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Investigation into the ring-substituted polyanilines and their application for the detection and adsorption of sulfur dioxide

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Abstract

It has been demonstrated in this study that the substituents on the monomer aniline benzene ring are able to introduce the significant differences to the resulting polyaniline's collective properties. We systematically evaluated the structural perturbation effects of two substituents (methyl and methoxy) of aniline monomer through the electrochemical method. Our results showed that the methoxy group induces the less structural perturbation than the methyl counterpart, because of its partial double bond restriction. The morphologies are different for the polyaniline and the ring-substituted polyanilines, in which substituted polyanilines feature the larger porosities with the addition of these side groups. The influential effects of the methoxy side group have been further illustrated and amplified by its superior sensing performance towards the environmentally-significant sulfur dioxide gas, evaluated through the construction of the quartz crystal microbalance (QCM)-based gas sensor with these polyaniline materials. The as-constructed gas sensor's sensitivity, selectivity and stability in terms of its SO₂ responses have been evaluated in details. The methoxy-substituted polyaniline was tested to show the unique gas sensing properties for the sulfur dioxide at the low concentrations (50–250 ppm) and function as the adsorbing material at the high concentrations (500–1250 ppm). Thus it can be used both as sensing material as well as a novel filter and/or storage reservoir for the removal of sulfur dioxide pollutant from the environments.

Keywords

Polyaniline; Gas sensing; SO₂; Quartz crystal microbalance; Adsorbing material

1. Introduction

Sulfur dioxide (SO₂) constitutes one of the major environmental pollutant gases and is responsible for the formation of the corrosive acid rain and acid smog after reacting with the water vapors in the atmosphere. The formed acid rains can further acidify and pollute the soils, which causes the serious environmental effects. With the increased concentrations of

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SO₂ in the air, it can trigger asthma as well as result in the severe damage to the respiratory system of the human beings. So the accurate and rapid method of monitoring and removal of the sulfur dioxide in the environment, especially in the atmosphere, is in constant need, with its real-time and on-site diagnostic measurement holding the significant position [1,2]. There are various analytical methods that have been developed for measuring the concentration of sulfur dioxide, such as the chromatography and numerous spectroscopic techniques. But these end-point techniques can not measure the dynamic ambient conditions, they are also costly and time-consuming and require the trained personnel to operate the expensive instruments. Compared to them, the quartz crystal microbalance (QCM)-based mass sensing is a cost-effective and real-time analytical method, avoiding the unnecessary off-site analysis, providing the real-time data for analysis, thus meeting the specific on-site monitoring requirements of the sulfur dioxide [3,4].

With the selection of the QCM transducer, a sensing material is needed to be coated on the QCM electrode. The adsorption and/or molecular interaction of the sensing material with the target sulfur dioxide gas molecules provides the sensitivity and selectivity for detection via the altered mass changes through the QCM resonator. Conducting polymer (CP) is a family of versatile organic materials to serve as the good candidate as the sensing materials, providing high surface areas and tunable functionality [5,6]. With our group's recent interests in the exploring the use of the conducting polymer in the sensor development with enhanced sensitivity and selectivity [7–9], the ring-substituted polyaniline and polyaniline itself were selected to serve as the coating material, facilitating the sulfur dioxide sensing [10–12]. Several educated considerations contribute to this choice. The first fundamental one lies in the fact that sulfur dioxide belongs to the category of the acidic gases. It is known that polyaniline has good acid/base properties, rendering the better molecular and/or physical interactions between the target gas and the sensing material, which is a prerequisite for the selective gas adsorption in the gas sensor design. Furthermore, the efficient synthesis and fabrication of the polyaniline films with the electrochemical techniques and their good environmental stability also support our selection in this gas sensor development [13,14].

In this work, we investigated the effects of the electron-donating groups (-OCH₃ and -CH₃) on the resulting polyaniline's analytical performance for SO₂. Specifically we have fabricated the ring-substituted polyaniline thin films on the QCM gold electrodes, using the electrochemical polymerization method and their real-time frequency responses to the different environmentally-important gases were characterized. The results show that the as-constructed poly (2-methoxyaniline) thin film adsorbs selectively the contaminant gas sulfur dioxide and gives signals that are quantitative. It has been concluded that at low concentrations of sulfur dioxide, the poly (2-methoxyaniline)-based QCM gas sensor can serve as an analytical sensor for its determination. With increasing SO₂ amounts, the poly (2-methoxyaniline) is able to function instead as an adsorbing material for the removal of the toxic SO₂ gas from the environment and a novel and unique filter and/or storage reservoir for this pollutant.

2. Experimental

2.1. Chemicals

2-Methoxyaniline (99.5%), 2-methylaniline (99.5%) and aniline (99.5%) were purchased from Sigma-Aldrich and used without further purification.

2.2. Experimental methods

The gold-coated quartz crystal was used as the working electrode. The Ag/AgCl and platinum wire with a diameter of 0.5 mm were used as the reference and counter electrodes respectively. The electrolytic solutions consist of 0.1 M aniline, 2-methylaniline or 2-methoxyaniline in 1.0 M H₂SO₄ respectively. The potentiodynamic method was used for the electro-polymerization of the different aniline monomers and the formation of the derivatized-polyaniline and polyaniline coatings on the surfaces of the QCM gold electrodes. The potential range was between -0.2 and 1.3 V and the scan rate was 50 mV/s. A total of 8 cycles were carried out. After polymerization, the polymeric films were rinsed with deionized water and ethanol. These electrochemical operations were performed with the Gamry potentiostat, which runs the Windows XP (Gamry Instruments Inc). The SEM images were obtained using a JEOL JSM-6510 scanning electron microscope integrated with the Oxford Instruments EDS (energy dispersive spectroscopy) unit.

The 10 MHz AT-cut quartz crystals are used. The prepared QCM gas sensor was integrated within a flow gas system, as shown in Fig. S1. The N₂ was used as the background gas. The gas concentrations were controlled by the mass flow controllers. The frequency of the QCM sensor was recorded with a measuring system consisting of a RQCM oscillator (research quartz crystal microbalance, MAXTEK Inc.), a frequency counter and a computer. The measurements were carried out at the room temperature and at a continuous flow rate of the gas mixture amounting to 200 sccm/min, where pure nitrogen and nitrogen containing the target gas at the given concentrations were introduced into the chamber alternatively.

3. Results and discussion

3.1. Electro-polymerization of aniline derivatives on the QCM gold electrode

Electro-polymerization has been a versatile method for directly forming the conducting polymeric thin films on the various substrate surfaces, ranging from the noble metals (Pt or Au), glassy carbon to the transparent electrode (indium tin oxide). The cyclic voltammetry technique was used in our experiment for the electro-polymerization of the different aniline derivatives [5,6,9]. The complete cyclic voltammograms of the electro-polymerization of the aniline, 2-methylaniline and 2-methoxyaniline are shown in Fig. 1.

The three different polymers share some similarities in the growth of the polymeric thin films. The common feature lies in the appearance of these initiation peaks of the respective monomers during their first polymerization cycles, though with the varied oxidation potentials (Table 1). As expected, the electron-donating methoxy group activates the aniline monomer most, corresponding to the lowest monomer initiation oxidation potential at 0.73 V (Fig. 1c, peak III). The poly (2-methoxyaniline) also displays its own unique characteristic

oxidation peak in the cyclic voltammogram: a second plateau-like peak (Fig. 1c, IV), which is centered around 1.1 V, could be identified and should be assigned to the partial oxidation of the methoxy substituent at the *ortho* position of the aromatic benzene ring. This second peak is missing for the other two polyaniline counterparts.

Starting from the second polymerization cycle, for the polyaniline and poly (2-methoxyaniline), the characteristic two pairs of redox peaks of polyaniline family begin to show up clearly during the growth of these polymeric films, representing the polyanilines' typical leucoemeraldine/emeraldine (Fig. 1a,c, peak I and I') and the emeraldine/ pernigraniline (Fig. 1a,c, peak II and II') transitions respectively (See Supplementary data Scheme S1 for a concept scheme) [5,6,9]. The peaks I' and II' refer to the corresponding reduction processes. But for the poly (2-methylaniline), only one pair of redox pair is dominant (Fig. 1b), which shows that the two characteristic transitions merge into one. It is believed by us that this merge stems from the structural perturbation effect of the added *ortho*-position methyl group. These added substituents will break, to some extent, the coplanarity of the recurrent benzenoid and/or quinoid rings along the polymeric chains [15–17], which in turn decreases the electronic transitions within the system (Fig. 2). So the intricate two oxidation state changes (peak I and I' of leucoemeraldine/emeraldine and peak II and II' of emeraldine/pernigraniline) can be not distinguished efficiently, providing the overall one oxidation/reduction pair (the combined peaks I/II and I'/II' in Fig. 1b) [16,17]. The methoxy group is, however, a unique substituent. As an extra side group at the *ortho* position next to the aniline's amino group as well, it should also induce the breakage of the coplanarity of these repeated aromatic rings, like that of the methyl group. Actually our cyclic voltammetric data show that the methoxy group does not lead to this behavior to such a great extent, as the two transition state changes can be still obviously identified (Fig. 1c, peaks I, II, I' and II'), though poly (2-methoxyaniline) features the decreased peak potential gaps of 0.12 V for the oxidation direction between peaks I and II and 0.21 V for the corresponding reduction wave between peaks I' and II', in comparison to the polyaniline's 0.54 V and 0.29 V of the oxidative and reductive peak gaps respectively (Table 1). These decreased peak potential gaps signal the expected trend of the methoxy group's structural perturbation effect, toward the one merged state of the methyl one. But due to the partial double bond formation between the oxygen and its connected carbon, the methoxy group is restricted structurally in comparison to the methyl counterpart, weakening its perturbation influences in the structural aspect (Fig. 2). Moreover, the lone pair of electrons on the oxygen donate to the aromatic systems, extending the large- π bonding of the polymeric systems, strengthening the whole system's electron communication [18–20].

After the electro-polymerization process, a layer of coherent and homogeneous polyaniline film can be clearly observed to have formed on the QCM gold electrode surfaces for the three polymers. Tables S1–S3 display, respectively, the net charge (Q_{net}), the number of electrons transferred and the mass deposited during the potentiodynamic growth of the 0.1 M aniline, 2-methylaniline and 2-methoxyaniline electro-polymerization in the 1.0 M H_2SO_4 solution for each sweeping cycle. The Q_{net} has been calculated from the difference between the Q_{anodic} and Q_{cathodic} from the integration of the cyclic voltammetric currents. Q_{anodic} and Q_{cathodic} refer to the charge associated with the anodic and cathodic processes

respectively. Their difference represents the net charge used for the polymer growth during each sweeping cycle. As reported in the literature [21–23], if the net charge has a polynomial relationship against the cycle number, the open polymer structures are formed, instead of the compact ones. The net charge of aniline, 2-methylaniline and 2-methoxyaniline electro-polymerization process has been plotted versus the cycle number respectively, as shown in Figs. S2–S4. Their polynomial functions of the net charge against the cycle number indicate the formation of the open polymer structures in these polyaniline derivatives, which is ideal and desired for the subsequent gas sensing testing. This is the reason why H_2SO_4 has been chosen for the electro-polymerization, which brings this effect, compared with the compact polymer structures generally formed by using HClO_4 .

These cyclic voltammograms of the electro-polymerization of the three different aniline family members provide their special growth pathways, which will contribute to their resulting different molecular interactions with the sulfur dioxide gas, on which we aim to demonstrate that the intricate simple substituents of aniline are able to result in great influences on the whole macromolecular performances, as will be discussed later.

3.2. The morphological study

The morphologies of the three polyaniline thin films have been characterized by the scanning electron microscopic technique as shown in Fig. 3. It can be seen that for the un-derivatized polyaniline (Fig. 3a), it displays a powdery morphology and has the relatively small porosity. With the addition of the methyl (Fig. 3b) and methoxy (Fig. 3c) side groups, the initial powdery morphology clearly changed to the band-like and globular-like appearances respectively. The globular-like morphology features the enlarged cavities in the poly (2-methoxyaniline) microstructures, which will provide the better gas permeability and result in its good sensing performance as discussed below [24,25].

3.3. Sulfur dioxide sensing test

With the three polymeric films readily available, they are subject to the tests of their real-time frequency responses to the sulfur dioxide gas ranging from 50 ppm to 250 ppm (Fig. 4a). The poly (2-methoxyaniline) shows the obvious advantage over its two other counterparts in terms of the sensitivity (Fig. 4b), 0.19 Hz/ppm versus polyaniline's 0.11 Hz/ppm and poly (2-methylaniline)'s 0.088 Hz/ppm (Table 2), within the low concentration region (below the 250 ppm threshold). The response time of poly (2-methoxyaniline) is also better than those of polyaniline and poly (2-methylaniline) (Table 3) [26,27].

It is reasonably expected from the polymer's structural viewpoint that the methoxy substituent can change the torsional angles between the adjacent recurrent benzenoid and quinoid rings in the polyaniline chain, simultaneously influencing the inter-chain distances. All of these will collectively adjust the sizes of the polymeric pores, affecting the relevant gas permeability in a direct sense and eventually the overall sensing performances of the as-designed gas sensor [28–30]. A second function of the introducing substituent is to modify the electronic properties of the polymer backbone itself, specifically involving the adjustment of the electron cloud density of the aniline aromatic ring and the resulting polyaniline's energy band gap [5,6,9]. In our opinion, these will contribute to strengthen the

molecular interaction between the acidic sulfur dioxide gas and the basic polyaniline film, owing to some of the hydrogen bonding-like character as illustrated in Fig. 5. A third influencing factor attributes to the change of pKa of the basic nitrogen sites of the polyaniline through the electronic effects of the methoxy substituent. As the electron-donating group, methoxy substituent is able to activate the aniline monomer, making its overall electro-polymerization process more efficient [31–33]. Specifically the methoxy group can enrich the electron cloud density of aniline aromatic ring by the delocalization of the oxygen lone pair of electrons, thus making the polyaniline more Lewis-base like to strengthen the acid (sulfur dioxide)-base (polyaniline) interaction (Fig. 5). The methyl group, however, has much weaker electron-donating ability compared with that of the methoxy group. Taking advantage of this, it has been shown from our experimental result that these lone-pair electrons on the methoxy group are likely to impart some hydrogen bonding-like character to offer the much favored molecular interaction with the sulfur atom of the sulfur dioxide (Fig. 5), which results in the improved sensing performances from the molecular level of the polymeric material [34,35].

3.4. Selectivity test

With the superior sensing performances of the methoxy-modified polyaniline identified as shown above, it has been subjected to the tests of its responses to the other different environmentally-significant gases, such as the O₂, H₂, CH₄, NO₂. As we have expected, the sensor selectively gave the strong responses to the acidic target gas SO₂, causing the negligible mass changes for the other neutral gases (O₂, H₂, CH₄) (Fig. 6a). NO₂, however, also being an acidic gas that causes much attention from the environmental protection viewpoint, introduced much interference compared to those neutral gases. But the poly (2-methoxyaniline) provided some partial selectivity between the two acidic gases in terms of the sensitivity: 0.19 Hz/ppm of SO₂ versus 0.10 Hz/ppm of NO₂ (Fig. 6b, c). It is believed by us that this partial selectivity of poly (2-methoxyaniline) towards the two acidic gases probably comes from the unfavorable partial repulsion interaction between the nitrogen of NO₂ and the polymer backbone's amine and/or imine nitrogen sites [36,37].

3.5. Stability test

The poly (2-methoxyaniline) sensor was kept in the ambient environment, without any special treatments on them. Its sensing responses towards SO₂ at the different time periods have been monitored continuously and exhibited in Fig. 7. As shown, the poly (2-methoxyaniline) is quite stable to give the distinct and satisfying responses towards the target gas after a long period of time.

3.6. Adsorption material at high concentration

With the increasing SO₂ amounts above the 250 ppm threshold, the poly (2-methoxyaniline) gradually displays some irreversible adsorption of the target gas (Fig. 8a), rendering the desorption process being not complete in the nitrogen atmosphere. Also the calibration curve deviates from the ideal linearity to reach its saturation state with the increased gas loading (Fig. 8b). It is believed by us that this unique and stronger adsorption property of the poly (2-methoxyaniline) than that of the polyaniline and poly (2-methylaniline), stems from this extra non-covalent or the hydrogen bonding-like interactions between the methoxy side

group and the sulfur center of the sulfur dioxide gas (Fig. 5), in addition to its basic backbone attraction to the acidic gas. It is because of this molecular-level modification that renders the acidic sulfur dioxide gas being not able to escape from the polymeric thin films in a comparably rapid manner under the nitrogen purging. This unique sulfur dioxide trap conveys the potential promising filter and storage properties of this environmentally-significant pollutant to the unique poly (2-methoxyaniline) thin film, shedding light on its possible application towards the efficient removal of this pollutant from the surroundings [38–40].

4. Conclusion

We have illustrated in this work that the simple substituents are able to make the big difference to the resulting polyaniline's collective properties. Our electrochemical experiments show that the methoxy group induces the less structural perturbation than the methyl group due to the partial double bond formation to restrict the side group and extending the whole large- π bonding of the conducting system. The SEM images describe the three polymeric thin films' morphological characters, featuring the larger porosities for the ring-substituted polyanilines, contributing to improve their gas permeability and the associated gas sensing capabilities. The substituents on the aniline monomer have been shown to have the influential roles in the polyanilines' properties, which were demonstrated in their different gas sensing performances. The QCM gas sensors have been constructed based on these ring-substituted polyaniline thin films. Their real-time frequency responses to the environmentally-important sulfur dioxide gas have been investigated. It has been concluded that at low concentrations of sulfur dioxide (below the 250 ppm threshold), the poly (2-methoxyaniline)-based gas sensor can be utilized as a sensor for its concentration determination. With the increased SO_2 amounts, the poly (2-methoxyaniline) is able to function instead as an adsorbing material for the removal of the toxic SO_2 gas from the atmosphere or the other surroundings and a unique and novel gas filter and/or storage reservoir for this pollutant.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2017.04.057>.

Fig. 1.

The electro-polymerization cyclic voltammograms of the aniline (a), 2-methylaniline (b) and 2-methoxyaniline (c) on the QCM gold electrode. Scan rate: 50 mV/s. The electrolytic solutions consist of 0.1 M aniline, 2-methylaniline and 2-methoxyaniline in 1.0 M H_2SO_4 respectively.

Fig. 3.
The SEM images of polyaniline (a), poly (2-methylaniline) (b) and poly (2-methoxyaniline) (c).

Fig. 4. (a) The real-time QCM frequency responses of polyaniline (green), poly (2-methylaniline) (red) and poly (2-methoxyaniline) (blue) towards the different concentrations of SO_2 ; (b) The calibration curves for the corresponding three polymeric thin films. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5.

The proposed molecular model for the sensor-analyte interactions between the poly (2-methoxyaniline) and the sulfur dioxide and the resulting influences of introducing the methoxy substituent.

Fig. 6.

(a) Selectivity of poly (2-methoxyaniline) sensor towards the different environmentally-significant gases; (b) The real-time QCM frequency responses of poly (2-methoxyaniline) towards the different concentrations of SO₂ and NO₂; (c) The calibration curves displaying the poly (2-methoxyaniline)'s partial selectivity between SO₂ and NO₂.

Fig. 7.
Stability of poly (2-methoxyaniline) sensor.

Fig. 8.

(a) The real-time frequency responses towards the consecutive change of the high sulfur dioxide concentrations. (b) The calibration curve spanning the different SO_2 concentrations.

Table 1

The comparison of the electrochemical properties of the three polymers.

	Poly (aniline)	Poly (2-methylaniline)	Poly (2-methoxyaniline)
Initiation potential (V)	1.12	1.10	0.73
$E = E_{II} - E_I$ (V)	0.54	N/A	0.12
$E = E_{II'} - E_{I'}$ (V)	0.29	N/A	0.21

Table 2

Analytical characteristic parameters of three polyanilines for the determination of SO₂ ^a.

Polymer	Film thickness (μm)	R ²	Sensitivity factor (Hz/ppm)
Poly (aniline)	1.91	0.9997	0.11
Poly (2-methylaniline)	1.69	0.9975	0.088
Poly (2-methoxyaniline)	1.06	0.9993	0.19

^aThe thickness of the polymeric films are calculated using the density of polyani-line of 1.33 g/cm³. The geometric area of the gold QCM electrode is 0.22 cm².

Table 3

The signal saturation time of three polyanilines to the different concentrations of SO₂^a.

Concentrations (ppm)	Poly (aniline) (min)	Poly (2-methylaniline) (min)	Poly (2-methoxyaniline) (min)
50	37.3	34.3	29.7
100	71.3	70.3	68.4
150	113.4	113.8	112.8
200	153.4	153.0	152.2
250	191.2	190.1	189.7

^aThe signal saturation time is the time to reach the 90% of maximum signal change. This time also includes the sampling time (the time for the gas to travel from the gas tank to the QCM sensor through the tubings.).