



Highly sensitive amperometric Nafion-based CO sensor using Pt/C electrodes with different kinds of carbon materials



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ABSTRACT

In this paper, a novel amperometric CO sensor using Nafion and Pt/C composite electrodes was fabricated. Three kinds of carbon materials (carbon fibers, multiwall carbon nanotubes and carbon blacks) were utilized as the supports of the sensing and reference electrodes for the CO sensors. The results revealed that the effective Pt loadings on the electrodes increased in the following order: carbon fibers (CFs) > multiwall carbon nanotubes (MWCNTs) > carbon blacks (CBs), leading to the increasing of the sensitivities toward CO in same order. In other words, the sensor using Pt/CFs as the sensing electrode (SE) showed the highest sensitivity with the value of 0.077 $\mu\text{A}/\text{ppm}$ and shortest response time in the range of CO concentration from 1 to 200 ppm at room temperature. Further, a reproducible and stable response against 50 ppm CO was obtained for the sensor with Pt/CFs SE materials. Moreover, a low detection limit of 0.1 ppm for CO was also examined, suggesting that the sensor can be convenient for detecting very low traces of CO.

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1. Introduction

Recently various kinds of gas sensors are required for monitoring carbon monoxide (CO) from the combustion exhaust such as automobiles, industrial plants and gas stoves, because CO is inflammable and can cause great harm to the body by bonding tightly with the hemoglobin, preventing the combination to oxygen [1–3]. Commonly, there are three types of sensors: semiconductor sensors based on SnO_2 [4–6], In_2O_3 [7,8], and so on, catalytic combustion sensors [9] and electrochemical sensors which are operated either in amperometric [10–12] or potentiometric mode [13–15].

Among the amperometric type electrochemical sensors, the gas sensor employing the Nafion membrane as the solid electrolyte, which shows good mechanical, outstanding chemical stability and excellent conductivities under the condition of high water vapor, has drawn more and more attentions recently [16–18]. Moreover, this type of sensors always works at room temperature and the response signals are almost proportional with the gas concen-

trations. For these sensors, the catalyst materials deposited on the Nafion membrane are indispensable for the gas detection. For example, K.C. Ho [19] has reported a NO gas sensor based on Pt/Nafion electrodes at a concentration of 500 ppm. Beyond that, the binary Pt-Ru electrode materials have also been prepared to detect H_2 by Y.C. Weng et al. [20]. Now it is well known that the addition of noble metals is an effective strategy to enhance sensing performance to target [21,22]. Nevertheless, the use of noble metals also has some drawbacks such as the self-aggregation of metal particles which may decrease the active surface areas for the interactions between gases and catalyst powders, expensive cost and poor selectivity.

A large number of ways have been adopted to overcome the above shortcomings. One of promising solution proposed for improvement is to deposit the metal nanoparticles (NPs) on some supports. Among them, alternative carbon materials like carbon blacks [23], ordered mesoporous carbons [24], carbon nanotubes [25–27] and carbon nanofibers [28–31] have been successfully prepared to support the metal NPs for applications in electrochemical catalysis and fuel cells because of their excellent conductivity and porous microstructure for dispersion of metal particles and gas transformation. Herein, a great deal of attentions have been drawn on the kinds of carbon supports for the homogeneous deposition of Pt NPs due to their unique surface structures, excellent mechan-

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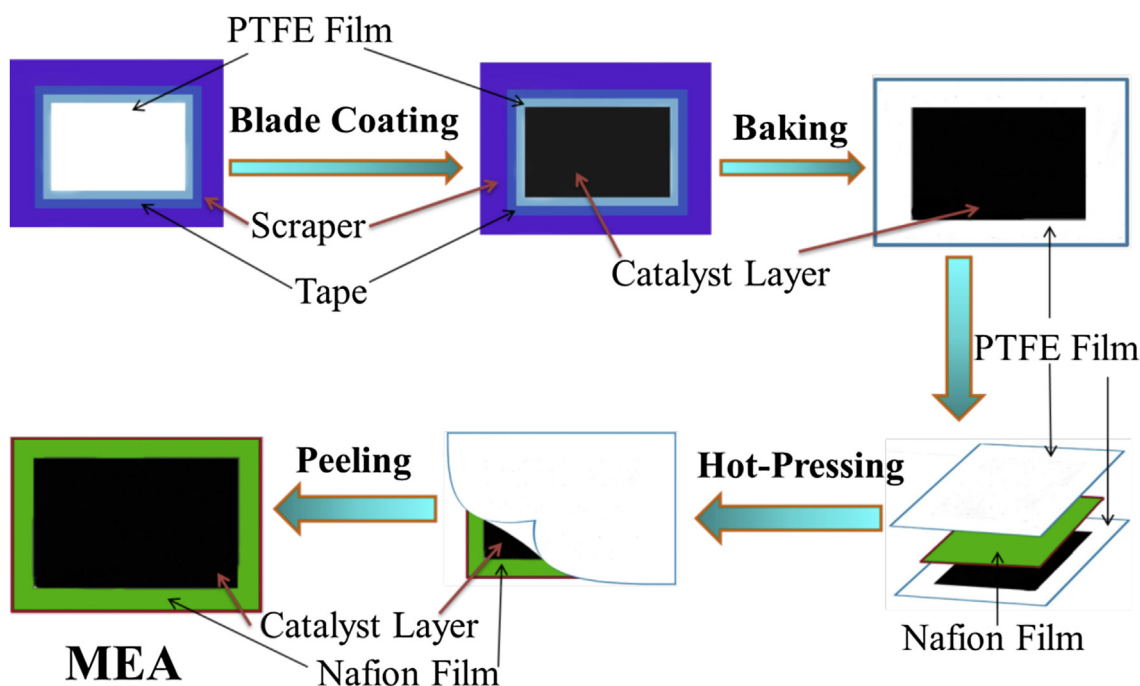


Fig. 1. Fabrication of the membrane electrode assembly (MEA) for the sensor.

ical properties, high electric conductivity and large surface areas [32,33]. For instance, Y.C. Liu et al. [34] have prepared a solid state H_2 sensor using Pt particles supported on activated carbon powders by the indirect wetting method and found that the sensitivity is $0.716 \mu A/ppm$ at a Pt loading of 3.0 mg/cm^2 . Besides, B. Zhao et al. [31] have employed the incipient wetness impregnation and electrodeposition methods to prepare a novel electrocatalyst, Pt NPs supported on activated carbon fibers, for the electrocatalytic hydrogenation of furfural to furfuryl alcohol. As far as we know, however, very few researchers have developed CO sensors by fabricating the sensing electrodes with noble metal particles supported on these carbon materials.

In this work, the Pt NPs deposited on CBs, MWCNTs and CFs, respectively, are utilized as the composite SE materials for the Nafion-based CO sensor. The differences of the microstructure for three types of catalytic powders have been discussed. Besides, when fabricating the amperometric sensor based on Nafion membrane, it is particularly critical to attain an excellent contact between Nafion membrane and catalytic materials for good proton and electronic conductivity. An effective way for obtaining the excellent contact is the hot-pressing method. After hot-pressing, the varieties of Nafion membranes attached with three kinds of catalytic materials (Pt/CBs, Pt/MWCNTs and Pt/CFs) have been obtained. Beyond that, the sensing properties and mechanism of the Nafion-based amperometric CO sensor have been investigated.

2. Experimental

2.1. Preparation of Pt NPs with different carbon supports

The Pt NPs are reduced from hexachloroplatinic acid (H_2PtCl_6 , Shanghai Wu Chemical Reagent Co., Ltd.) by using sodium borohydride ($NaBH_4$, Aladdin) as the reductant on three carbon supports: CBs (CABOT, U. S. A.), MWCNTs (XFNANO Co., Ltd.) and CFs (Beijingdaoking Co., Ltd.). The detailed procedure is as follows.

First, the carbon support is suspended in deionized water with $50 \text{ mM } H_2PtCl_6$ solution and trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, Sinopharm Chemical Reagent Co., Ltd.) acted as the stabilizer at a carbon support/trisodium citrate weight ratio of 4:1:3 by ultrasonication for 30 min. Next, $50 \text{ mL } NaBH_4$ solution, which is obtained by dissolving the $NaBH_4$ powders into $50 \text{ mL } 0.1 \text{ M } NaOH$ solution to prevent the hydrolysis, is added into the resulting suspension dropwise with continuously magnetic stirring at $50^\circ C$ for 2 h. Then, such prepared Pt/C powders are cleaned with deionized water and dried at $80^\circ C$ for 12 h.

2.2. Fabrication and measurement of the amperometric CO sensor

The amperometric CO sensor is fabricated using the fuel cell prototype as described in our previous work [35]. The prototype contains a membrane electrode assembly (MEA) composed of two catalyst layers hot pressed at $90^\circ C$ and 8 MPa on a Nafion membrane which is pre-treated in $5\% H_2O_2$ solution, $0.5 \text{ M } H_2SO_4$ solution and deionized water at $80^\circ C$, respectively. The MEA, which is inserted between the gas diffusion cap and isolation disc, is obtained by the scrapping method as shown in Fig. 1. 10 mg as-prepared Pt/C catalyst powders are well-distributed in $100 \mu L$ of pre-arranged dispersant which includes $100 \mu L$ $5 \text{ wt.}\%$ Nafion solution used for attaining strong interactions between Nafion membrane and catalytic powders, $50 \mu L$ ethylene glycol (EG) and $200 \mu L$ deionized water on polytetrafluoro-ethylene (PTFE) film. Then two pieces of resulting films are dried at $90^\circ C$ and hot-pressed with the Nafion membrane. Finally, the PTFE films are peeled away and the MEA is immersed in deionized water for 12 h. Three kinds of MEAs containing Pt NPs supported on CBs, MWCNTs and CFs are labeled as M_a , M_b and M_c , respectively. Correspondingly, CO sensors fabricated by above three types of MEAs are defined as S_a , S_b and S_c , respectively. Based on the remaining volume of catalyst inks on the surface of PTFE films after hot-pressing, the Pt loadings of

Table 1
Pt loadings in the SE and RE for different MEAs.

Sample	Pt Loading(mg/cm ²)	
	SE	RE
M _a	0.35	0.34
M _b	0.36	0.35
M _c	0.63	0.54

the SE and reference electrode (RE) for three MEAs are calculated and listed in Table 1.

The phase information and lattice parameters of prepared samples were investigated by X-ray diffraction analysis (XRD, using Cu K α radiation at 0.1541 nm, Rigaku). The Gemini VII surface area and porosity system was used to measure the N₂ adsorption-desorption isotherms to estimate the specific surface area of three kinds of Pt/C catalysts with and without dispersant. To obtain the microstructure of three types of as-synthesized samples, the field emission scanning electron microscopy (FESEM) was employed with a JEOL JSM-2100F microscope at an accelerating voltage of 200 kV.

The cyclic voltammetry measurements (CVs) for the amperometric CO sensor were carried out between -0.6 and 0.8 V with a scanning rate of 20 mV/s by the electrochemical workstation (CHI611C, Shanghai Instrument Corporation, China). Besides, the chronoamperometry was applied to record the sensing properties toward CO by the conventional static method described in our previous reports [36] using the same workstation without an initial potential. Moreover, all the electrochemical and sensing performances were measured at room temperature (23 – 25 °C) in the laboratory with 20% – 25% RH. In the case of sensing experiments, each injection of target gas is followed by an exposure to the ambient air. As a result, the current signal (ΔI) toward CO is defined as the difference in the presence (I_p) and absence (I_a) of the target gas. Thus the ΔI value is correlated with the CO concentration and the slope is acted as the sensitivity.

3. Result and discussion

Fig. 2 shows the XRD patterns of three carbon materials before and after supporting the Pt NPs. Two obvious peaks at the position of $2\theta = 24.6^\circ$, 43.8° for CBs ($2\theta = 26.2^\circ$, 44.4° for MWCNTs and CFs) are observed, indicating the graphite crystallite of the carbon materials. Moreover, it can also be seen that five peaks for three types of Pt/C samples appear at $2\theta = 39.8^\circ$, 46.2° , 67.4° , 81.3° and 85.7° , respectively, which corresponds to the standard data (JCPDS Card No. 040802), showing a cubic structure of Pt NPs in these samples. No apparent diffraction peaks of any other impurity are observed, indicating high purity of the Pt/C samples. The average crystallite

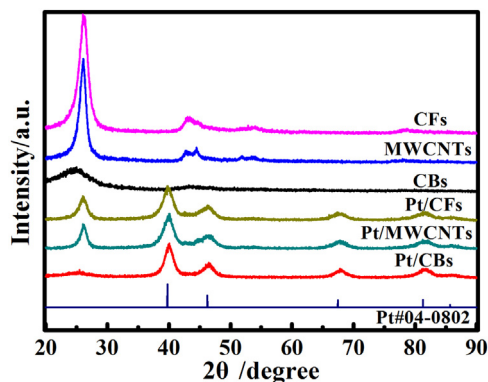


Fig. 2. XRD patterns of different carbon materials before and after supporting the Pt nanoparticles.

Table 2
The textural properties of as-prepared catalyst samples with and without dispersant.

Sample	BET Surface Area(m ² /g)		Average Pore Diameter(nm)
	Without Dispersant	With Dispersant	
Pt/CBs	159.1	9.5	51.2
Pt/MWCNTs	74.6	16.7	43.1
Pt/CFs	101.9	21.6	28.5

sizes of Pt supported on CBs, MWCNTs and CFs, which are calculated using the full width at half maximum (FWHM) of the Pt (2 2 0) peak by the Debye-Scherrer equation, are about 10.8 , 9.4 and 7.6 nm diameter, respectively.

The morphology and microstructure of as-synthesized Pt/C samples are determined by FESEM as shown in Fig. 3. The insets of three images show the morphology of carbon supports before the deposition of Pt NPs. It can be found that the Pt NPs are better distributed on the surface of CFs during the growth (Fig. 3c), which may be due to the roughness of the CFs surface. In contrast, the surface is more smoother for MWCNTs, indicating the aggregation of Pt NPs which can facilitate to form larger Pt particles (Fig. 3b). In the case of deposition of Pt NPs on CBs, it seems likely to occur on the graphitic shell filled with a lot of micropores as described in the Ref. [37]. As a result, a strong aggregation for Pt NPs has been observed. Besides, the self-aggregation of carbon black powders can also cause the coalescence of Pt NPs. Hence, the largest particles have been developed for Pt NPs supported on CBs (Fig. 3a). Furthermore, these observations presented in SEM images are well consistent with the calculation results from XRD measurement. To further confirm the microstructure of three catalyst powders, the specific surface area for as-prepared samples are calculated by BET method as shown in Table 2. It can be seen that the Pt/CFs have the largest BET surface area (21.6 m²/g) and the smallest average pore diameter (28.5 nm), in agreement with the results of XRD and SEM measurements.

To obtain the qualitative information about the amount and distribution of the Pt/C catalyst powders on Nafion membrane during the preparation of MEA using the hot-pressing method, Fig. 4 represents the differences of Nafion membrane (A) and PTFE films (B) after hot-pressed. It can be seen that the catalyst layer of M_c has the best quality with highest uniformity and the Nafion membrane basically remains original shape without any severe distortion after hot-pressed, as shown in Fig. 4A(c). In addition, the minimum residual catalyst inks on the PTFE film has also been observed after hot-pressed in Fig. 4B(c), indicating the maximum of Pt loadings on M_c. Nevertheless, when the Pt NPs are supported on CBs, a certain amount of distortion has occurred for the Nafion membrane and a large number catalyst inks have been left over on the PTFE film after hot-pressed, which lead to the smallest amount of Pt loadings on M_a. For the Pt/MWCNTs catalyst powders (b), the amount of Pt loadings for M_b are between that for M_a and M_c, which correspond to the results calculated by the weighing method as shown in Table 1. Here, these consequences may be attributed to the hydrophobicity of the carbon supports and the interactions between Pt NPs and carbon supports. Compared with CBs, MWCNTs and CFs have the more hydrophobic surfaces and segregate the catalyst layer from PTFE film easier, which leads to the less residual catalyst inks. On the other hand, both the dispersity and interaction for Pt NPs on CFs are stronger relative to that on MWCNTs, indicating larger effective surface areas of electrodes for M_c.

Fig. 5 demonstrates the CVs of the as-prepared sensor (S_c) in air (a) and 200 ppm CO (b) between -0.6 and 0.8 V at 20 mV/s. Note that two CV curves are almost similar and no oxidation or reduction peaks have been observed, which may result from a certain amount charging current originally existed in the Nafion membrane [32,38]. Additionally, the current for S_c is smaller to 200 ppm CO gas

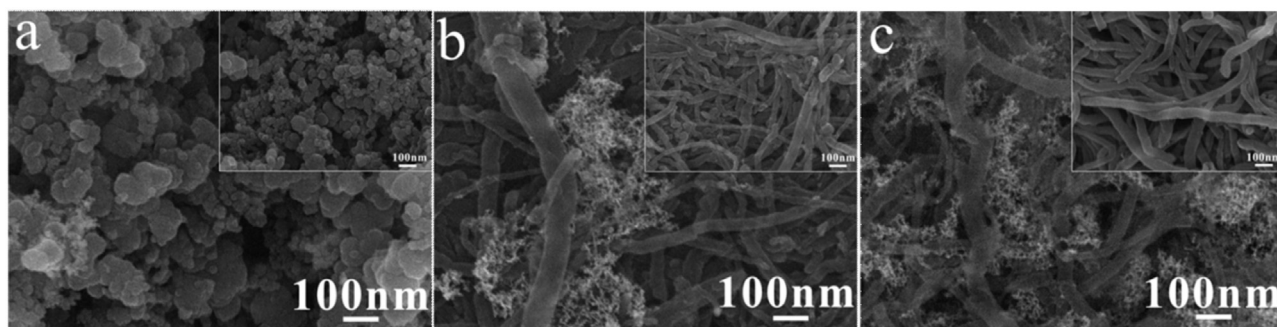


Fig. 3. FESEM images of Pt nanoparticles deposited on CBs (a), MWCNTs (b) and CFs (c). Inserts are carbon materials without Pt.

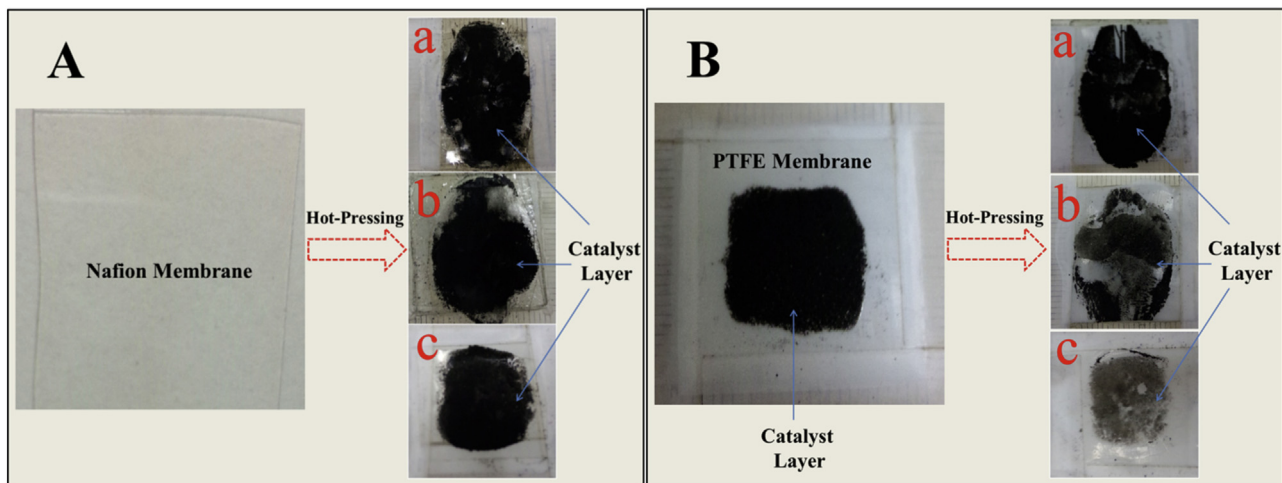


Fig. 4. Pictures of Nafion (A) and PTFE (B) membrane using (a) Pt/CBs, (b) Pt/MWCNTs and (c) Pt/CFs for the catalyst after hot-pressing.

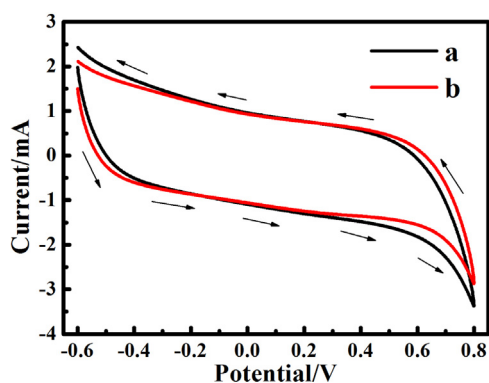


Fig. 5. Cyclic voltammograms of S_c in air (a) and 200 ppm CO (b) at 20 mV/s.

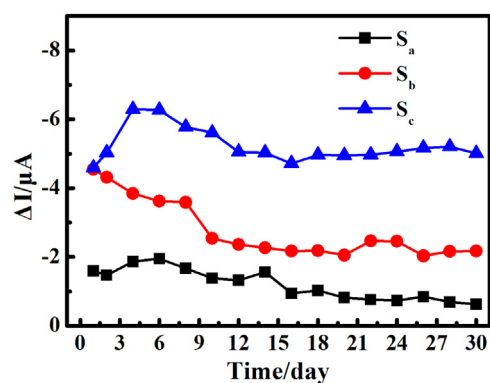


Fig. 6. The stability of three sensors toward 50 ppm CO.

than air at the same potential owing to the electrons generated in the oxidation of CO. Accordingly, all the sensing performance measurements of the amperometric sensor are performed without any applied potential by the chronoamperometry.

Fig. 6 shows the stability of three sensors in 30 days toward 50 ppm CO. The ΔI of S_c increased sharply in early days and then gradually became stable after 30 days. On the contrary, S_b had a highest value of ΔI (4.31 μA) toward 50 ppm CO which was almost same as S_c at the beginning. However, the response signal drastically decreased down to 2.49 μA after the aging experiment for 30 days. For S_a , the ΔI continuously decreased with aging days to keep the minimum value after 30 days. The degeneration for sensing performances of three sensors can be explained by the aggregation of Pt NPs, which has resulted in the loss of effective

surface areas for Pt/C catalysts. Since response signals of three sensors have tended to remain constant, all sensing properties are performed after 30 days aging in the following text.

In order to discuss the effects of carbon supports in catalysts on the sensing properties of CO sensor, the ΔI of three sensors toward 50 ppm CO is obtained and the response/recovery time defined as the time for the sensing current to 90% value of response current during adsorption/desorption have also been discussed. As shown in Fig. 7a, S_c has the largest value (5.03 μA) of ΔI against 50 ppm CO among three sensors, followed by S_b and S_a , respectively. These results are in very good agreement with the sensitivity experiment described in Fig. 7b (0.032 $\mu\text{A}/\text{ppm}$ for S_a , 0.037 $\mu\text{A}/\text{ppm}$ for S_b and 0.077 $\mu\text{A}/\text{ppm}$ for S_c). It has been well-known that there are plentiful micropores on the surface for CFs, resulting in highly dispersed

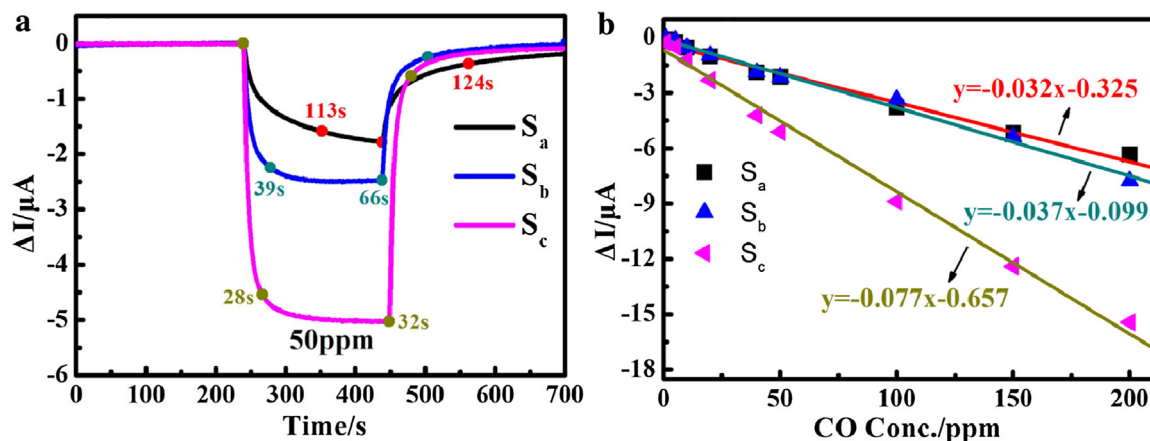


Fig. 7. (a) The typical response transients to 50 ppm CO for different sensors; (b) Relationships between response current and CO concentrations for sensors with different kinds of catalysts.

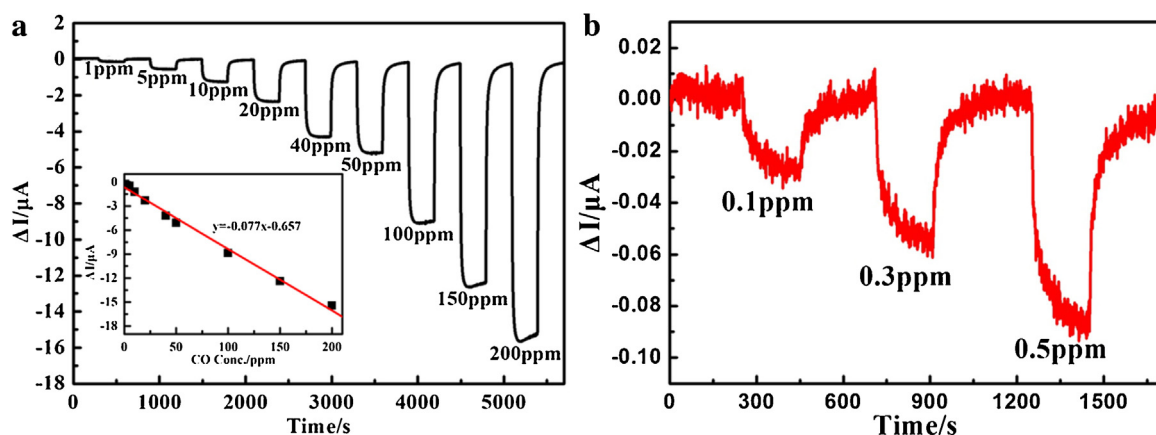


Fig. 8. The typical response transients of S_c to different concentrations of CO in the range of (a) 1–200 ppm and (b) 0.1–0.5 ppm.

deposition of Pt NPs. As described in [39], D.H. Lin et al. have found that the sufficient pores and high dispersion of Pt NPs on ordered mesoporous carbon exhibit high electrocatalytic activity for CO oxidation. Similarly, L.J. Gao [40] also finds that the CO oxidation has been enhanced by the ultrathin graphitic overlayers on Pt (1 1 1) surface. Thus, it can be concluded that the promotions of catalyzed reactions of CO may be caused by the larger concentrations of adsorbed CO on Pt NPs, which is normally assumed to follow the Langmuir–Hinshelwood mechanism [41]. It has been well-proved that there are two indispensable factors for this mechanism: One is the surface diffusion of the CO adsorbed on the catalyst and another is the OH (ads), which is known to combine with the adsorbed CO to form CO_2 , generated by electrochemical adsorption of H_2O . Additionally, CFs also owns a good hydrophobic property because of the fibrous structure, which can greatly alleviate the corrosion of carbon materials. These special features of CFs have led to optimal capabilities including the effective surface area and amount of Pt loadings, which are both the essential factors on the sensing performances of sensors. Thus in comparison with other two sensors, S_c has a largest effective surface area with the maximum value of Pt loadings (Table 1), indicating the highest sensitivity toward CO. Beyond that, the response and recovery times of S_c toward 50 ppm CO are 28 and 32 s, which are about 2 times and 4 times as fast as S_b and S_a , respectively. The faster response for S_c is mainly attributed to the low resistance and short diffusion distance of CFs compared with MWCNTs and CBs.

To study more detail information about the sensing performance of S_c toward CO, the typical response transients to different con-

centrations of CO in the range of 1–200 ppm are shown in Fig. 8a. It is obvious that the response current of sensor increases with the increasing CO gas concentration. From the inset of Fig. 8a, it can also be found that the sensitivity calculated from the slope of linear relationship between ΔI and the CO concentrations is $0.077 \mu\text{A}/\text{ppm}$. Subsequently, certain small CO concentrations (0.1, 0.3 and 0.5 ppm) are also introduced to give the information about the low detection limit for S_c as shown in Fig. 8b. It is noted that there is a clear output signal of 30 nA to 0.1 ppm CO, which is called as the low detection limit. Therefore, this amperometric sensor seems to be convenient for monitoring very low traces of CO in the environment.

Fig. 9a represents a typical response and recovery transients to 50 ppm CO for S_c . Here, the drift percentage of ΔI to 50 ppm CO for the sensor is calculated by the equation: $\text{Error}\% = (\Delta I - \Delta I_0)/\Delta I_0 * 100\%$, where ΔI_0 is the response signal of the first cycle and ΔI is that of other cycles. It has been revealed that the deviation percentages of ΔI for 50 ppm are all below 2%, showing an excellent reproducibility for this amperometric CO sensor.

The selectivity is also an important sensing performance parameter for gas sensor in practical application, so the ΔI of S_c toward 50 ppm of certain interference gases (H_2 , NO, NO_2 , SO_2 and C_2H_4) is shown in Fig. 9b. The present sensor has much higher response current toward 50 ppm CO in comparison to other interference gases, which displays the good selectivity. There may be mainly two factors to illuminate the high selectivity. Firstly, an effective mean for enhancing selectivity is the addition of noble metals (such as Pd, Au and Pt) [4,42,43]. For example, K. Wang [43] has fabricated a

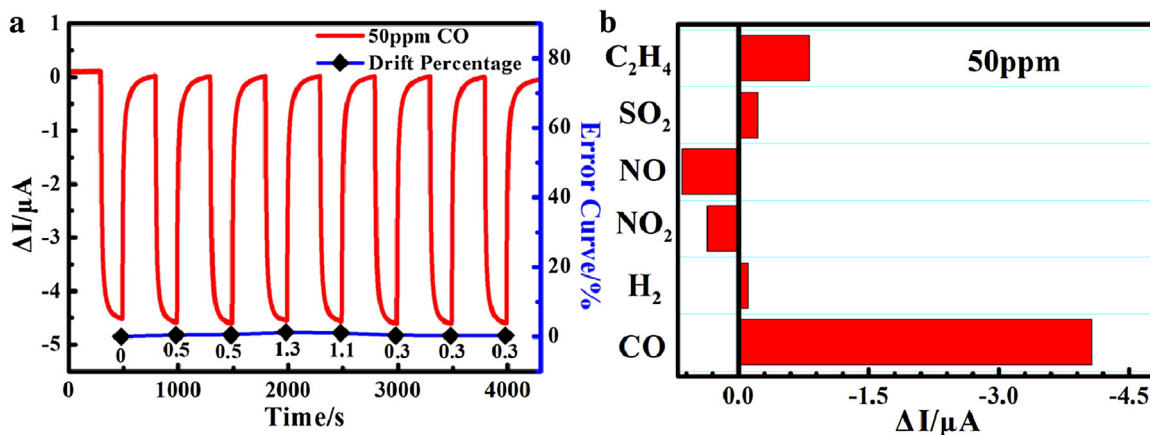


Fig. 9. (a) Continuous response and recovery curves of S_C for 50 ppm CO; (b) Cross-sensitivity of S_C to various kinds of gases at a concentration of 50 ppm.

highly sensitive CO sensor by Pt-loaded SnO_2 porous nanosolid. In this work, the sensing performance of the sensor toward CO has obviously improved by using Pt as the additive. Besides, as shown in Fig. 3(c), the Pt NPs have good dispersion on the surface of CFs. According to the Langmuir–Hinshelwood mechanism for CO oxidation, the strong capacity of CO adsorption on the highly-dispersed Pt NPs deposited on CFs has contributed to enhance the sensitivity to CO, comparing with other tested gases. As a result, the high selectivity has been obtained for the amperometric Nafion-based CO sensor.

As reported in [35,44], the mechanism of this amperometric CO sensor can be understood. When the present device is exposed in

CO gas, there are two reactions happening simultaneously at the SE:



The protons generated in the SE can transfer to the RE through the Nafion membrane. The electrons, however, can only get to the RE through the external loop because of the semipermeability of Nafion membrane. Afterwards, the reaction (2) has also occurred in the RE (Fig. 10):

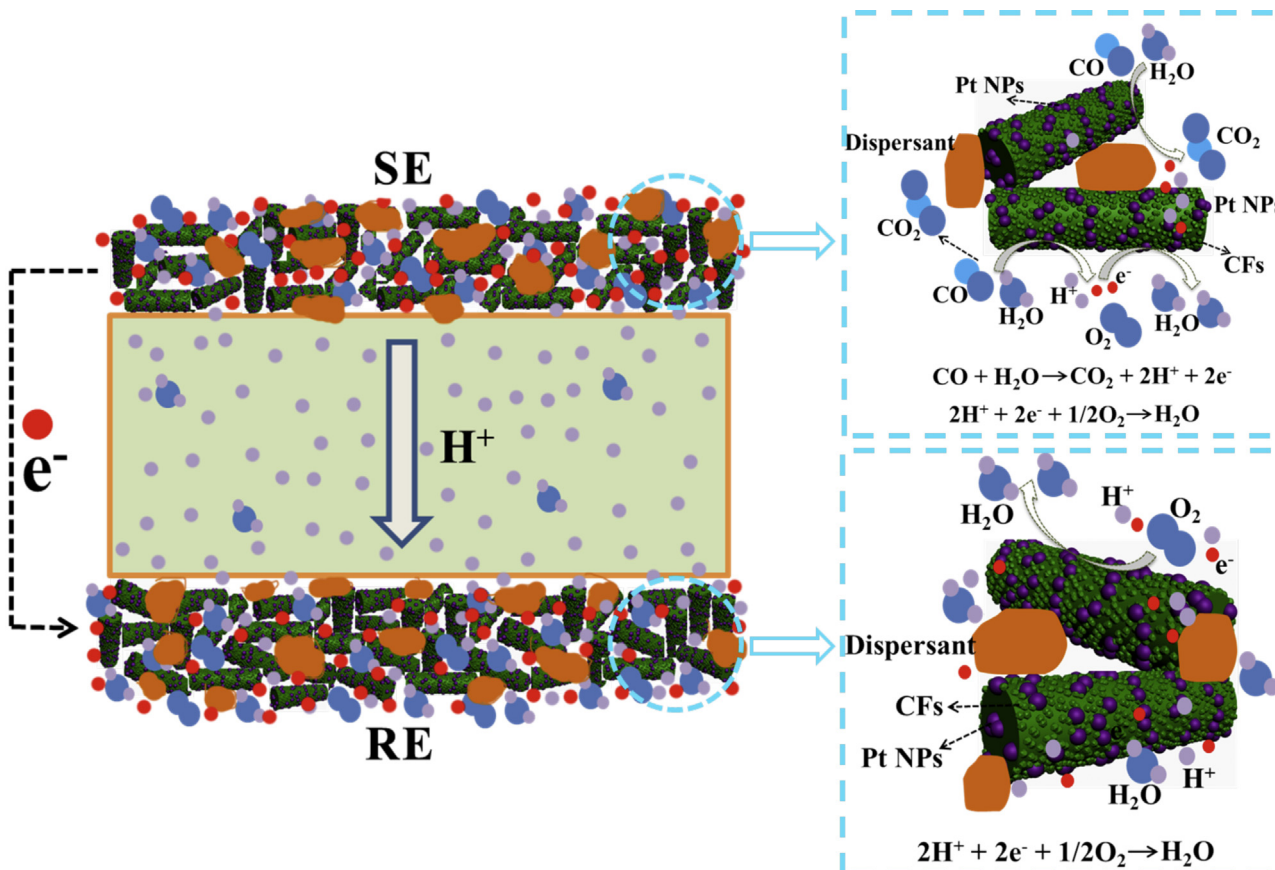


Fig. 10. The sketch of the sensing mechanism for MEA in the amperometric CO sensor.

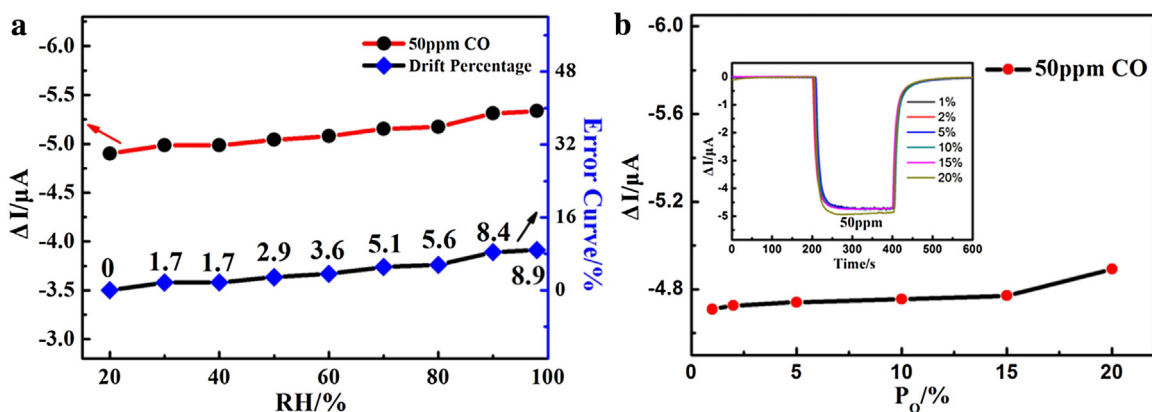


Fig. 11. Response current of S_c toward 50 ppm CO at different relative humidity (a) and oxygen concentrations (b).

In summary, the oxidation of CO gas has taken place in the MEA:



During the oxidation, the amount of electrons migrated has been recorded by the electrochemical workstation, which is directly proportional to the CO concentration.

From the above discussion, it can be suggested that both the moisture and oxygen in the testing environment have played the significant roles in the oxidation of CO. Consequently, the effects of different concentrations of moisture and oxygen on the sensing performances of the sensor are shown in Fig. 11a and b, respectively. From Fig. 11a, it is seen that the ΔI to 50 ppm CO increased with the increase of the relative humidity (RH) and the drift percentage of the response signal, which is calculated by comparing the value of ΔI with the response current at 20% RH, is below 10%, indicating a tolerable result for moisture. From the prototype of this amperometric CO sensor, it has been known that the RE is segregated with surroundings and can basically maintain a high RH owing to the existence of the water-container. On contrary, the SE has directly contacted with the ambient air without extra water supply. Based on these conditions, the increasing RH surroundings can increase the reaction rate for Eq. (1) and decrease the rate for Eq. (2), but has a neglected influence on the rate for Eq. (3). Thus, the response of sensor increases with increasing value of RH. Additionally, it can be observed from Fig. 11b that the value of ΔI diminishes with the decrease of oxygen concentration. Obviously, the rates for Eqs. (2) and (3) are simultaneously decreased with the reducing of oxygen concentration, contributing to a low oxidation rate to CO gas, which is the main reason for the influences of oxygen concentration on the sensing performance.

4. Conclusion

In summary, this report has fabricated a new type of amperometric CO sensor based on Nafion solid electrolyte and Pt NPs supported on three kinds of carbon materials (CBs, MWCNTs and CFs). XRD measurement shows that the Pt NPs have a cubic structure and the average size of Pt NPs supported on CFs is estimated to be smaller than that of others. The SEM images suggest that Pt NPs dispersed extensively on CFs, indicating a large electrochemically active surface area. The M_c , prepared by the hot-pressing method, displays the best quality of catalyst layers with largest Pt loadings for the electrodes. The sensitivities to CO gas of these three sensors are in the order: S_c (0.077 $\mu A/ppm$) > S_b (0.037 $\mu A/ppm$) > S_a (0.032 $\mu A/ppm$). It is also found that S_c exhibits the low detection limit of 0.1 ppm to CO, indicating the application in the condition with very low traces of CO. Additionally, S_c also has a good selectiv-

ity, reproducibility and stability with fast response/recovery times toward 50 ppm CO at room temperature.

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