



Humidity sensing properties of novel ruthenium polypyridyl complex

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ABSTRACT

We report the characterization of novel ruthenium polypyridyl complex (Ru-PC) based sensor film with a thickness of 50 nm coated on a quartz substrate using a spin coating method for humidity detection. The resulting complex $[Ru(L1)_2(L2)]$ was synthesized in a one-pot reaction starting from $[RuCl_2(p\text{-cymene})]_2$, where the ligands (L1 = 4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt and L2 = 4,4'-dicarboxy-2,2'-bipyridine) were characterized by NMR, mass spectrometry (MALDI), elemental analysis and UV–vis spectroscopy. The humidity adsorption and desorption kinetics of the ruthenium complex were investigated using the Quartz Crystal Microbalance (QCM) technique. The Langmuir model was used to determine adsorption and desorption rates and Gibbs free energy over the 11–97% relative humidity range. Our experimental results show that Ru-PC films have a great potential for humidity sensing applications at standard conditions (i.e. room temperature).

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1. Introduction

Stringent control of the humidity is essential in many of the industrial applications. The petroleum, medical, food industries all manufacture moisture-sensitive products. Furthermore, clean rooms, greenhouses, research and development labs, computer rooms, and nuclear reactors often require fixed moisture levels [1–4].

To date many types of humidity sensors have been developed that use a variety of detection methods including: current, resistance, capacitance, conductivity, absorption and luminescence [1–7].

Recently ruthenium(II) polypyridine complexes have been identified as potential humidity sensors. The principal reason is their remarkable chemical stability and photophysical properties. These complexes have a wide range of applications in many research fields such as light harvesting systems and photochemically driven molecular devices, as well as photocatalysts and as biological surveys [8–15]. Moreover, ruthenium dyes are also promising candidates for a variety of sensors and switches [16–18] due to their

semiconducting properties. The sensing properties of ruthenium(II) polypyridine dyes are usually based on lifetime or intensity detection methods and the selective response to certain gases due to the appropriate properties of used sensitive dye. Several studies have been carried out so far to monitor humidity sensing properties of ruthenium dyes with different morphologies showing that they are very active for humidity and gases [6,16–18].

Ru-PC was designed and synthesized with the ligands 4,4'-dicarboxy-2,2'-bipyridine (L2) and bathophenanthroline bearing disulfonic acid disodium salt (L1) [8]. L1 and L2 were selected to increase the sensitivity of the compound to moisture over the salt of a sulfonic acid and COOH groups. The compound can also show a high pH sensitivity due to these functional groups [10,19].

QCM is one of the oldest and reliable techniques to measure adsorption and desorption kinetics of molecules on the air and thin film interfaces. However, the major focus of this work has been to investigate adsorption and desorption kinetics of a new ruthenium complex (Ru-PC) bearing sulfonate and carboxylate groups, not to improve the well known QCM technique. There are many studies in the literature about the QCM based humidity sensing mechanism of other materials. Nevertheless, to the best of our knowledge, QCM based humidity sensing system that utilizes ruthenium(II) polypyridine dyes has not been reported yet. With the usage of different functional groups over the backbone of the compounds, it is also possible to improve sensing properties of the device depending applied method.

QCM has been widely used for thickness measurements of metal films deposited onto the crystal and investigations of the kinetics

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of adsorption/desorption of adsorbate molecules. The QCM method monitors the frequency shift (Δf) of a coated quartz crystal with sensing element due to adsorption of molecules on the surface of the sensing material [20]. The mass change (Δm) of surface of the quartz crystal is calculated by using Sauerbrey equation [20]:

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

where f_0 is the resonant frequency of the fundamental mode of the QCM crystal, A is the area of the gold disk coated onto the crystal, ρ is the density of the crystal, and μ is the shear modulus of quartz.

The frequency shift is directly proportional to the adsorbed mass on the Ru-PC modified gold QCM electrodes. Finally, the Langmuir adsorption model was used to analyze the adsorption and desorption kinetic parameters of Ru-PC films, showing that the Ru-PC has strong affinity for water vapour molecules between 11% and 97% relative humidity (RH) values.

2. Experimental details

$[\text{RuCl}_2(p\text{-cymene})]_2$, 1,10-phenanthroline-disulfonic acid disodium salt (L1) and 4,4'-dicarboxy-2,2'-bipyridine were purchased from Aldrich. All organic solvents were purchased from Merck and Fluka, and used as without modification. $[\text{Ru}^{\text{II}}(\text{bis}(4,7\text{-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt}) (4,4'\text{-dicarboxy-2,2'-bipyridine})]$, $[\text{Ru}^{\text{II}}(\text{L1})_2(\text{L2})]$, was synthesized according to procedures in the literatures [8,10,12] as shown in Fig. 1. The $[\text{Ru}^{\text{II}}(\text{bis}(4,7\text{-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt}) (4,4'\text{-dicarboxy-2,2'-bipyridine})]$, $[\text{Ru}^{\text{II}}(\text{L1})_2(\text{L2})]$, [Ru-PC] was synthesized and characterized as follows:

$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.1 g, 0.163 mmol) was dissolved in DMF (50 ml) and 4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt (L1) (0.351 g, 0.654 mmol) then added (Fig. 1). The reaction mixture was heated to 80 °C under an inert atmosphere for 12 h with constant stirring. To this reaction flask 4,4'-dicarboxy-2,2'-bipyridine (L2) (0.08 g, 0.33 mmol) was added and refluxed for 12 h. Finally, the reaction mixture was cooled to room temperature and the solvent was removed by using a rotary evaporator under vacuum. The solid was extracted with methanol, filtered and dried under vacuum. On a Sephadex LH-20 column the crude complex was purified with methanol as an eluent. The crude complex was re-crystallized from MeOH/ethyl acetate. 216 mg of the product with 93% yield was obtained. UV (MeOH); λ_{max} : 483 (1.38), 314 (2.66), 278 (4.21), 221 (4.28). $^1\text{H NMR}$ (400 MHz, D_2O) δ ppm: 9.56 (t, $J=1.7$ Hz, 1H, NCHCH, L2), 9.43 (t, $J=1.3$ Hz, 1H, NCHCH, L2),

8.73 (s, 1H, NCHCH, L1), 8.62 (s, 1H, NCHCH, L1), 8.10 (t, $J=1.1$ Hz, 1H, CCHC, L2), 8.02 (t, $J=1.3$ Hz, 1H, CCHC, L2), 7.78 (d, $J=3.6$ Hz, 1H, NCHCHC, L2), 7.73 (d, $J=3.8$ Hz, 1H, NCHCHC, L2), 7.62 (m, $J=1.4$ Hz, 4H, CCHCHC, L1), 7.44 (q, $J=1.1$ Hz, 2H, NCHCHC, L1), 7.40 (q, $J=1.2$ Hz, 2H, NCHCHC, L1), 7.24 (m, $J=2.4$ Hz, 4H, CCHCHCSO₃Na, L1), 7.18 (m, $J=2.6$ Hz, 4H, CCHCHCSO₃Na, L1), 6.95 (m, $J=2.4$ Hz, 4H, CCHCHCSO₃Na, L1), 6.89 (m, $J=2.4$ Hz, 4H, CCHCHCSO₃Na, L1). MS (MALDI): $m/z=1419.1$ [M+H]⁺. Anal. Calc. For C₆₀H₃₆N₆Na₄O₁₆S₄Ru (1418.25): C, 50.81; H, 2.56; N, 5.93. Found: C, 50.79; H, 2.39; N, 5.88%.

Gold coated quartz crystal electrodes were placed into ethanol and ultrasonically cleaned, then rinsed by de-ionized water. 1 mg/ml Ru-PC was dissolved in deionized water. 5 μl of solution was spin-coated on to quartz crystal with 2000 rpm. After drying at room conditions, it was kept in dessicator at room temperature for 3 h. Then the quartz crystal coated with Ru-PC film was used to record both the reference frequency at 11% and the frequency changes up to 97% relative humidity. The thicknesses of films were measured using a Dektak profilometer from Veeco and found to be 50 nm.

A closed box, partly filled with saturated salt solutions, generated a humid environment with good accuracy in the free room above the salt. The value of the relative humidity depends on the type of salt given in Ref. [21]. The same experimental setup given in our previous work [21] was used to measure the adsorption kinetics of Ru-PC films above saturated LiCl (11% RH) and K₂SO₄ (97% RH) aquatic solution level inside a half filled closed container.

A Time-resolved Electrochemical Quartz Crystal Microbalance (EQCM) with the model of CHI400A Series from CH Instruments (Austin, USA) was used to measure the change in the resonance frequency of quartz crystals between gold electrodes via both serial and usb interface connected to a computer. The QCM works with oscillation frequencies between 7.995 and 7.950 MHz. The density (ρ) of the crystal is 2.684 g/cm³, and the shear modulus (μ) of quartz is 2.947×10^{11} g/cm s². Around oscillation frequency of 7.995 MHz, a net change of 1 Hz corresponds to 1.34 ng of materials adsorbed or desorbed onto the crystal surface of an area of 0.196 cm² [22].

The signals coming from a QCM electrode and a commercial RH humidity sensor were simultaneously measured during the adsorption and desorption process. Both the relative humidity and temperature were also recorded during measurements while maintaining the temperature around 23 °C. For this purpose, a EI-1050 selectable digital relative humidity and temperature probe with a response time of 4 s and a resolution of 0.03% RH was used with a USB controlled LabJack U12 ADC system combined with a single

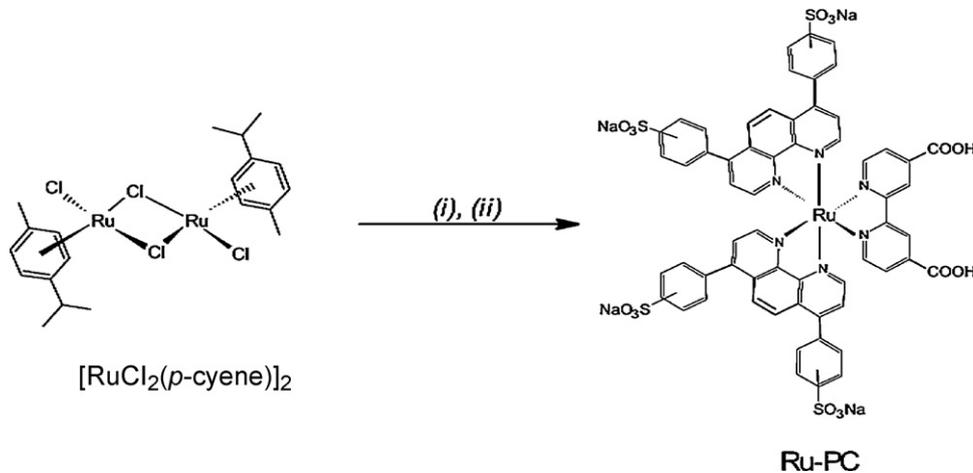


Fig. 1. Synthesis of $[\text{Ru}^{\text{II}}(\text{bis}(4,7\text{-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt}) (4,4'\text{-dicarboxy-2,2'-bipyridine})]$, $[\text{Ru}^{\text{II}}(\text{L1})_2(\text{L2})]$, [Ru-PC]: one-pot synthetic route for Ru-PC. (i) L1, DMF, 80 °C, inert atmosphere, overnight; (ii) L2, 15 °C, overnight.

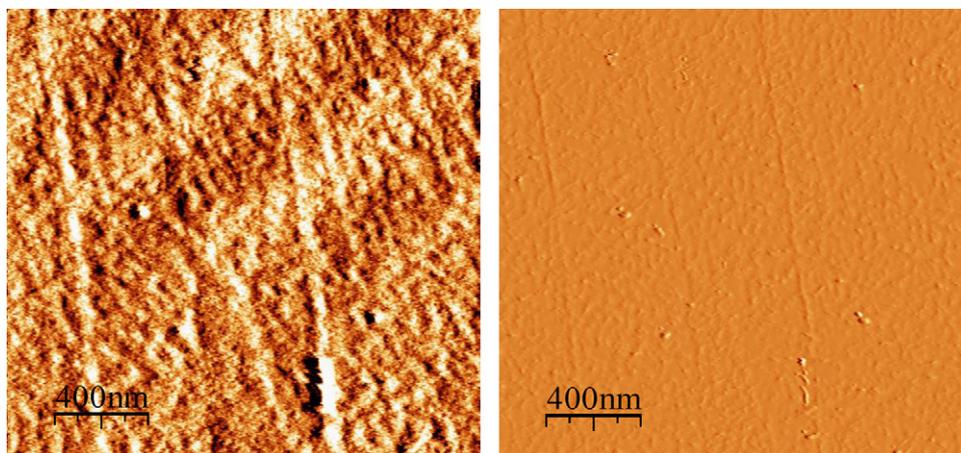


Fig. 2. AFM topographic and face images in tapping mode of Ru-PC film. Sample was prepared by drop-casting of a solution of Ru-PC ($c = 1.5 \times 10^{-5}$ M) in MeOH onto HOPG substrate and measured in air.

chip sensor module (SHT11) manufactured by Sensirion (Staefta, Switzerland).

3. Results and discussion

The surface morphology of Ru-PC thin films on highly ordered pyrolytic graphite (HOPG) was observed by atomic force microscopy (AFM) in tapping mode (Fig. 2). These measurements were performed under ambient conditions using a commercial scanning probe microscope. The AFM topographic images obtained were processed using the WSxM program. A freshly prepared solution of sample in MeOH ($20 \mu\text{l}$, 1.5×10^{-5} M) was deposited by drop-casting on HOPG surface, and then letting the drop dry at room temperature in ambient air conditions. AFM studies on uneven graphitic surfaces revealed the film formation. Ru-PC thin films were relatively uniform and smooth (Fig. 2). As expected, the film thickness strongly depended on the concentration of the drop-cast solution. Small variations within the same drop-cast substrate were observed, probably because of non-uniform evaporation of the cast solution on the substrate as well as the steps of the HOPG surface.

The sensing properties of Ru-PC on QCM, primarily originate from hydrogen bond formation of adsorbed water molecules with functional groups of the Ru-PC. When the Ru-PC film is exposed to moisture, water molecules get easily trapped in between the heteroatoms of the compound. The sensing reaction between water molecules and the Ru-PC is summarized in Fig. 3. The mass increase on the QCM surface due to adsorption of water molecules can be easily measured by monitoring the change in the QCM resonance

frequency as seen in Fig. 4. During the desorption process in low humidity values, water molecules bound to the Ru-PC by weak hydrogen bonds leave the film surface on QCM. As a result, a significant sharp decrease in total QCM resonance frequency is observed due to mass change on the film surface.

Fig. 4(a) and (b) shows the frequency response of the Ru-PC film covered QCM during adsorption and desorption process at fixed relative humidity (RH) values between 11% and 97% RH. Fig. 4(b) shows no hysteresis after long time moist adsorption and desorption process between 11% and 97% RH. All the adsorption and desorption data given in Fig. 4 show exponential dependence. In Fig. 4(c), there are two exponential fit lines due to two different adsorption behaviours below and above 50% RH, in high and low adsorption regions. It rapidly rises in low humidity region up to around 50%, most probably due to the hydrogen bonding capability of $-\text{SO}_3^-$ and $-\text{COOH}$ functional groups of Ru-PC film surface itself, which cause a sharp increase in the sensitivity of the compound to moisture in short time periods. But above 50%, it goes toward saturation due to possible diffusion process of water molecules inside the Ru-PC film and/or possible water condensation process on the film surface.

The Langmuir adsorption isotherm model is frequently used to describe adsorption kinetics of gas molecules onto organic or inorganic films [23–29]. Here QCM is used to measure the fractional coverage as a function of time during the adsorption of water vapour molecules by Ru-PC film. An increase in the frequency shift reflects the molecular mass uptake or loss. Hence the difference between the oscillation frequency shift (Δf) of coated and uncoated

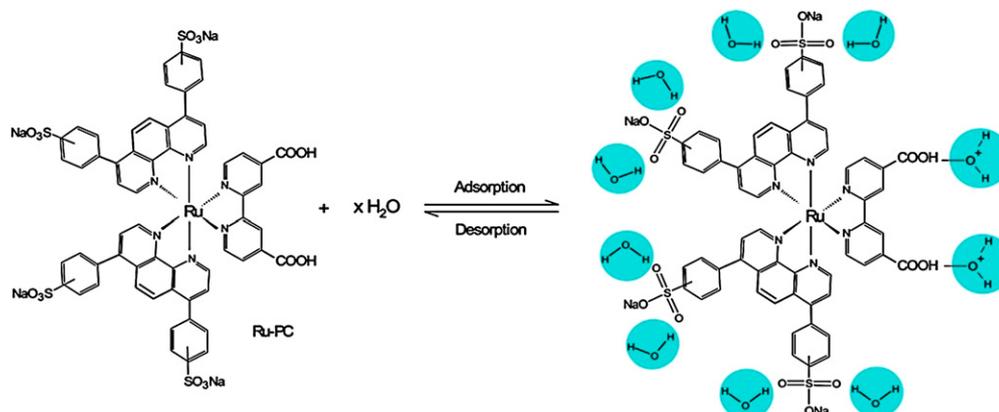


Fig. 3. The sensing reaction based on hydrogen bond formation between water molecules and the functional groups of Ru-PC.

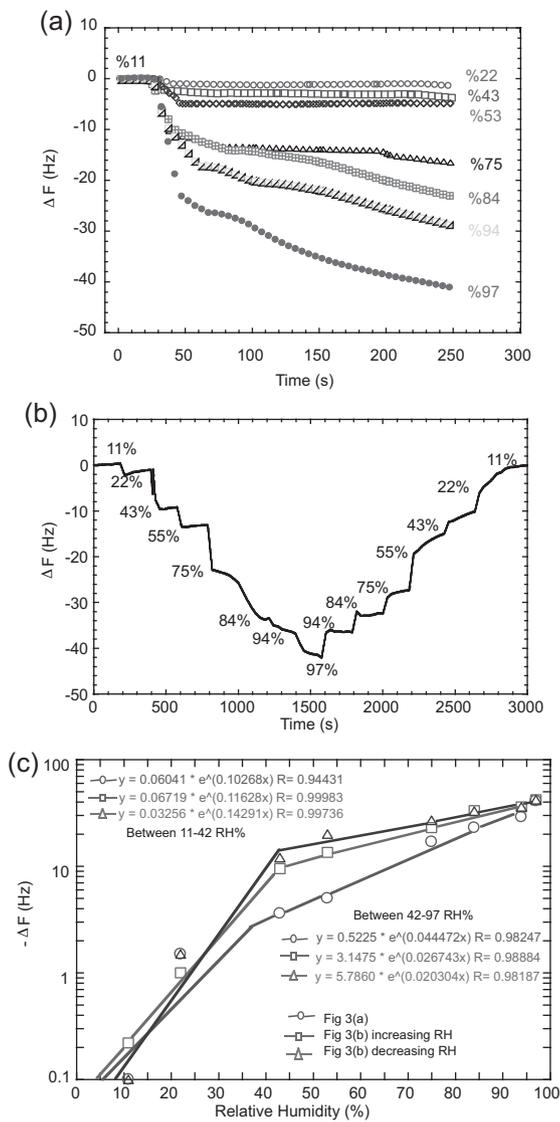


Fig. 4. QCM frequency shifts for adsorption and desorption cycles between 11% RH and various RH values: (a) and (b), QCM frequency shifts (Hz) as a function of time (s) for different increasing and decreasing relative humidity values between 11% and 97% RH. The adsorption and desorption data taken from (a) (\circ) and (b) (increasing RH: \square) (decreasing RH: \triangle) show an exponential dependence on relative humidity when the frequency shifts are taken as logarithmic (c). The magnitude of the error bars is chosen as 15%. The blue line (circular symbol) shows the exponential fit to the adsorption data given in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

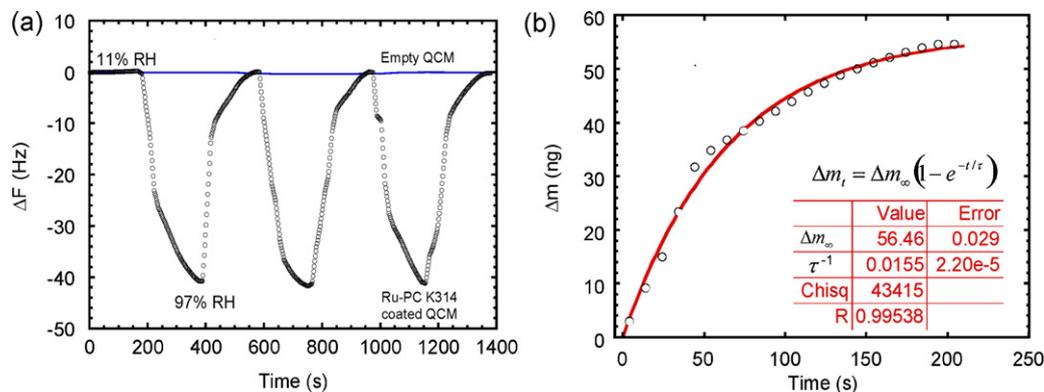


Fig. 5. Experimental QCM frequency shifts (circles) for 3 cycles of adsorption and desorption process between 11% RH and 97% RH values (a), and the least square fit (solid line) of the adsorption part given in (a) to the Langmuir adsorption isotherm model given in Eq. (4) (b).

QCM is directly proportional to the adsorbed mass of moisture molecules. The relationship between the surface adsorption kinetics and the frequency shift (Δf) of QCM can be expressed as follows:

$$\frac{d\Delta f}{dt} = (\Delta f_{\max} - \Delta f)k_a C - k_d \Delta f \quad (2)$$

where Δf and Δf_{\max} are the QCM resonance frequency shifts, k_a and k_d are the adsorption and desorption rate constants, C is the concentration of water molecules in air, t is the time. Standard steam tables were used to determine the partial pressure of water vapour at each temperature [30]. Saturated salt solutions are frequently used for humidity measurements. At any temperature, the concentration of a saturated solution is fixed. With the excess solute, the solution remains saturated in a sealed metal or a glass chamber [21]. The temperature was kept constant during measurements around 23 °C. The vapour molar concentration C was calculated from the ideal gas equation ($PV = nRT$). At the corresponding partial pressure for the relative humidity measured at the equilibrium point as given in Table 1 shown in Refs. [21,30].

The time variation of the change in the frequency due to adsorption can be obtained by

$$\Delta f(t) = \Delta f_{\max} K' (1 - e^{-k_{\text{obs}} t}) \quad (3)$$

where K' is the association constant and k_{obs} is the inverse of the relation time as defined by $K' = (1 + (k_d/k_a C))^{-1}$ and $k_{\text{obs}} = k_a C + k_d$, respectively. In the QCM technique, the frequency shift is proportional with the change in the adsorbed mass by the film on the QCM electrodes. The time dependent frequency shift can be fitted by Langmuir isotherm adsorption. From the curve fit, the association constant (K') of the water vapour molecules was found as 0.96 and $k_{\text{obs}} = 0.0155 \text{ s}^{-1}$. Using Sauerbrey relation given in Eq. (1) ($\Delta m = -(1.34 \text{ ng/Hz}) \Delta f$), the time dependent variation of the mass of adsorbed water vapour molecules on the Ru-PC film surface Δm_t can be estimated using:

$$\Delta m_t = \Delta m_\infty (1 - e^{-t/\tau}) \quad (4)$$

where Δm_∞ is the maximum adsorbed amount of the humidity molecules on the surface at $t \rightarrow \infty$ and τ is the response time defined as $\tau^{-1} = k_a [\text{water vapour molecule}] + k_d$. From the least square fit to Eq. (4), the response time of the adsorption process is calculated as 64.56 s. The average recovery time of 3 adsorption and desorption cycles can be measured as 175 s from Fig. 5(a). The accuracy of the sensor depends on the EQCM accuracy that used in the experiment. For our QCM system, the frequency resolution: <0.1 Hz. Time-resolved EQCM allows 0.1 Hz to be resolved in milliseconds.

Fig. 5(a) shows the time dependence of experimental QCM frequency shifts (circles) for 3 adsorption and desorption cycles (11–97% RH). Fig. 5(b) shows the least square fit (solid line) of

the adsorption components of Fig. 4(a) using Langmuir adsorption isotherm model given in Eq. (4).

The average values of adsorption and desorption rate were obtained to be $0.704 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$ and $0.015 \pm 0.0013 \text{ s}^{-1}$, from the least square fit of adsorption component of the three cycles, respectively. The Gibbs free energy ΔG of adsorption/desorption, at a constant temperature, is defined by

$$\Delta G = -RT \ln \frac{k_a}{k_d} \quad (5)$$

The Gibbs free energy for adsorption is calculated using Eq. (5) for each cycle. The average Gibbs free energy for adsorption was $-9.45 \pm 0.5 \text{ kJ/mol}$. The negative sign shows that there water absorption is an exothermic process ($\Delta G < 0$) and as a consequence reaction is spontaneous.

Our QCM results show that the Ru-PC films are very sensitive toward humidity changes, yielding reproducible adsorption and desorption kinetic behaviour to humidity changes. This is most probably due to the hydrogen bonding capability of $-\text{SO}_3^-$ and $-\text{COOH}$ groups which cause an increase in the sensitivity of the compound to moisture in short time periods.

This work shows that the Ru-PC could potentially be used as a humidity sensor.

4. Conclusion

The response to relative humidity changes of Ru-PC films with 50 nm thickness obtained by spin coating technique was investigated by QCM technique. The adsorption kinetics under constant relative humidity between 11% and 97% was explained using Langmuir adsorption model at 23 °C constant QCM temperature. The average values of adsorption and desorption rates were obtained to be $0.704 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$ and $0.015 \pm 0.0013 \text{ s}^{-1}$, respectively. The average Gibbs free energy for adsorption of 3 cycles is obtained as $-9.45 \pm 0.5 \text{ kJ/mol}$, indicating that the Ru-PC films show a favoured kinetic reaction against moist molecules in air. QCM results show that Ru-PC films are extremely sensitive to humidity and give reproducible adsorption/desorption kinetics against to humidity changes due to the existence of sulfonate and carboxylate groups in the structure.

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References

- [1] R. Narayanaswamy, O.S. Wolfbeis (Eds.), *Optical Sensors: Industrial, Environmental and Diagnostic Applications*, Springer-Verlag, Heidelberg, 2004, pp. 251–280.
- [2] M.M.F. Choi, O.L. Tse, Humidity-sensitive optode membrane based on a fluorescent dye immobilized in gelatin film, *Anal. Chim. Acta* 378 (1999) 127–134.
- [3] D.S. Ballantine, H. Wohltjen, Optical wave-guide humidity detector, *Anal. Chem.* 58 (1986) 2883–2885.
- [4] M. Matsuguchi, T. Kuroiwa, T. Miyagishi, S. Suzuki, T. Ogura, Y. Sakai, Stability and reliability of capacitive-type relative humidity sensors using crosslinked polyimide films, *Sens. Actuators B: Chem.* 52 (1998) 53–57.
- [5] Y. Sadaoka, M. Matsuguchi, Y. Sakai, Y. Murata, Optical humidity sensing characteristics of composite thin-films of hydrolyzed Nafion-dye with a terminal n-phenyl group, *J. Mater. Sci.* 27 (1992) 5095–5100.
- [6] D.B. Papkovsky, G.V. Ponomarev, S.F. Chernov, A.N. Ovchinnikov, I.N. Kurochkin, Luminescence lifetime-based sensor for relative air humidity, *Sens. Actuators B: Chem.* 22 (1994) 57–61.
- [7] J.M. Costa-Fernández, M.E. Díaz-García, A. Sanz-Medel, A critical comparison of different solid supports to develop room-temperature phosphorescence sensing phases of air moisture, *Sens. Actuators B: Chem.* 38 (1997) 103–109.

- [8] M. Grätzel, Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells, *J. Photochem. Photobiol. A: Chem.* 164 (2004) 3–14.
- [9] Md.K. Nazeeruddin, S.M. Zakeeruddin, J.J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Grätzel, Electrochemical studies of the Co(III)/Co(II)(dbbip)₂ redox couple as a mediator for dye-sensitized nanocrystalline solar cells, *Coordin. Chem. Rev.* 248 (2004) 1317–1328.
- [10] Md.K. Nazeeruddin, M. Grätzel, Separation of linkage isomers of trithiocyanato (4,4',4''-tricarboxy-2,2',6,2''-terpyridine)ruthenium(II) by pH-titration method and their application in nanocrystalline TiO₂-based solar cells, *J. Photochem. Photobiol. A: Chem.* 145 (2001) 79–86.
- [11] K. Ocakoglu, C. Zafer, B. Cetinkaya, S. Icli, Synthesis, characterization, electrochemical and spectroscopic studies of two new heteroleptic Ru(II) polypyridyl complexes, *Dyes Pigments* 75 (2007) 385–394.
- [12] K. Ocakoglu, F. Yakuphanoglu, J.R. Durrant, S. Icli, The effect of temperature on the charge transport and transient absorption properties of K27 sensitized DSSC, *Sol. Energy Mater. Sol. C* 92 (2008) 1047–1053.
- [13] C. Sahin, C. Tozlu, K. Ocakoglu, C. Zafer, C. Varlikli, S. Icli, Synthesis of an amphiphilic ruthenium complex with swallow-tail bipyridyl ligand and its application in nc-DSSC, *Inorg. Chim. Acta* 361 (2008) 671–676.
- [14] C. Metcalfe, J.A. Thomas, Kinetically inert transition metal complexes that reversibly bind to DNA, *Chem. Soc. Rev.* 32 (2003) 215–224.
- [15] K. Ocakoglu, Y. Yildirim, F.Y. Lambrecht, J. Ocal, S. Icli, Biological investigation of I-131-labeled new water soluble Ru(II) polypyridyl complex, *Appl. Radiat. Isotopes* 66 (2008) 115–121.
- [16] A.P. de Silva, H.Q.N. Gunaratne, T. Gunlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Signaling recognition events with fluorescent sensors and switches, *Chem. Rev.* 97 (1997) 1515–1566.
- [17] S.J. Glenn, B.M. Cullum, R.B. Nair, D.A. Nivens, C.J. Murphy, S.M. Angel, Lifetime-based fiber-optic water sensor using a luminescent complex in a lithium-treated Nafion (TM) membrane, *Anal. Chim. Acta* 448 (2001) 1–8.
- [18] O. McGaughey, J.V. Ros-Lis, A. Guckian, A.K. McEvoy, C. McDonagh, B.D. Mac-Craith, Development of a fluorescence lifetime-based sol-gel humidity sensor, *Anal. Chim. Acta* 570 (2006) 15–20.
- [19] A.R. Oki, R.J. Morgan, An efficient preparation of 4,4'-dicarboxy-2,2'-bipyridine, *Synth. Commun.* 25 (1995) 4093–4097.
- [20] G. Sauerbrey, *Z. Phys.* 155 (1959) 206–222.
- [21] S. Okur, M. Kus, F. Özel, V. Aybek, M. Yilmaz, Humidity adsorption kinetics of calix [4] arene derivatives measured using QCM, *Talanta* 81 (2010) 248–251.
- [22] A. Erol, S. Okur, B. Comba, Ö. Mermer, M.C. Arkan, Humidity sensing properties of ZnO nanoparticles synthesized by sol-gel process, *Sens. Actuators B: Chem.* 145 (2010) 174–180.
- [23] D.S. Karpovich, G.J. Blanchard, Direct measurement of the adsorption-kinetics of alkanethiolate self-assembled monolayers on a microcrystalline gold surface, *Langmuir* 10 (1994) 3315–3322.
- [24] S.J. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1967, ISBN 0-12-300956-1.
- [25] Y.L. Sun, R.J. Wu, Y.C. Huang, P.G. Su, M. Chavali, Y.Z. Chen, C.C. Lin, In situ prepared polypyrrole for low humidity QCM sensor and related theoretical calculation, *Talanta* 73 (2007) 857–861.
- [26] P.G. Su, Y.P. Chang, Low-humidity sensor based on a quartz-crystal microbalance coated with polypyrrole/Ag/TiO₂ nanoparticles composite thin films, *Sens. Actuators B: Chem.* 129 (2008) 915–920.
- [27] P.-G. Su, Y.-L. Sun, C.-C. Lin, A low humidity sensor made of quartz crystal microbalance coated with multi-walled carbon nanotubes/Nafion composite material films, *Sens. Actuators B* 115 (2006) 338–343.
- [28] S. Qiu, L. Sun, H. Chu, Y. Zou, F. Xu, N. Matsuda, Study of adsorption behaviors of meso-tetrakis (4-N-methylpyridyl) porphine p-toluenesulfonate at indium-tin-oxide electrode/solution interface by in-situ internal reflection spectroscopy and cyclic voltametry, *Thin Solid Films* 517/9 (2009) 2905–2911.
- [29] L.-X. Sun, T. Okada, Simultaneous determination of the concentration of methanol and relative humidity based on a single Nafion(Ag)-coated quartz crystal microbalance, *Anal. Chim. Acta* 421 (2000) 83–92.
- [30] Y.A. Cengel, M.A. Boles, *Thermodynamics an Engineering Approach*, 5th ed., McGraw-Hill Science Engineering, 2006, p. 719.

Biographies

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