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RESEARCH ARTICLE

ADSORPTİON KINETICS of CONDUCTING POLYMER POLYPRROLE with H_2O, CO_2 and O_2

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ABSTRACT

Polypyrrole (PPy) thin film has been used to investigated the sensor response properties against humidity (HO_2), carbon Dioxide (CO_2) and Oxygen (O_2) in the atmospheric environment. TEM and AFM micrographs of thin films show PPY structures of big grain sizes which ranging from 200 nm-500nm. The adsorption-desorption kinetics of the PPy data of the materials have been obtained by using Quartz Crystal Microbalance technique (QCM). Langmuir model has been used to investigate H_2O, CO_2, and O_2 gases and to compare their adsorption and desorption kinetics of polypyrrole thin films, high-purity nitrogen gas was used as references and cleaning the desorption process. Both QCM and electrochemical deposition technique results polypyrrole coated sensors exhibited promising environmental gas sensor response at room temperature.

INTRODUCTION

Nowadays gases contaminations may cause one of the largest problems facing our life on the earth. Also this contaminations can affect in the ozone hole that leads to a lot of bad side influences in our lives and may affect all aspects of life around us. How has the use of industry materials, transportation in all forms, factories, compressed gas and burning of forests, human waste disposal, agricultural pesticides, insecticides and how has the use of automotive and aerospace industries affect in the environment around us?. All of these things cause lots of contaminations and produce carbon which can affect in our environments negatively. In recent years, remarkable process in synthesis of conducting polymers has offered a great possibility for novel applications in various fields, such as biomedical applications (Rim *et al.,* 2013; Muskovich *et al.,* 2012; Mattioli-Belmonte *et al.,* 2005), energy storage (Gomez-Romero, 2002; Scrosati, 1998), biosensors (Lawal and Adeloju, 2013; Zhang *et al*., 2010; Quinto *et al*., 2000) due to considerable flexibilities in electronic properties by modifying their chemical structures (Yoon *et al*., 2008). A particular interest among various conducting polymers such as polypyrrole (PPy) (Kate *et al*., 2011; Penza *et al.,*1998) for sensor devices (Adhikari and Majumdar, 2004; Amer *et al*., 2010; Aubert *et al.*, 1999; Radhakrishnan and Paul, 2007).

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The sensor responses of gases property have been investigated by several groups in literature Amer *et al.,* 2010; Radhakrishnan and Paul, 2007; Arena *et al.,* 1994; Li *et al.,* 2011; Paul *et al.,* 2009; Paul *et al.,* 2009). In this work, conducting polymers of PPy was deposited by using electrochemical deposition technique (ECD) and employed as a adsorbing material for gases by using QCM technique for their sensor applications. Langmuir model has been used to compare adsorption and desorption kinetics of bare PPy against H_2O, CO_2 and O_2 gas with respect to inert N_2 gas. H_2O, CO_2 and O_2 gases (with the concentration between 0-2000 ppm) was used as active gases for adsorption processes, whereas high-purity nitrogen gas was used for desorption process. The thermodynamic properties of the sensing materials have been obtained by using Quartz Crystal Microbalance (QCM) technique. Electrical responses of the thin film of the PPy derivatives between gold interdigitated electrodes (IDE) with 3 μm gap have also been measured at the same time for comparison.

MATERIALS AND METHODS

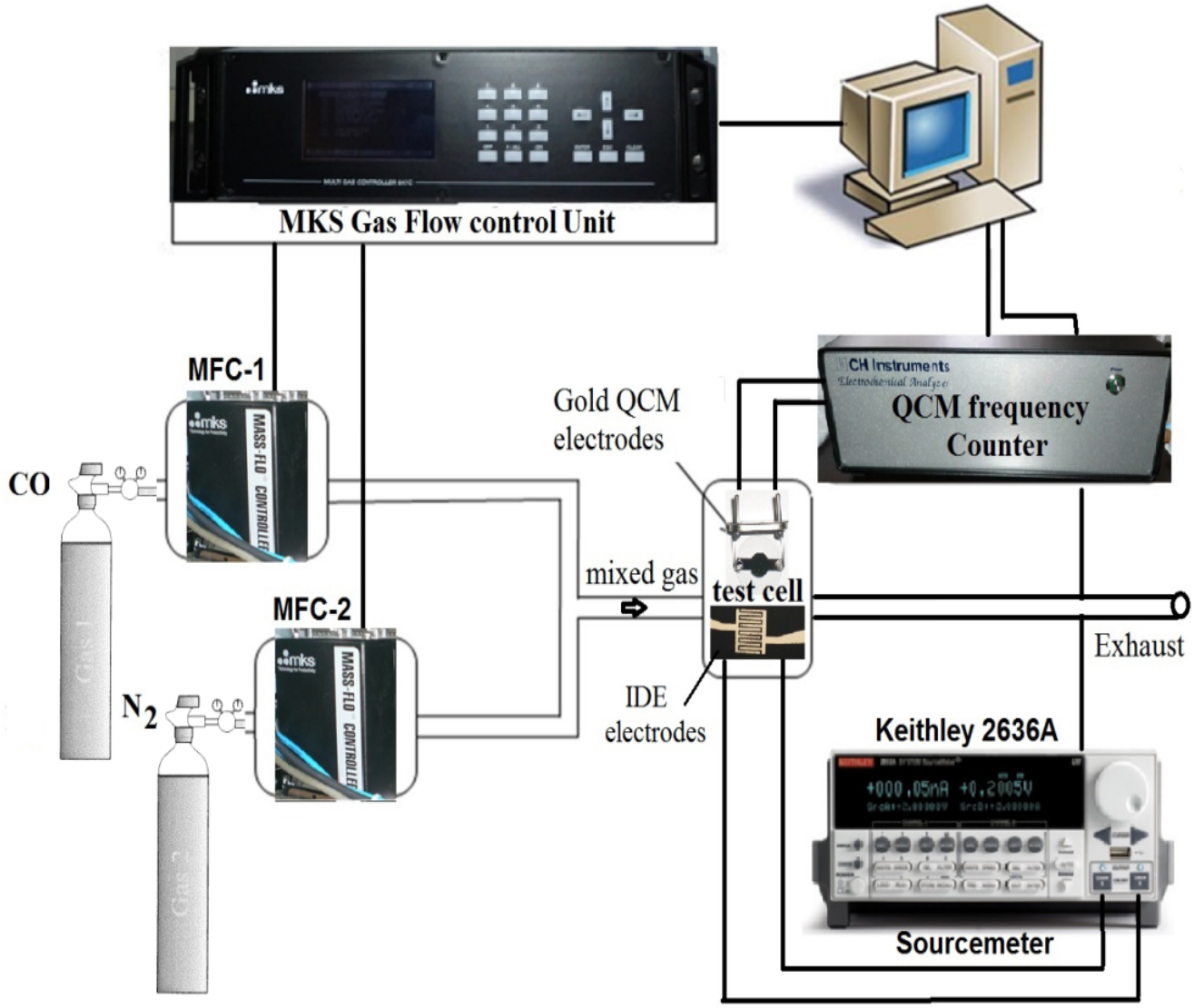
Chemical materials were obtained from Aldrich Chemical Co. All other chemicals were of analytical grade and used without further purification. Silicon carbide of high purity nanoparticles (that exceeds 99.9%) with average 40 nm in size, specific surface area of 39.8 m^2/g and bulk density of 0.11g/cm^3 were obtained from Beijing Deke Daojin Science and Technology Co., Ltd. China (Mainland). Electrochemical fabrication technique was used for PPy thin films during the synthesis of polypyrrole monomers.

QCM and IDE measurements

Figure (1) shows the experimental setup 2-channel gas flow system to measure QCM and IDE signals under gases exposure to investigate the adsorption and desorption H_2O, CO_2 and O_2 molecules. A quartz crystal microbalance (QCM) is a type of acoustic wave microsensors that are capable of ultrasensitive mass measurements. Under favorable conditions, a typical QCM can measure a mass change of 0.1-1 ng/cm^2 .

Figure (2). Under favorable conditions, a typical QCM can measure a mass change of 0.1-1 ng/cm^2. A time-resolved electrochemical quartz crystal microbalance (EQCM) with the model of CHI400B Series from CH Instruments (Austin, USA) has been used to measure the adsorption kinetics of CO gas molecules and the change in the resonance frequency of quartz crystals between gold electrodes. The resonator of the QCM can measure frequencies in the range of 7.995MHz -7.950 MHZ. The mass change (Δm) on surface of the quartz crystal is calculated from the frequency change (Δf) by using Sauerbrey

Figure 1. The experimental setup with 2-channel gas flow system to measure QCM and IDE signals under variable O_2, CO_2 and humidity exposure to investigate the adsorption and desorption on PPy films.



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$$\Delta m = -\frac{A\sqrt{\mu\rho}}{2f_0^2} \times \Delta f = -C \times \Delta f \qquad (1)$$

where f_0 is the resonant frequency of the fundamental mode of the QCM crystal, The density (ρ) of the crystal is

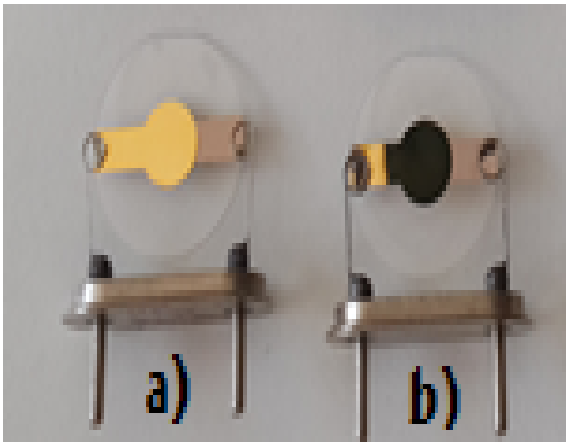

Figure 2. QCM electrodes: (a) empty, (b) PPy deposited QCM electrodes using Electrochemical Deposition Technique

2.684 g/cm^3 and the shear modulus (μ) of quartz is 2.947×10^{11}g/cm s^2. A net change of 1Hz corresponds to 1.34 ng of materials adsorbed onto the crystal surface of an area of 0.196 cm^2. Electrical responses of the thin film of the PPy derivatives on gold interdigitated electrodes (IDE) with 3 □m gap have also been measured at the same time for comparison. To describe the adsorption kinetics of gas molecules onto an organic or inorganic films, Langmuir adsorption isotherm model is frequently used (Zhang *et al*., 2010). According to this model, the rate of surface reaction to form a monolayer on the surface is given with the following equations:

$$\frac{d\theta}{dt} = k_a(1-\theta)C - k_d\theta \quad (2)$$

Where θ is a unit less quantity, which express the fraction of surface coverage, C is the gas concentration in the air, k_a and k_d are the adsorption and desorption constants, respectively. Integration of Eq. (2) leads to:

$$\theta(t) = K'(1-e^{-k_{ads}t}) \quad (3)$$

where k_{ads} is the inverse of the relaxation time and K' is the association constant defined as;

$$K' = \frac{k_aC}{k_aC+k_d} \text{ and } k_{ads} = k_aC + k_d \quad (4)$$

Here, QCM has been used to measure the fractional coverage θ as a function of time during the adsorption of gas molecules by PPy thin films, while the increase in frequency shift reflects the molecular mass uptake or loss. Thus the difference between the oscillation frequency shift (Δf) of coated and uncoated QCM is directly proportional to the adsorbed mass of gases molecules. The relationship between the surface adsorption kinetics and frequency shift (Δf) of QCM can be expressed as following;

$$\Delta f(t) = \Delta f_{max}K'(1-e^{-k_{ads}t})$$

(5) Using Sauerbrey relation, ($\Delta m = -(1.34 ng/Hz)\Delta f$), the time dependent variation of mass of the adsorbed gas molecules on the PPy thin films surface Δm_t can be defined as following:

$$\Delta m_t = \Delta m_\infty(1-e^{-t/\tau}) \quad (6)$$

$$\tau^{-1} = k_a \times C[\text{CO molecules}] + k_d \quad (7)$$

Δm_∞ is the maximum amount of adsorbed gas molecules on the surface for $t \to \infty$ and τ is the relaxation time.

RESULTS AND DISCUSSION

Structure Analysis

TEM Result

Figure 2. shows nanostructures PPy TEM image with 200 nm-400nm grain sizes was taken by the transmission electron microscope JEOL JEM-2100F.

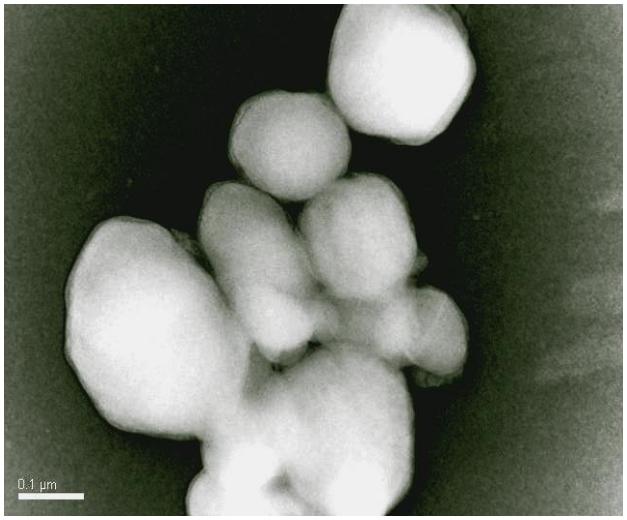

Fig 2. TEM image of PPy

Atomic Force Microscopic (AFM) Results

AFM images of the PPy sample in area (9.38 μm *9.38μm) are shown in Figure (3) were taken by using Nanosurf Flex AFM. Figure (3.a & b) reveal topography scan forward and 3D line fit 1.51 μm while Figure (3.c) demonstrates the 3D amplitude scan forward line fit 14.5 mV and Figure (4.d) displays 3D topography Diverted data 74.9 nm. Figure (4) shows the change in the sensore response of the PPy thin films at the relative humidity (RH) value 95% (red circles), at the CO_2 (blue squares) and O_2 (filled green circles) concentrations of 100% as function of time for 200s.

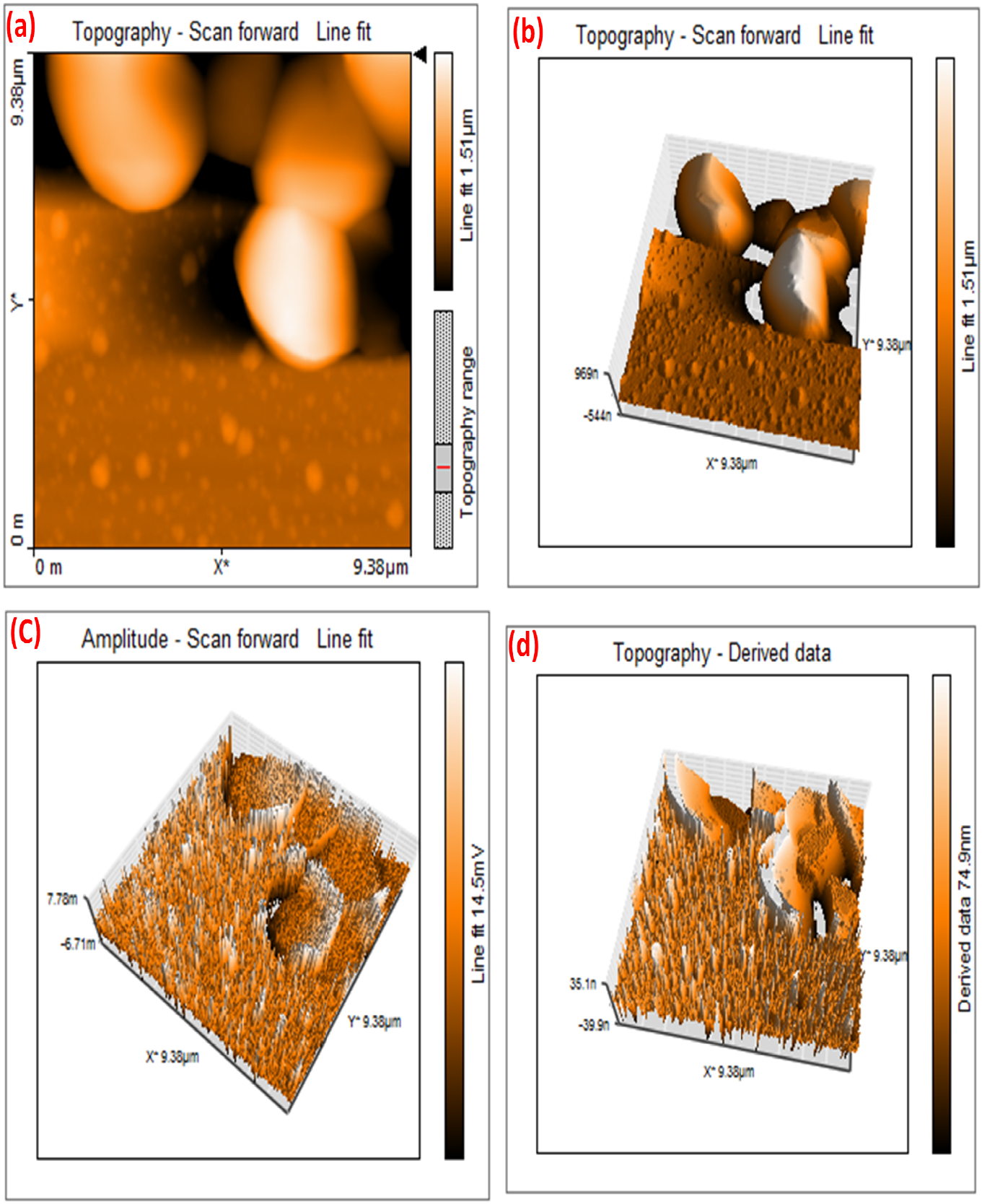

Figure 3. AFM micrograph of PPY (a) Topography scan forward, (b) 3D Topography scan Forward, (c) 3D Amplitude scan forward and (c) 3D topography diverted data

Table 1. QCM results: the least square fit results to the QCM data using the Langmuir adsorption isotherm model given in Equation (6)

y = m1 + m2*(1 - exp(-m3*x))		
	Value	Error
m1	1,5929	0,34347
m2	43,159	0,33208
m3	0,036846	0,00050377
Chisq	15087	NA
R	0,96158	NA

y = m1 + m2*(1 - exp(-m3*x))		
	Value	Error
m1	-2,1228	0,032182
m2	23,195	0,029598
m3	0,019759	6,3237e-5
Chisq	221,59	NA
R	0,99845	NA

y = m1 + m2*(1 - exp(-m3*x))		
	Value	Error
m1	-3,0221	0,060712
m2	21,322	0,057668
m3	0,02828	0,00015072
Chisq	607,99	NA
R	0,99433	NA

Table 1. Adsortion and desorption coefficients of PPy thin films against H_2O, CO_2 and O_2

ADSORPTION & DESORPTION	H_2O	CO_2	O_2
Ka ADSORPTION	16.748	8.981	1.29E+01
Kd DESORPTION	3.35E-03	1.80E-	2.57E-03

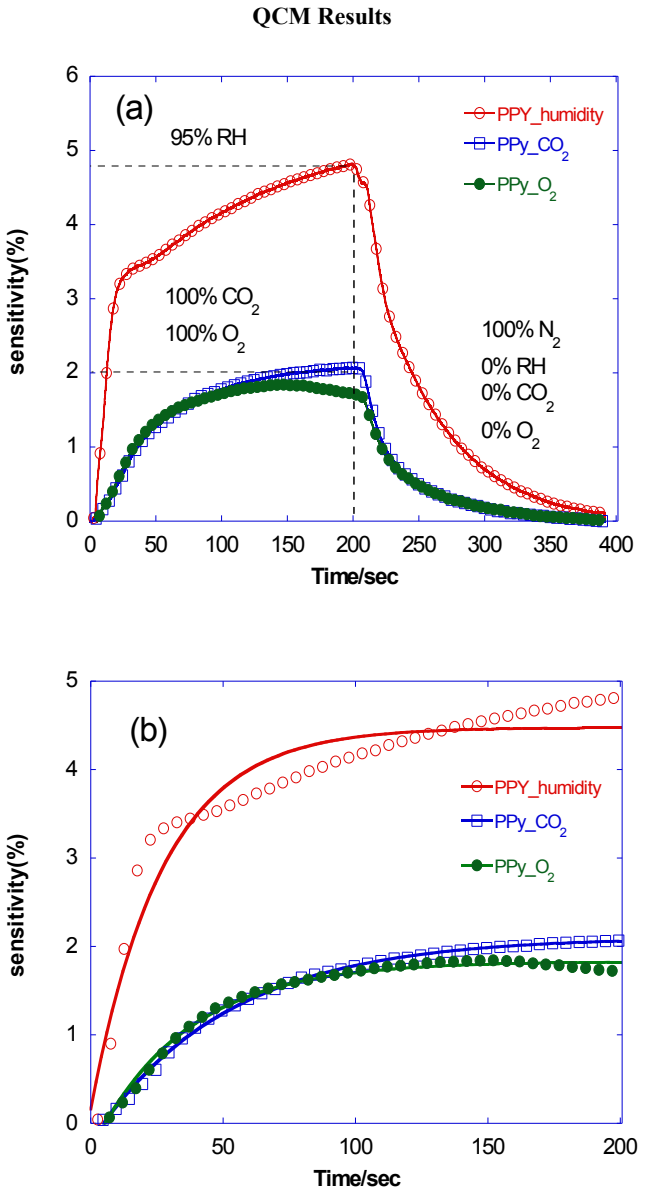

Figure (4. a) The change in sensitivity of the PPy sensing film at the relative humidity (RH) values 95% (red circles) (b) at the CO_2 (blue squares) and O_2 (filled green circles) concentrations of 100%

The ratio of active gas/N_2 flow through the test cell for 95% relative humidity conditions as a function of time are shown. aktive gas/N_2 flows were used alternately to obtain the recovery and response characteristics of the PPy sensing element for humidity, CO_2 and O_2 sensing. The sensitivity of the PPy thin film increased to 48%, 21 % and 18 % due to the increased amount of physisorbed active gas molecules as a consequence of increasing relative humidity and concentration of CO_2 and O_2 gases respectively as shown in Figure (4.b). Adsortion and desorption coefficients is given in Table 1. Shows the adsorbed masses of gas H_2O, CO_2 and O_2 molecules. Table 2. Reveals adsorption and desorption coefficients of PPy thin films have been found at least twice of that of the CO_2 and O_2 active gasses. This shows that affinity forces due to dipole-dipole interation between PPy and H_2O is higher compare to CO_2 and O_2.

Conclusion

TEM and AFM micrographs of PPY thin films with the big grain sizes ranging from 200 nm- 500nm in structure have been prepared by an electrochemical deposition technique in order to fabricate the PPy thin films for used as QCM electrodes. These QCM PPy piezoelectric sensors were used to investigate the possible sensor response mechanisms and adsorption-desorption kinetics of the atmospheric gasses such as humidity, CO_2 and O_2. The coefficients of adsorption and desorption of humidity is observed twice more than of CO_2 gas. While depending on the Langmuir measurement model the coefficients of adsorption and desorption of CO_2 gas is more at least twice than the O_2 active gas. This indicates that affinity forces due to dipole-dipole interaction between PPy and H_2O is higher compare to CO_2 and O_2 gases. Hence, conducting PPy thin films can be utilized as a suitable material for gases sensor applications.

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