojunction has been fabricated, the film, like other traditional heterojunctions or p n junctions, should show a typical rectifying effect. If we just consider the phases of increasing supplied current in Figs.3(b) and 4(b) at $T = 300\,\mathrm{K}$, the $I - V$ characteristic curves can be obtained as shown in Fig.5(a), exhibiting an obvious nonlinear and asymmetric feature. The $I - V$ characteristics show an evident rectifying effect with a rectifying ratio (γ) of about 4, i.e. $\gamma \approx 4$, at $\pm 0.02\,\mathrm{V}$, indicating that the heterojunction has been fabricated between the two sides of the PAPNPA film as shown in Fig.2(b). The solid squares represent the supplied current flowing from 'N side' to 'A side' while the open squares refer to the reverse supplied current. Furthermore, in the same way, a more obvious nonlinear and asymmetric $I - V$ characteristic curve at $T = 77\,\mathrm{K}$ is obtained as shown in Fig.5(b). The junction exhibits a more obvious rectifying effect with $\gamma \approx 20$ at $\pm 0.06\,\mathrm{V}$. Therefore, we believe that a heterojunction has been fabricated between the two sides of the film and the junction shows a temperature-dependent feature.

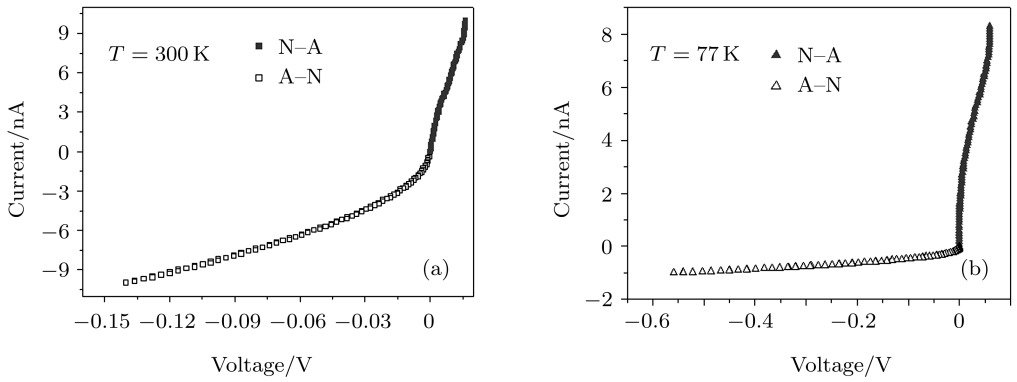


Fig.5. $I-V$ characteristic curves of pn junction between 'A side' and 'N side' of the PAPNPA film, measured separately at $T = 300\,\mathrm{K}$ (a) and $T = 77\,\mathrm{K}$ (b).

The accompanied structural change takes place in the 'A side' due to the photoinduced isomerization on the azobenzene side-chain. Moreover, it has been reported that the trans to cis photoinduced isomerization can increase the resistance of PAPNPA film due to the interaction between the light field and the molecules upon the irradiation of UV light.[15] We conclude that there were formed a depletion layer on the 'A side' and an accumulation layer on the 'N side' near the interface due to higher level Fermi energy on the 'A side' as shown in Fig.6. Thus, the film can exhibit a rectifying effect. Furthermore, we attribute the temperature-dependent feature of rectifying effect to the variation in barrier height in terms of weak temperature dependence of the semiconductor band gap,[16] and on the other hand, the series resistance is also an important parameter describing the electrical characteristics of the rectifying junctions[17] as the conductivity of PAPNPA film decreases exponentially with temperature decreasing as described in Ref.[15]. Our further investigation on the obtained PAPNPA film is in progress.



Fig.6. Schematic illustration of heterojunction including a depletion layer in 'A side' and an accumulation horizon in 'N side'.

4. Conclusions

An innovative heterojunction has been fabricated in a single thin HCl-doped PANI film containing azobenzene side-chain. We have measured and investigated the electric properties of the film. From the measured abnormal $V - I$ curves we conclude that there are accumulated positive charges on the 'A side', which, however, is still an open question and needs

further investigating. The $I-V$ characteristic curves indicate that a heterojunction is formed between the two sides of the film, which shows an obvious rectifying effect. We propose that the free-standing film of polyaniline containing azobenzene side-chain may be used in organic electronic devices such as plastic rectifiers, capacitor and batteries.

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