

# NO<sub>2</sub> gas sensing based on vacuum-deposited TTF–TCNQ thin films<sup>☆</sup>

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## Abstract

The sensing characteristics of tetrathiafulvalen–tetracyanoquinodimethane (TTF–TCNQ) thin films for detecting nitrogen dioxide gas are studied. TTF–TCNQ complex, which is obtained by dissolving TTF and TCNQ powders in a solvent, is thermally evaporated onto a Al<sub>2</sub>O<sub>3</sub> substrate screen-printed with interdigitated gold electrodes. The gas sensing properties for the NO<sub>2</sub>–TTF–TCNQ interaction, including conductance transient and sensitivity, are discussed. When the special sensing condition of short contact time or lower concentration range is satisfied, a linear relationship is obtained by plotting the rate of conductance change versus NO<sub>2</sub> concentration, from which a sensitivity value of  $8.0 \pm 0.1 \times 10^{-3}$   $\mu\text{S/s ppm}$  is obtained. The rate of conductance change measured at room temperature is linear with respect to the NO<sub>2</sub> gas concentration up to 30 ppm. Moreover, by comparing with the literature, the conductivity calculated for the vacuum evaporated TTF–TCNQ thin films suggests that the molecular structure of the complex is randomly oriented.

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*Keywords:* Conductance; Interdigitated electrode; Nitrogen dioxide sensor; Upper sensing limit; TTF–TCNQ complex

## 1. Introduction

The semiconductor-type gas sensor widely applied in industry and daily life shows high reversibility and reliability. Various inorganic metal oxides and some highly conjugated organic compounds such as SnO<sub>2</sub> [1] and metal phthalocyanines [2–4], play very important roles on sensing of gases. In addition to metal phthalocyanines, a few organic compounds, such as tetrathiafulvalen (TTF), tetracyanoquinodimethane (TCNQ) derivatives [5–8] and TTF–TCNQ complex [9] also show the potential on gas sensing.

The TTF–TCNQ complex was synthesized and tested to have high conductive capability which is approaching to metallic Cu [10]. The research on the TTF–TCNQ complex, ranging from fundamental thin film preparation [10–12] and its morphology characterization [11–13] to application in electrochromic displays [14], have been reported. However, little effort is devoted to sensor application using this complex as a sensing material.

Jouve et al. [9] discovered, for the first time, that the TTF–TCNQ-doped PE film is sensitive to NO<sub>2</sub> gas under room temperature. Unlike the semiconductor-type sensors, the sensing mechanism seems to involve a fully “irreversible” chemical reaction between NO<sub>2</sub> gas and TTF–TCNQ complex.

NO<sub>2</sub> gas is a highly toxic gas with a pungent odor, and is harmful to the environment. The maximum tolerable concentration is no greater than 5 ppm for the environmental regulations in many countries. Since TTF–TCNQ complex is sensitive to NO<sub>2</sub>, it is worth trying to test the complex as a sensing material for NO<sub>2</sub>. Unlike the ordinary amperometric or semiconductor-type NO<sub>2</sub> gas sensors that possess a reversible behavior when exposed to and removed from NO<sub>2</sub>, the sensor we study allows the sensing material to react and to be consumed. Since the mechanism governing the sensing behavior varies from one material to the another, even for the same detected gas, a proper model suitable to explain this sensing characteristic is also needed. Vernon [15] performed series of experiments on tarnishing film (rust) growth on metal. Mott and Gurney [16] and Booth [17] also derived mathematical expressions to explain this phenomenon. The aim of this research is to investigate the gas sensing property of vacuum-deposited TTF–TCNQ thin film for NO<sub>2</sub> detection. Our experimental data for the sensor response can be explained by the tarnishing film model proposed in the literature.

## 2. Experimental

TTF–TCNQ complex is obtained by dissolving both TTF (Fig. 1(a)) and TCNQ (Fig. 1(b)) powders into acetonitrile, then a 1:1 molar ratio complex precipitates (Fig. 1(c)). The preparation step is depicted in [10]. The complex powder is

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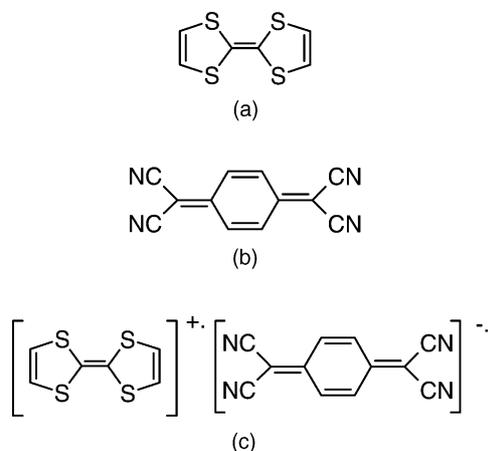


Fig. 1. (a) Tetrathiafulvalene (TTF); (b) tetracyanoquinodimethane (TCNQ); (c) TTF–TCNQ complex.

further purified by recrystallization in acetonitrile. Sensing thin film is thermally evaporated onto  $\text{Al}_2\text{O}_3$  substrate with an interdigitated gold electrode with 200  $\mu\text{m}$  electrode spacing under  $3 \times 10^{-5}$  Torr vacuum, as described in Fig. 2(a). The interdigitated gold electrode was fabricated by printing gold paste onto the  $\text{Al}_2\text{O}_3$  substrate, then heated at 750  $^\circ\text{C}$  for 20 min. Afterward, the film is applied a potential of 4 V dc across the two electrodes. By measuring the change in current, the conductance response of the film, which varies with different concentrations of  $\text{NO}_2$  gas, can be monitored. The sensing film that face against the gas inlet at a flow rate of 200 ml/min is placed in the sensing chamber, as shown in Fig. 2(b). The sensing procedure was carried out under room temperature.  $\text{NO}_2$  gas is diluted with pure  $\text{N}_2$  that is assumed and demonstrated to be inert in this system. Various concentrations are tested by controlling a gas flow system (Fig. 2(c)). Conductance is recorded by a potentiostat/galvanostat (EG&G, model 273A).

### 3. Theory

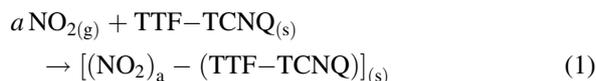
The mathematical expression of this theory is based on “totally irreversible chemical reaction.” At least four different approaches have been reported to deal with this diffusion-reaction phenomenon. In the so-called Danckwerts [18] approach, only diffusing substance was considered, so there is no information about how the tarnishing film was formed and affected. Obviously, this approach is not adequate to describe our system. Ghez [19] utilized a moving tarnishing film boundary and introduced a first-order reaction mechanism to obtain a general relationship between the film growth rate and the time. Deal and Grove [20] also proposed a model using flux balances when diffusing substance is experiencing: (1) mass transfer from bulk to film surface; (2) diffusion through tarnishing film; and (3) first-order reaction with fresh material. They obtained a relationship similar to the Ghez’s approach for oxidation process of

silicon, which is a significant step in microchip manufacturing. Booth [17] derived a “tarnishing film model” even earlier by applying simple concept of mole balance of diffusing substance and reacted product in diffusion control region. By relaxing the assumption of first-order reaction, the tarnishing film model, instead, uses only stoichiometric factor which is much beneficial and realistic when the reaction order is unknown in advance. Furthermore, the model is capable of describing the film growth when the film is not initially fresh. Based on the advantages that Booth’s tarnishing film model can offer, we adapt this model with a few modifications of our own to ensure the compatibility of model with sensing system and extend to include the reaction control region.

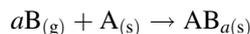
#### 3.1. Basic assumptions

The following assumptions are made regarding our modified tarnishing film model:

- (i) An irreversible reaction is assumed and can be written as,



where “ $a$ ” is a stoichiometric factor between the reactants. By denoting  $\text{NO}_2$  as B and TTF–TCNQ complex as A, the product (tarnishing reaction film)  $(\text{NO}_2)_a - (\text{TTF-TCNQ})$  can be abbreviated as  $\text{AB}_a$ . Eq. (1) is simplified as



- (ii) The moving boundary or the reaction plane at which the reaction takes place is located at the interface between the fresh TTF–TCNQ complex and the reacted  $(\text{NO}_2)_a - (\text{TTF-TCNQ})$ , or  $\text{A-AB}_a$  interface, as shown in Fig. 3.
- (iii) A quasi-steady-state hypothesis is introduced which means that concentration of diffusing substances is not a function of time ( $\partial C_B / \partial t = 0$ ). Substituting the hypothesis into the “equation of continuity” inside the tarnishing zone ( $0 < x < l$ ) where no reaction takes place and no fluid flow occurs, the equation of continuity is simplified as

$$\nabla^2 C_B = 0$$

thus,

$$\frac{dC_B}{dx} = \frac{C_{\text{BS}} - C_{\text{B0}}}{l} = \text{constant} \quad (= -z) < 0 \quad (2)$$

After applying boundary condition:  $x = 0$ ,  $C_B = C_{\text{B0}}$ ,  $x = l$ ,  $C_B = C_{\text{BS}}$ , a linear concentration profile in 1-D is obtained

$$C_B = C_{\text{B0}} + (C_{\text{BS}} - C_{\text{B0}}) \frac{x}{l} = C_{\text{B0}} - zx \quad (3)$$

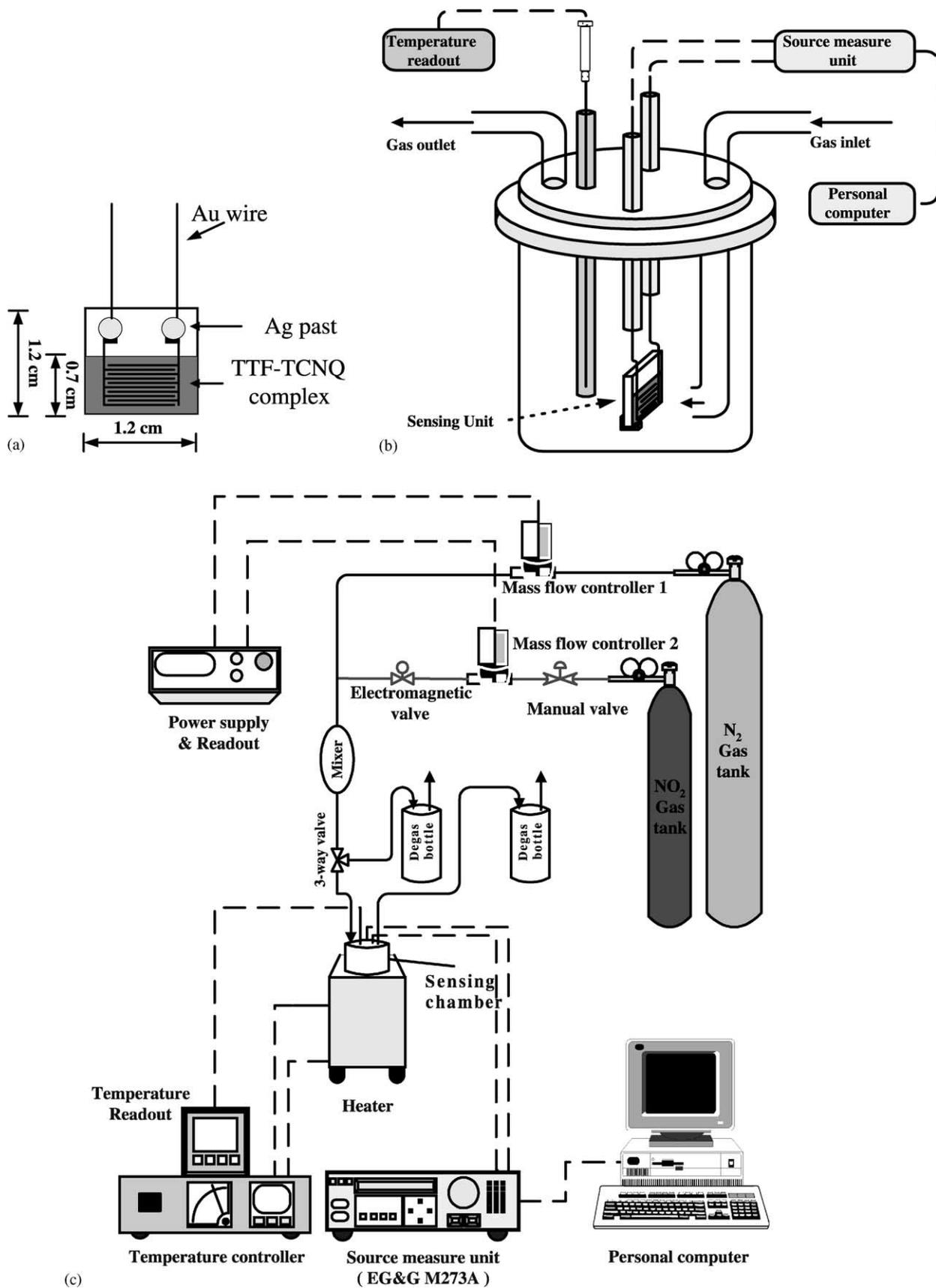


Fig. 2. (a) Sensing unit; (b) sensing chamber; (c) gas flow control system.

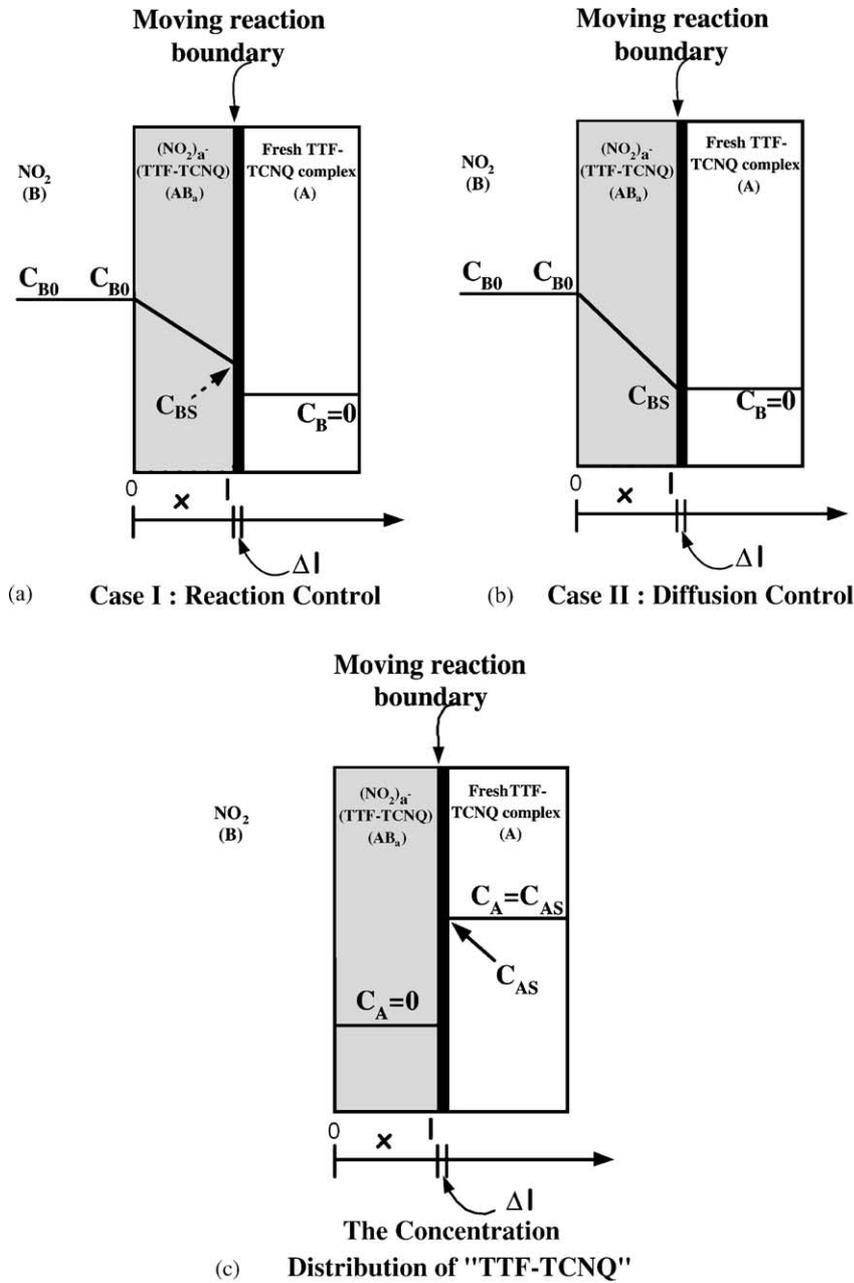


Fig. 3. Schematic concentration profile of (a) diffusing substance, NO<sub>2</sub>, in reaction control; (b) NO<sub>2</sub> in diffusion control; (c) fresh TTF–TCNQ in any situation.

where  $z$  is a constant, representing the concentration gradient for species B diffusing through the tarnishing film.

(iv) Total conductance ( $G = 1/R = \sigma A_h/L$  ( $\Omega^{-1}$  or S)) of “A” and “AB<sub>a</sub>” layer can be expressed by two parallel resistors, as shown in Fig. 4

$$\frac{1}{R} = \frac{1}{R_{AB_a}} + \frac{1}{R_A}; \quad G = G_{AB_a} + G_A \quad (4)$$

where  $\sigma_A$  is the conductivity of A (S/cm),  $\sigma_{AB_a}$  the conductivity of AB<sub>a</sub>, and  $\sigma_A > \sigma_{AB_a}$ ,  $A_h$  the cross-sectional

area perpendicular to electric current direction,  $L$  the length along current flow direction, and

$$G_{AB_a} = \sigma_{AB_a} \frac{A_h}{L} = \sigma_{AB_a} \frac{lW}{H} \quad (5)$$

$$G_A = \sigma_A \frac{A_h}{L} = \sigma_A \frac{mW}{H} \quad (6)$$

By combining Eqs. (4)–(6), the total conductance can be written as

$$G = G_{AB_a} + G_A = \frac{W}{H} (\sigma_{AB_a} l + \sigma_A m) \quad (7)$$

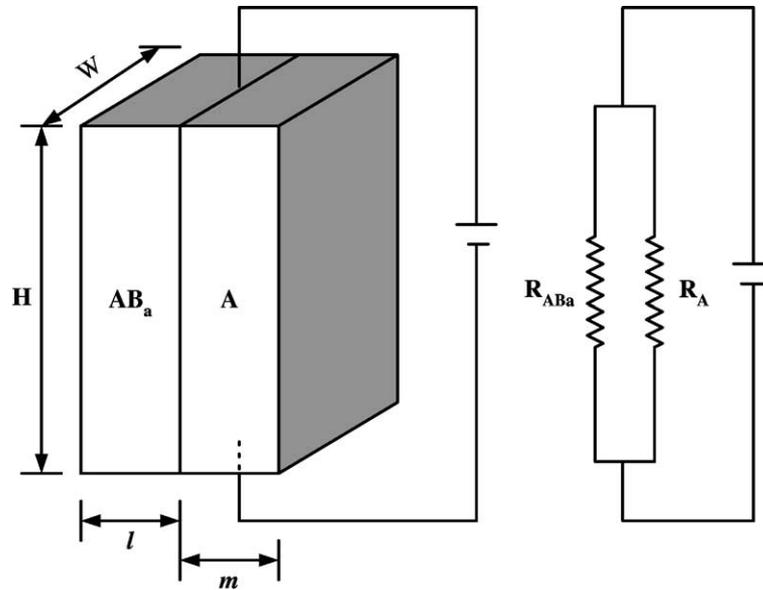


Fig. 4. Total conductance of two layers and representative circuitry.

- (v) The film volume does not change during the reaction, which means

$$l + m = \text{constant} = C; \quad \text{or} \quad m = C - l \quad (8)$$

Substituting  $m$  from Eq. (8) into Eq. (7), we have

$$G = G_{AB_a} + G_A = \left[ \frac{W}{H} \sigma_A C \right] + \left[ \frac{W}{H} (\sigma_{AB_a} - \sigma_A) l \right] \quad (9)$$

The growth rate of tarnishing film ( $AB_a$ ) can be described by the following equation

$$\frac{dn_{AB_a}}{dt} = -\frac{dn_A}{dt} = A_v \frac{dl}{dt} \frac{1}{v} \quad (10)$$

where  $A_v$  is the cross-sectional area perpendicular to the direction of tarnishing film growth,  $v$  the molar volume of  $AB_a$ , and  $l$  the thickness of  $AB_a$ .

Differentiating Eq. (9) with respect to time and combining with Eq. (10), one obtains the rate of conductance change ( $dG/dt$ ) that is proportional to the growth rate of tarnishing film ( $dn_{AB_a}/dt$ ), as shown below

$$\frac{dG}{dt} = \frac{W}{H} (\sigma_{AB_a} - \sigma_A) \frac{dl}{dt} = \frac{W}{H} (\sigma_{AB_a} - \sigma_A) \frac{v}{A_v} \frac{dn_{AB_a}}{dt} < 0 \quad (11)$$

There are two limiting cases, corresponding to two quite different mechanisms, which need to be considered. That is, the reaction control (case 1) and the diffusion control (case 2) regimes.

### 3.2. Case 1: reaction control (rate of diffusion $\gg$ rate of reaction)

Typical concentration profile of B under reaction control case is obtained from Eq. (2), in which the concentration

gradient is constant for a given arbitrary bulk concentration  $C_{B0}$ , as illustrated in Fig. 3(a). The rate-determining step is the reaction, as written in Eq. (1). This takes place at the moving reaction boundary. According to rate law, the rate of the reaction is temperature and concentration dependent

$$-r_A = \frac{-r_B}{a} = -\frac{dC_A}{dt} = \frac{-1}{V} \frac{dn_A}{dt} = k'(T) C_A^\alpha C_B^\beta \quad (12)$$

where  $V$  is the control volume within which reaction takes place,  $k'$  the specific rate constant,  $T$  is temperature,  $\alpha$  and  $\beta$  are reaction orders with respect to species A and B, respectively. It is noted that  $C_A$ , as written in Eq. (12), is the concentration “inside” the reaction boundary, and thus is not a constant. However, it can be replaced by the fresh or the unreacted concentration of A,  $C_{AS}$ , because of the infinitesimal reaction time and thickness involved within the reaction layer, as shown in Fig. 3(c). Eq. (12) thus becomes

$$-r_A = \frac{-r_B}{a} = -\frac{dC_A}{dt} = \frac{-1}{V} \frac{dn_A}{dt} = k'(T) C_{AS}^\alpha C_{BS}^\beta \quad (12')$$

where  $C_{AS}$  is the fresh concentration of TTF–TCNQ that is close to the reaction boundary, as shown in Fig. 3(c). And  $C_{BS} = C_{B0} - z l$  at  $x = l$  (from Eq. (3)). Rewriting Eq. (10) by using the relations from Eqs. (3) and (12'), one obtains

$$-\frac{dn_A}{dt} = A_v \frac{dl}{dt} \frac{1}{v} = V k' C_{AS}^\alpha C_{BS}^\beta$$

or,

$$\frac{dl}{dt} = \frac{v V k' C_{AS}^\alpha}{A_v} (C_{B0} - z l)^\beta \quad (13)$$

By a somewhat complicated derivation from Eqs. (11) and (13), the rate of conductance change under a given

temperature surrounding is written as

$$\frac{dG}{dt} \propto \frac{dl}{dt} \propto (C_{B0} - zl)^\beta \quad (14)$$

If  $\beta$  is equal to 1 (first-order reaction is generally accepted and may be valid in this system as well), the film growth rate can be written as

$$\frac{dl}{dt} = \frac{vVk' C_{AS}^z}{A_v} (C_{B0} - zl)^1$$

or,

$$\int_l^{l+\Delta l} \frac{dl}{C_{B0} - zl} = \frac{vVk' C_{AS}^z}{A_v} \int_0^t dt$$

Furthermore, the growth of tarnishing film is varied exponentially with the sensing time, as

$$\Delta l = \left( \frac{C_{B0}}{z} - l \right) \left\{ 1 - \exp \left[ - \left( \frac{vVk' C_{AS}^z}{A_v} \right) zt \right] \right\}$$

For a fresh film ( $l=0$ ) during the initial stage (small  $t$ ,  $\Delta l=0$ ) of this sensing procedure, the surface concentration  $C_{BS}$  may be viewed as a constant very close to the bulk concentration  $C_{B0}$ . The film growth rate (or the conductance change rate) is proportional to the bulk concentration of  $\text{NO}_2$  ( $C_{B0}$ ). Then, Eq. (14) is reduced to

$$\frac{dG}{dt} \propto \frac{dl}{dt} \propto (C_{B0})^1 \quad (15)$$

### 3.3. Case 2: diffusion control (rate of reaction $\gg$ rate of diffusion)

In this case, the rate-determining step is no longer determined by the reaction but the diffusion process through the tarnishing film ( $\text{AB}_a$ ). The concentration profile for B is presented in Fig. 3(b). Because of fast reaction, the  $\text{NO}_2$  concentration at the moving boundary ( $C_{BS}$ ) is depleted to zero, thus Eq. (2) becomes

$$\frac{dC_B}{dx} = \text{constant} = \frac{C_{BS} - C_{B0}}{l} = \frac{0 - C_{B0}}{l}$$

By considering the conservation of diffusing substance (B) across the reaction boundary (tarnishing reaction model) [17], the mole flux balance equation can be derived as follows

$$J_B|_{x=l} = -D \frac{dC_B}{dx} \Big|_{x=l} = \frac{d}{dt} \left( \frac{a\rho_{\text{AB}_a} l}{M_{\text{AB}_a}} \right) \quad (16)$$

or,

$$-D \frac{0 - C_{B0}}{l} = \frac{a\rho_{\text{AB}_a}}{M_{\text{AB}_a}} \frac{dl}{dt} \quad (17)$$

thus,

$$\frac{dl}{dt} = \frac{M_{\text{AB}_a} D C_{B0}}{a\rho_{\text{AB}_a} l} \quad (18)$$

Integrating Eq. (18) gives

$$\int_l^{l+\Delta l} l \, dl = \frac{M_{\text{AB}_a} D C_{B0}}{a\rho_{\text{AB}_a}} \int_0^t dt$$

or,

$$(l + \Delta l)^2 - (l)^2 = \frac{2M_{\text{AB}_a} D C_{B0}}{a\rho_{\text{AB}_a}} t$$

Finally,

$$\Delta l = \frac{-2l + \sqrt{(4l^2 + 8M_{\text{AB}_a} D C_{B0} t / a\rho_{\text{AB}_a})}}{2} \quad (19)$$

where  $M_{\text{AB}_a}$  is the molecular weight of  $\text{AB}_a$ ,  $\rho_{\text{AB}_a}$  the density of  $\text{AB}_a$ ,  $D$  the room temperature diffusivity of  $\text{NO}_2$  (B) through tarnishing film ( $\text{AB}_a$ ),  $\Delta l$  the growth thickness of tarnishing film in a time interval  $t$ . When the film is freshly made ( $l = 0$ ), Eq. (19) can be further simplified

$$\Delta l = \sqrt{\frac{2M_{\text{AB}_a} D C_{B0} t}{a\rho_{\text{AB}_a}}} \quad (20)$$

The conduction change rate for  $\text{AB}_a$  is obtained from Eqs. (11) and (18)

$$\frac{dG}{dt} = \frac{W}{H} (\sigma_{\text{AB}_a} - \sigma_A) \frac{dl}{dt} = \frac{W}{H} (\sigma_{\text{AB}_a} - \sigma_A) \frac{M_{\text{AB}_a} D C_{B0}}{a\rho_{\text{AB}_a} l} \quad (21)$$

Eq. (21) implies that the conductance change rate ( $dG/dt$ ) is proportional to the concentration gradient ( $0 - C_{B0}/l$ ) of  $\text{NO}_2$  diffusing through tarnishing film. If we keep the growing thickness to be very small and negligible by experiment techniques, says “very short contact time or very low concentration,” we can consider that  $\Delta l \ll l$ . This means that  $l$  may be kept constant (see Fig. 3(b)). Thus, we can simplify Eq. (21) into

$$\frac{dG}{dt} \propto C_{B0} \quad (22)$$

## 4. Results and discussions

Eq. (1) is merely a possible expression trying to capture the concept of “tarnishing reaction model” [17]. However, the actual product may not be the same as the one being proposed. As long as the stoichiometric factor ( $a$ ) between the reactants (A and B) holds, the result will be coincident with the one we deduced above, while the tarnishing film still remains on the substrate.

Typical response of freshly made TTF–TCNQ sensing thin film in a “long sensing time” procedure is demonstrated in Fig. 5(a). The conductance of the film remains constant under  $\text{N}_2$  exposure which indicates that the carrier gas,  $\text{N}_2$ , being used is inert indeed. A continuous decrease of conductance for a fresh film was then recorded after introducing

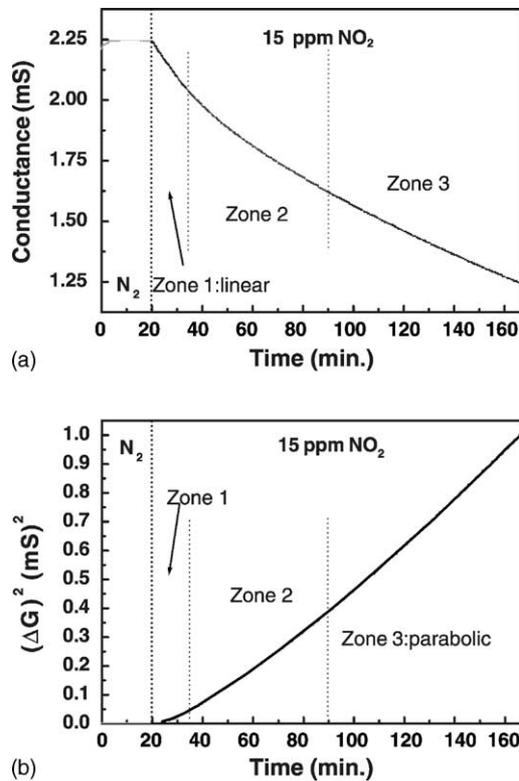


Fig. 5. (a) The typical conductance response for TTF-TCNQ thin film exposed to NO<sub>2</sub> gas. (b) Plot of square of conductance change vs. time.

15 ppm NO<sub>2</sub> to the carrier gas. According to the model mentioned above, for each limiting case, we have the relationship ( $dG/dt$ ) that is proportional to  $dI/dt$  (Eqs. (11) and (17)), so that we consider that the film growth ( $\Delta l$ ) can be evaluated by the conductance change ( $\Delta G$ ). By re-plotting the data in Fig. 5(a) with  $(\Delta G)^2$  (proportional to  $(\Delta l)^2$ ) versus time, we arrive at Fig. 5(b).

There are three zones in this plot, zones 1, 2 and 3. In zone 1, there is a linear relationship between  $\Delta G$  and time (Fig. 5(a)). But in zone 3, it is  $(\Delta G)^2$  that is linearly proportional to time (Fig. 5(b)), which strongly supports the diffusion control case (Eq. (20)) in Section 3 that we just derived. An explanation for zone 1 is that the rate is determined by surface reaction which is a constant value stated in [16]. In our previous discussions, this statement is correct only if a fresh film is exposed to a certain concentration of NO<sub>2</sub> and first-order sensing reaction is proceed during a very early stage of fresh film sensing ( $l = 0$ ), as analyzed in the reaction control case in Eq. (15). As for zone 2, it might be the transition-state zone between zone 1 (short time, first-order reaction control) and zone 3 (long time, diffusion control).

As discussed earlier, the sensing curve will exhibit simple relation of  $\Delta G \propto t$  even in the case of diffusion control that can be described by a parabolic law, if a very short contact time or very low concentration condition is satisfied. The continuous sensing curve is shown in Fig. 6(a). The decreasing trend of conductance varies with the bulk concentration.

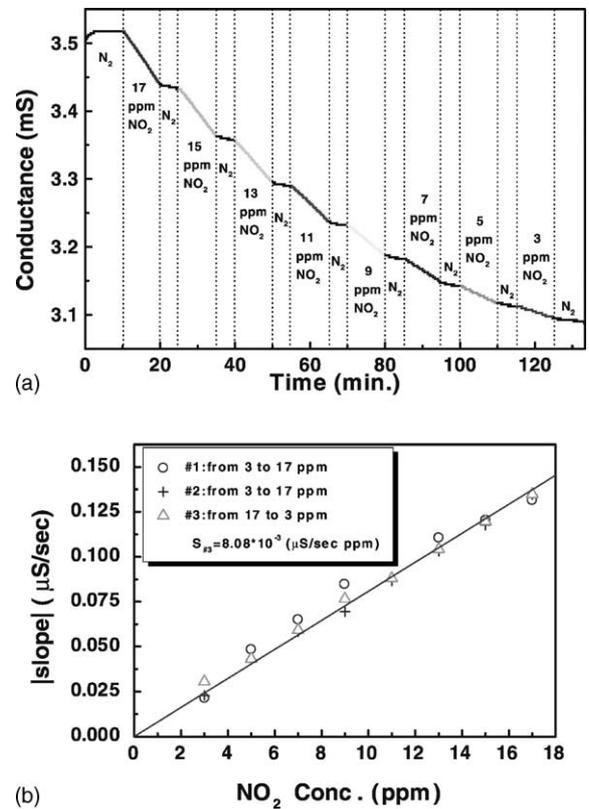


Fig. 6. (a) Continuous sensing curve for NO<sub>2</sub> gas from higher concentration (17 ppm) to lower concentration (3 ppm). (b) Reproducible sensitivity for one film with different sensing procedures (lower concentration to higher for #1 and #2; from higher to lower concentration for #3). The data in (b) #3 is taken from the slope of (a).

By plotting the conductance change rate ( $dG/dt$ , slope of sensing curve) versus the bulk NO<sub>2</sub> concentration, the calibration curve for sensing is obtained (#3 in Fig. 6(b)). The reproducibility is also shown for the film, which is experienced from two different sensing procedures (lower concentration to higher for #1 and #2, and higher to lower concentration for #3 in Fig. 6(b)) with a sensitivity,  $S$  ( $dG/dt \times \text{concentration}$ ), of  $8 \pm 0.1 \times 10^{-3}$  μS/s ppm. Because the film used is not fresh and is also slightly reactive with O<sub>2</sub> in air, it would be hard to preserve a “fresh film” after the film is made. So we do not believe the linear relation in Fig. 6 comes from the reaction control in Eq. (15) but from the diffusion control under “very short contact time or very low concentration” derived in Eq. (22). Here, the sensitivity is defined as the conductance change rate per unit ppm of NO<sub>2</sub> concentration, which is rarely seen. However, since the rate is constant for specific NO<sub>2</sub> concentration, it is easily recorded and determined with the aid of computer and/or other electronic devices.

As mentioned previously, the tolerable NO<sub>2</sub> concentration presents in air is usually less than 5 ppm according to the environmental regulations, which happens to meet the low concentration requirement as mentioned in Section 3. That is the reason why we limit our sensing experiments to NO<sub>2</sub> concentrations lower than 20 ppm to satisfy the actual application.

The lower limit of detection, in the ppb range for example, can be achieved by performing the sophisticated measurement of faint conducting current. As for higher concentrations, there is no guarantee that the sensing slope will be proportional to the concentration of NO<sub>2</sub>, as evidenced by the parabolic relationship.

The main purpose in designing such a long sensing time (20 min in each concentration) is to ensure that this linear decreasing trend exists. There is no need to take such a long period in ordinary sensing routines. Since the conductance declining rate is constant, 10–20 s are more than enough to predict the slope of conductance transient, and the undetermined NO<sub>2</sub> concentration is revealed with the help of the calibration curve or sensitivity. This kind of sensing has potential in making the gas detecting procedures easier by shortening the detecting time, as no response time needs to be waited and determined, which usually is very time consuming.

Linear sensing limit (higher limit) shown in Fig. 7 is approximately 30 ppm. It may vary with the growth of tarnishing film where the thickness cannot be regarded as a constant in case 2 and is strongly dependent of sensing procedures encountered.

TTF–TCNQ thin film is also sensitive to other gases [9]. Among them, NO is another one which also leads to a totally irreversible behavior, just like NO<sub>2</sub> does. However, as long as the stoichiometric coefficients and diffusion coefficients for NO are similar to those of NO<sub>2</sub>, probably there is no significant difference in distinguishing both gases. Other gases, such as O<sub>2</sub>, H<sub>2</sub>O, VOCs were also reported [9] to be partially reversible when brought in contact with a TTF–TCNQ thin film. In this case, it is impossible to apply current theory to obtain the required sensitivity and selectivity.

Finally, we shall discuss the conductivity ( $\Omega^{-1} \text{ cm}^{-1}$  or S/cm) rather than conductance ( $\Omega^{-1}$  or S) measured. The concept of conductivity evaluation can be roughly imagined by considering Fig. 8, which is solely a pair of interdigitated electrodes covered with a layer of TTF–TCNQ. The conductivity can be calculated as follows

$$\sigma = \frac{GL}{A_h} = \frac{2.25 \times 10^{-3} \text{ S} \times 0.02 \text{ cm}}{2 \times 10^{-5} \text{ cm} \times 0.6 \text{ cm}} = 3.75 \text{ S/cm} \quad (23)$$

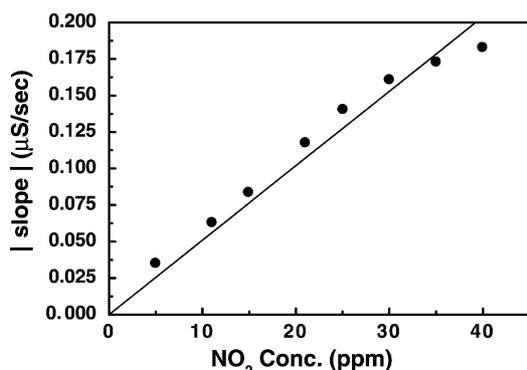


Fig. 7. Linear sensing limit of the film is about 30 ppm.

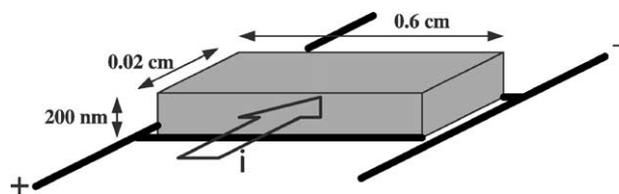


Fig. 8. Scheme of roughly evaluation of conductivity.

where  $G$  is the conductance, chosen from the conductance of freshly prepared film (2.25 mS in Fig. 5(a)). Comparing the data in [12] ( $\sigma_b = 600\text{--}900 \text{ S/cm}$ ,  $\sigma_b/\sigma_a \sim 10^3$ , which means  $\sigma_a$  may be in the range of 0.6–0.9 S/cm, where  $a$  and  $b$  represent the  $a$  and  $b$  axes for the monoclinic crystal structure of TTF–TCNQ complex) with our result, the order we evaluated is in the range between  $\sigma_b$  and  $\sigma_a$  and is closer to  $\sigma_a$ . It is concluded that the TTF–TCNQ conductive complex prepared under vacuum conditions is randomly distributed, thus the lowest conductivity ( $\sigma_a$ ) prevails and strongly affects the conductivity result. With further purification or improvement on the crystalline orientation, one is expected to increase the conductance (or conductivity), and so the extension on the sensor life may be realized.

As for the commercial aspect, a device like this should possess potential to be developed as a disposable sensor. A simple estimation can be made by considering the cost of raw materials (TTF: US\$ 138.3/g; TCNQ: US\$ 16.7/g, Aldrich, catalogue 2003–2004) with material losses during the thin film preparation (assume that only 10% of TTF–TCNQ is coated on the sensing electrodes). If total mass of 2 g (1 g TTF + 1 g TCNQ, molecular weight is the same for both, which is 240) is considered for TTF–TCNQ, then the total volume deposited is

$$V_t = \frac{W}{\rho} = \frac{2 \text{ g}}{1.615 \text{ g/cm}^3} = 1.24 \text{ cm}^3$$

For each sensing film, the deposited volume is

$$v = 1.2 \text{ cm} \times 0.7 \text{ cm} \times 200 \text{ nm} = 1.68 \times 10^{-5} \text{ cm}^3$$

With a total raw material consumption of 2 g, the total number of sensing chip to be coated can be calculated by assuming 90% of raw materials loss

$$N = \frac{0.1V_t}{v} = 7371 \text{ chips}$$

So, the material cost for each sensing chip is only

$$\frac{138.3 + 16.7}{7371} = \text{US\$ } 0.021 \text{ per chip}$$

With the encouragement of this cost estimation, we believe that the disposable sensor of this type does have a commercial potential.

## 5. Conclusions

In this research, we use thermally evaporated TTF–TCNQ complex as an active material in detecting NO<sub>2</sub> gas.

According to its irreversible behavior, a complete deduction of reaction/diffusion control model based on several assumptions is obtained so as to describe the phenomenon we encountered. Initial linear region (zone 1) was governed by the first-order reaction (case 1); and the long time region (zone 3) is diffusion control (case 2). As for the calibration curve, since the sensing film is no longer a fresh film, only “diffusion control” case is applicable in this sensing system. The linear relation of sensing curve will stand, as long as the “short contact time or low concentration” condition holds. In an acceptable range that tarnishing film thickness can be regarded as a constant, it shows good reproducibility with a sensitivity of  $8 \pm 0.1 \times 10^{-3} \mu\text{S/s ppm}$ . However, the sensitivity and the sensing limit will depend on the thickness of tarnishing film and the way TTF–TCNQ film is prepared. Even though this material is sacrificial in nature, the constant conductance change rate can even shorten the detecting time, while typical sensors must wait for steady-state response. The order of conductivity evaluated is compatible to the literature reported, and is thought to be morphology dependent. The cost of each sensing chip is quite low and it is suitable to be used as a disposable sensor.

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