al Kimiya: Jurnal Ilmu Kimia dan Terapan
p-ISSN: 2407-1897, e-ISSN: 2407-1927
Vol. xx, No. yy (zz-zz), Month and Year in Masehi/Month and Year in Hijriyah (filled by Publisher)

THE ARTIFICIAL NOSE-BASED PMMA-rGO COMPOSITE COATED QCM SENSOR TO SNIFF COFFEE AROMA AT DIFFERENT ROASTING DEGREE

FERRY CHRISMIADI NALLE[1,3*], AHMAD SABARUDIN [1]*, AND SETYAWAN PURNOMO SAKTI[2,3*]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University, Malang 65142, Indonesia

[2]Department of Physics, Faculty of Mathematics and Natural Sciences, Brawijaya University, Malang 65142, Indonesia

[3]Sensor Technology Laboratory (SenTLab), Department of Physics, Faculty of Mathematics and Natural Sciences, Brawijaya University, Malang 65142, Indonesia

*Corresponding Author email: ferrynalle15@student.ub.ac.id; sabarjpn@ub.ac.id; sakti@ub.ac.id

Article Information

Received: xxxx
Revised: xxxx
Accepted: xxxx
Published: xxxx

DOI: xxxx

Keywords:
PMMA; rGO; QCM sensor; Coffee aroma; Surface roughness.

Abstract

The quality of a product, including coffee, can be determined by its aroma, which is influenced by various chemical compounds. Human olfactory-based assesment and other technologies have been developed to assess coffee aroma; however, these methods are often costly and require highly trained professionals. Gravimetric-based sensors, such as quartz crystal microbalance (QCM) sensors, offer high sensitivity, ease of use, and the capacity to modify their effective surface with nanomaterials. In this research, an artificial nose-based QCM sensor has been modified using a material-sensitive polymethyl methacrylate-reduced graphene oxide (PMMA-rGO) composite.The composite materials were synthesised using an in-situ polymerisation method in the presence of dual solvent. IR characterisation revealed PMMA and PMMA-rGO spectra to be highly similar, suggesting successful trapping of rGO within the PMMA matrix via physical interaction. Increasing the content of rGO resulted in a slight increase in the surface roughness of the QCM sensor.The composite-based QCM sensor demonstrated the capacity to detect coffee aroma at three distinct roasting temperatures (220℃, 225℃, and 230 ℃). The highest response was observed in sample PR1, with a value of -35.2 Hz (220℃), -44.3 Hz (225℃), and -83 Hz (230℃) for the variation in the amount of rGO in the polymer matrix. The presence of rGO with their surface area properties enhanced the QCM sensor to detect coffee aroma.

INTRODUCTION

Indonesia becoming one of the world's top coffee producers [1], [2] and coffee quality is crucial in building consumer trust in food products. Aroma is a key factor in assessing coffee quality. Traditional aroma analysis techniques, such as nuclear magnetic resonance (NMR) [3] and chromatography (GC-O) [4], are reliable but have several disadvantages like lengthy-analysis time, not portable, and complex procedure. To overcome this challenge, quartz-based sensors come up with their uniqueness. Quartz crystal microbalance (QCM) sensors offer a promising alternative, as they are highly sensitive, portable devices, fast response time and easily modify their surfaces with nanomaterials [5].

Poly (methyl methacrylate) (PMMA) is extensively utilized in the development of various polymeric hybrid materials due to its cost-effectiveness, favorable physical and mechanical properties. These characteristics make PMMA a highly adaptable material for applications across interdisciplinary fields [6]. Reduced graphene oxide (rGO) is an outstanding material from the carbon-family, highly conductive and lightweight [7]. PMMA and rGO composites have been applied in various sensing contexts, including humidity [7] and ammonia detection [8], [9]. When combined these two materials, it can enhance QCM sensor sensitivity to specific analytes, such as food aromas. Several research has been conducted by surface modification QCM sensors for detecting aroma compounds such as methyl salicylate in black tea [10], β-myrcene in mango[11], β-pinene in Indian cardamom [12], and detection of bioactive compounds in turmeric (*Curcuma longa* L.)[13].

The mode of synthesis plays an important role to get the PMMA-rGO with specific properties. The synthesis of PMMA-rGO has been achieved through various method. Pham et al. 2012 [14] using surfactant in their PMMA-rGO synthesis. The PMMA latex was mixed GO, followed by hydrazine reduction. Mallik et al. [15] were synthesised the PMMA-rGO nanocomposite in the presence of iron metal induced deoxygenated rGO with continuous ultrasonication. Gaikward et al.[9] were synthesized the PMMA/rGO composite via drop cast on fabricated interdigitated copper electrodes. In our research, the PMMA-rGO was synthesized via in-situ polymerization approach in the presence of ethanol-water as a co-solvent system. The usage of alcohol-water mixture was predominantly used because it can control the solubility, good filler dispersion, and enhance the electrical and mechanical properties [14], [15], [16], [17]. The rGO was added after the PMMA was formed.

This study aims to synthesize PMMA and PMMA-rGO composites and then applying these materials on the QCM sensor for detecting roasted coffee aroma. The composites were prepared via modified *in-situ polymerization* using a co-solvent system. Robusta coffee was selected for its unique aroma profile, and for the roasting temperature varied from 220℃, 225℃, and 230℃.

EXPERIMENT

Material

All chemicals used in this work were analytical grade and without further purification. Methyl methacrylate (MMA, 99,9%), α, α'-azoisobutyronitrile (AIBN) and reduced-graphene oxide (rGO, 99,9%) were purchased by Sigma Aldrich. Ethanol (99%), methanol (99%), and acetone (99%) were provided by Merck. We also used deionized water in all the experiments. We purchased the 8 MHz AT-Cut QCM sensor with dual silver electrodes from PT Great Microtama, Surabaya.

Instrumentation

Our lab-scale artificial nose was used to find the smell of coffee, and the Fourier transform infrared (ATR-FTIR) Shimadzu IR Spirit-T was used to identify the functional groups of nanocomposite materials. We measured the surface roughness using a non-contact Topography Measurement System (TMS) 1200 from Polytec GmbH. We used the Omicron Lab Bode 100 impedance analyzer to find the threshold frequencies of the QCM sensor before and after deposition.

Procedure

The Synthesis of Polymethyl Methacrylate-reduced Graphene Oxide (PMMA- rGO) Composite.

The PMMA-rGO was synthesized by using facile in situ polymerization method with minor modification[6], [9], [15], [18], [20]. Precisely, (MMA) was mixed with AIBN in the ratio of 18.8% by weight. Ethanol-water acts as a medium reaction with a proportion of 1:4 (% by volume). The reaction was kept at ± 65℃ under continuous stirring for 2 hours. The solution changed from colorless to white, which indicates the PMMA was formed. After that PMMA solution was, the rGO (0.2 %, 0.6%, and 1%) was mixed with 1 mL acetone and then sonicated for 5 minutes before adding it to the PMMA solution. The reaction then was continuous for one hour. After that, the PMMA-rGO solid was washed with methanol and hot water several times. Finally, the PMMA-rGO dried at 40℃, for 24 hours. The PMMA was prepared by the same method without rGO. The samples PMMA without rGO was denoted as **PR0** and PMMA-rGO was marked as **PR0.2, PR0.6,** and **PR1**.

Material deposition method

The coating process of PR0, PR0.2, PR0.6, and PR1 on the surface of the QCM sensor was performed using the spin-coating method. First, the materials were weighed about 1 mg and then mixed with 1 mL of acetone to make a concentration of 1% solution for each. Then, 50 µL of the solution is dropped onto the surface of the QCM, which spins at 2000 rpm for 60 seconds. The deposition is done on both sides of the QCM sensor. After deposition, the QCM sensors are heated for one hour at 200℃.

The sensing operation setup

All the QCM coated with PMMA and PMMA-rGO was placed onto a sample holder and put into a closed-type chamber (**Figure 1**). About 150 grams of Robusta green coffee were

al Kimiya: Jurnal Ilmu Kimia dan Terapan
p-ISSN: 2407-1897, e-ISSN: 2407-1927
Vol. xx, No. yy (zz-zz), Month and Year in Masehi/Month and Year in Hijriyah (filled by Publisher)

placed in our own lab-scale artificial nose [21]. The roasting temperature were 220℃, 225℃, and 230℃ and replicated in thrice. The sensing measurement process was taken in an hour.

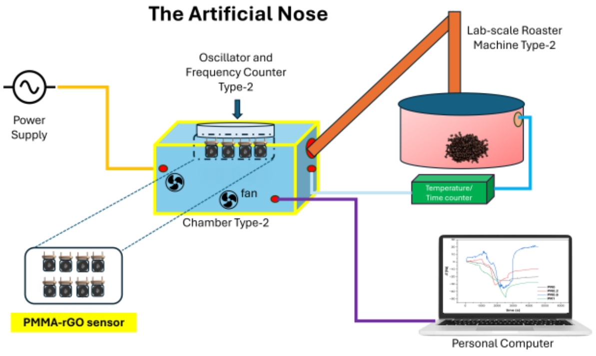


Figure 1. The illustration of artificial nose-based QCM sensor

The calculation

To estimate the amount of coating material on the surface of QCM sensor, we can use the Sauerbrey equation [19], [22-24]:

$$\Delta f = -C_f . \Delta m \text{............................}(1)$$

There is a change in frequency (Δ*f*) from before and after deposition in Hz, a crystal sensitivity constant (0.1834 Hz/ng/cm2), and a coating material mass (Δ*m*) on the surface of the QCM. The Sauerbrey is not used only to determine the amount of deposited mass on the surface of QCM; in this case, we use this equation to determine the decreasing frequency (Hz) when exposed to the coffee aroma.

RESULT AND DISCUSSION

The frequency changing (Δf)

To estimate the amount of coating material on the surface of QCM, we can use the shifting frequency (Δ*f*) before and after the deposition process. After that, this shifting frequency is used to determine the deposited mass (Δ*m*) via the Sauerbrey equation **Table 1.** shows that the materials successfully coated all the QCM sensors. This is due to a change in the frequency (f) of the QCM sensor. Additionally, by using the Sauerbrey equation, we can estimate the amount of material (Δ*m*) on the QCM surface.

Table 1. The frequency changes (Δ*f*) of QCM sensor before and after deposition

No	Sample Code	Initial Frequency before coating (f_0,Hz)	Frequency after coating (f_1,Hz)	Δf (Hz)	Δm (ng)
1	PR0	8008352	8008242	-1.1×10^{-4}	2.1×10^{-2}
2	PR0.2	8008462	8008352	-1.1×10^{-4}	2.1×10^{-2}
3	PR0.6	8007033	8006813	-2.2×10^{-4}	4.3×10^{-2}
4	PR1.0	8007143	8006484	-6.59×10^{-4}	12.8×10^{-2}

The Surface Characteristics

ATR-FTIR analysis

Figure 2. shows the pattern of IR spectrum for PMMA and PMMA-rGO. There are several bands for PMMA, such as around 2850 cm^{-1} indicates the -C-H stretching, around 1710 cm^{-1} specifically for -C=O (carbonyl) stretching, and the bands around 1342 cm^{-1} reflect the -C-O-C (ester) bending mode. The bands for PMMA-rGO were similar to the PMMA. These finding suggests that the rGO was successfully trapped on the polymer matrix. Additionally, the interaction between PMMA and rGO in the nanocomposite structure via physics interaction rather than chemically bonded. This result is quite like previous study [6], [9], [20].

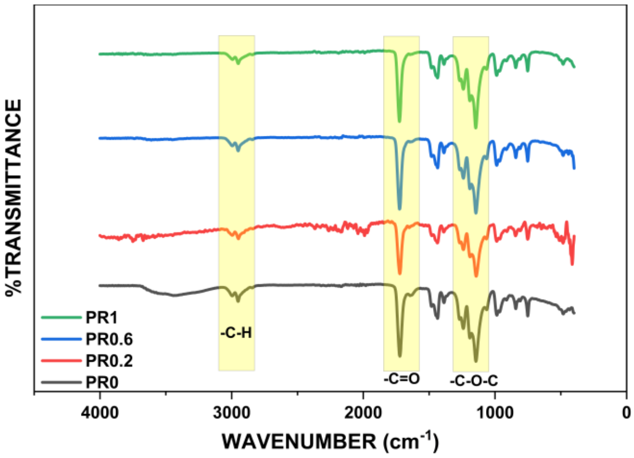
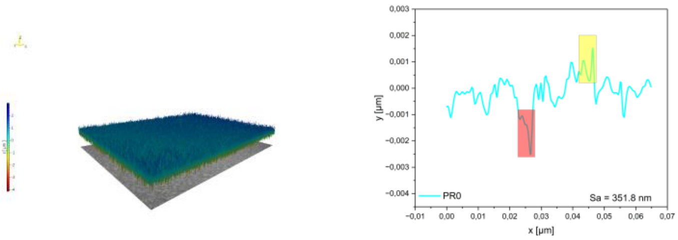


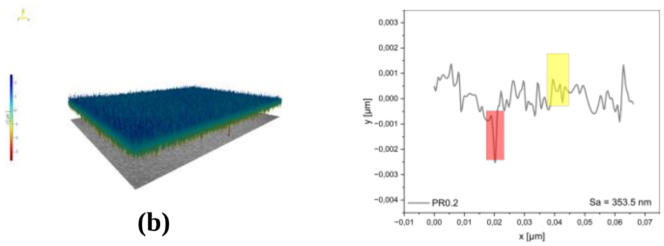
Figure 2. IR spectra for PMMA-rGO

TMS analysis

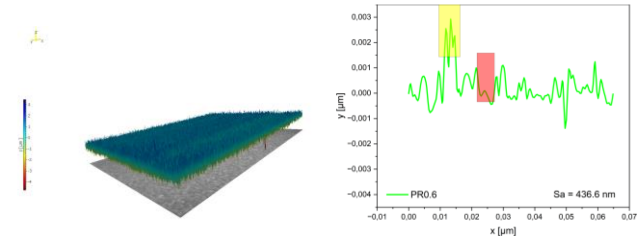
Figure 3 summarizes the surface characteristics of PMMA and PMMA-rGO. All the QCM-coated samples consist of peak and valley modes at their surfaces. The intensity of the peak and valley was quite intense, alongside the presence of rGO. By increasing the amount of rGO on the PMMA matrix, the intensity of peak-valley mode on the QCM surface was increased. This result suggests that the presence of rGO changes the morphological contour of the QCM sensor surfaces. The pattern of peak valley then reflects the surface roughness (*Sa*) value.



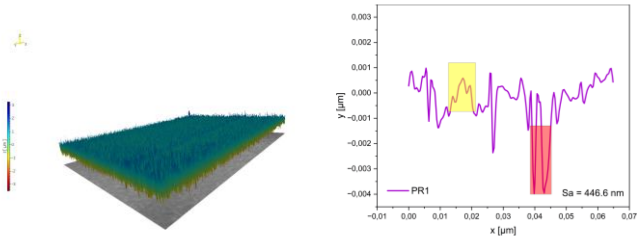
(a) **(a1)**



(b) **(b1)**



(c) **(c1)**



(d) **(d1)**

Figure 3. TMS profiling image of the surface of PMMA-rGO-coated QCM sensor in peak (yellow mark)-valley (red mark) mode (a1-d1) and 3D-mode (a-d)

The value of surface roughness (Sa) was increasing with the increased amount of rGO in the composite. When PMMA is on the surface of the QCM sensor, it makes the surface rougher, which gives the analyte (coffee aroma) more places to interact with it. Furthermore, by adding the graphene to the polymer matrix and then applying it to the QCM sensor, their surface becomes more rough. Because graphene has a lot of surface area, this behavior shows that rGO gives the analyte more places to interact with it. This large surface area can be used as a target for analyte detection.

The sensing performance

In this study, Robusta coffee sample was roasted at three different roasting temperatures, 220°C, 225°C, and 230°C. Based on **Figure 4a-c**, all the QCM sensors can detect coffee aroma at three different temperatures. When the roasting temperature was increased, the more coffee aroma was produced. The highest frequency shift (Δf) was found in the 230°C degree of roasting. **Figure 4d** shows the relationship between amount of rGO in the polymer matrix toward QCM sensing performance.

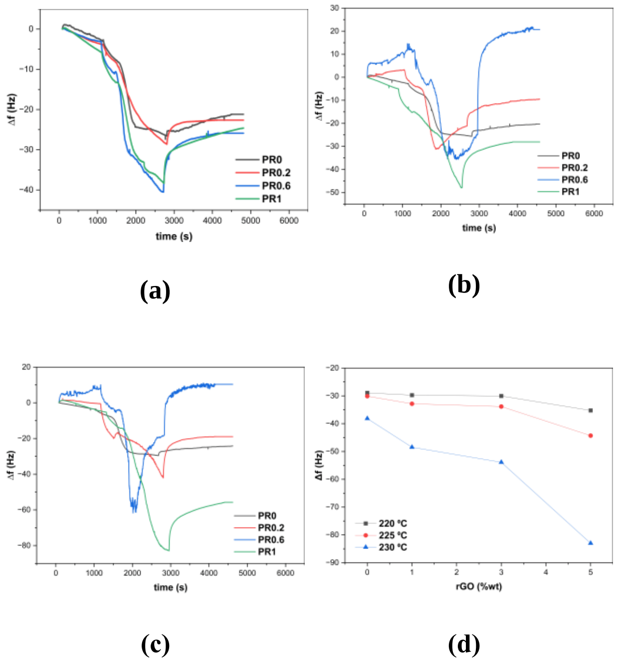


Figure 4. PMMA/rGO coated QCM sensor response toward real roasted coffee aroma at different degree of roasting: (a) 220℃, (b) 225℃, (c) 230℃, and relationship between the amount of rGO (%wt.) in nanocomposite vs Δ*f*

For all degrees of roasting, the QCM sensing performance was increased with the increasing amount of rGO. The highest frequency shift *(*Δ*f*) was found in sample PR1, at 220℃, 225℃, and 230℃ orderly -35.2 Hz, -44.3 Hz, and -83 Hz (**Figure 4d).** By increasing the amount of graphene into polymer matrix, the QCM sensing performance was significantly increasing. By increasing the roasting temperature, more coffee aroma was produced. The more rGO was added into the polymer matrix, the QCM sensor enabled to detect more coffee aroma. The study from Aycı et al.[25] suggests that the higher surface area, the higher possibility of analyte (gas molecules) to interact with the thin film (coating material). In this study, the higher surface roughness is related to the amount of graphene on the surface of QCM sensor. The higher concentration of graphene, the more surface roughness is produced. Basically, graphene provides a large surface area. When applied to the QCM sensor in polymer matrix, the surface roughness may be increased. Consequently, the coffee aroma can find the best area to interact with the coating material.

CONCLUSION

The artificial nose based PMMA-rGO coated QCM sensor could detect coffee aroma at different roasting. temperature. The higher the temperature, the more coffee aroma is produced. The highest frequency shift (Δ*f*) was found in sample PR1, at 220℃, 225℃, and 230℃ orderly -35.2 Hz, -44.3 Hz, and -83 Hz. By increasing the content of rGO on the polymer matrix, the surface roughness slightly increases, which contributes to the sensing performance, because of their high surface area. In the future, the coating process needs to be improved to get better results as well as their sensing performance, including its stability and reproducibility.

ACKNOWLEDGEMENT

The authors thankfully acknowledge financial support from the Endowment Fund (LPDP) of the Ministry of Economics, Indonesia.

REFERENCES

[1] F. Ashardiono and A. Trihartono, "Optimizing the potential of Indonesian coffee: a dual market approach," *Cogent Social Science*, **10**(1), 2024, https://doi.org/10.1080/23311886.2024.2340206

[2] M. Purnomo, Y. Yuliati, A. Shinta, and F. D. Riana, "Developing coffee culture among indonesia's middle-class: A case study in a coffee-producing country," *Cogent Social Science*, **7**(1), 2021, https://doi.org/10.1080/23311886.2021.1949808

[3] J. C. C. Freitas, M. Ejaz, A. T. Toci, W. Romão, and Y. Z. Khimyak, "Solid-state NMR spectroscopy of roasted and ground coffee samples: Evidences for phase heterogeneity and prospects of applications in food screening," *Food Chemistry*, **409**, May 2023, https://doi.org/10.1016/j.foodchem.2022.135317

[4] R. Crnjar, P. Solari, and G. Sollai, "The Human Nose as a Chemical Sensor in the Perception of Coffee Aroma: Individual Variability," *Chemosensors*, **11**(4), Apr. 2023, https://doi.org/10.3390/chemosensors11040248

[5] Z. Ma, T. Yuan, Y. Fan, Y. Chen, Y. Bai, and J. Xu, "Mesoporous-Structure MOF-14-Based QCM p-Xylene Gas Sensor," *Nanomaterials*, **13**(11), Jun. 2023, https://doi.org/10.3390/nano13111743

[6] G. Sahoo, N. Sarkar, D. Sahu, and S. K. Swain, "Nano gold decorated reduced graphene oxide wrapped polymethylmethacrylate for supercapacitor applications," *RSC Advances*, **7**(4), pp. 2137–2150, 2017, https://doi.org/10.1039/c6ra26930c

[7] F. Temel and I. Ozaytekin, "The enhanced humidity sensing performance of calixarene/PMMA hybrid layers: QCM sensing mechanism," *Journal of Materials Science: Materials in Electronics*, **33**(5), pp. 2801–2815, Feb. 2022, https://doi.org/10.1007/s10854-021-07484-z

[8] A. Raza, R. Abid, I. Murtaza, and T. Fan, "Room temperature NH_3 gas sensor based on PMMA/RGO/ZnO nanocomposite films fabricated by in-situ solution polymerization," *Ceramics International*, **49**(16), pp. 27050–27059, Aug. 2023, doi: https://doi.org/10.1016/j.ceramint.2023.05.247

[9] S. S. Gaikwad, A. S. Khune, N. N. Ingle, and M. D. Shirsat, "Chemiresistive sensor based on PMMA/rGO composite for detection ammonia," *Sensors and Actuators A: Physical*, **377**, Oct. 2024, https://doi.org/10.1016/j.sna.2024.115665

[10] P. Sharma, B. Tudu, L. P. Bhuyan, P. Tamuly, N. Bhattacharyya, and R. Bandyopadhyay, "Detection of Methyl Salicylate in Black Tea Using a Quartz Crystal Microbalance Sensor," *IEEE Sensors Journal*, **16**(13), pp. 5160–5166, Jul. 2016, https://doi.org/10.1109/jsen.2016.2564978

[11] S. B. Ali *et al.*, "Sensitive Detection of β-Myrcene in Mango Using Ethyl Cellulose Modified Quartz Crystal Microbalance Sensor," 2019. [Online]. Available: www.sciencedirect.comwww.materialstoday.com/proceedings

[12] N. Debabhuti *et al.*, "A study of vegetable oil modified QCM sensor to detect β-pinene in Indian cardamom," *Talanta*, **236**, Jan. 2022, https://doi.org/10.1016/j.talanta.2021.122837

[13] F. Hardoyono and K. Windhani, "Identification and detection of bioactive compounds in turmeric (Curcuma longaL.) using a gas sensor array based on molecularly imprinted polymer quartz crystal microbalance," *New Journal of Chemistry*, **45**(38), pp. 17930–17940, Oct. 2021, https://doi.org/10.1039/d1nj03640h

[14] V. H. Pham, T. T. Dang, S. H. Hur, E. J. Kim, and J. S. Chung, "Highly conductive poly(methyl methacrylate) (PMMA)-reduced graphene oxide composite prepared by self-assembly of PMMA latex and graphene oxide through electrostatic interaction," *ACS Applied Materials Interfaces*, **4**(5), pp. 2630–2636, May 2012, https://doi.org/10.1021/am300297j

[15] A. K. Mallik *et al.*, "Reduced Graphene Oxide (rGO) Prepared by Metal-Induced Reduction of Graphite Oxide: Improved Conductive Behavior of a Poly(methyl methacrylate) (PMMA)/rGO Composite," *ChemistrySelect*, **4**(27), pp. 7954–7958, Jul. 2019, https://doi.org/10.1002/slct.201901281

[16] M. D. Hossain, W. S. Kim, H. S. Hwang, and K. T. Lim, "Role of water on PMMA/clay nanocomposites synthesized by in situ polymerization in ethanol and supercritical carbon dioxide," *Journal of Colloid Interface Science*, **336**(2), pp. 443–448, Aug. 2009, https://doi.org/10.1016/j.jcis.2009.04.044

[17] G. Oehl, N. Naga, and G. Ziegmann, "Facile Synthesis of Poly(methyl methacrylate) Silica Nanocomposite Monolith by In Situ Free Radical Polymerization of Methyl Methacrylate in the Presence of Functionalized Silica Nanoparticles," *ACS Omega*, **9**(14), pp. 16279–16287, Apr. 2024, https://doi.org/10.1021/acsomega.3c10338

[18] P. A. Saeed and A. Sujith, "A simple approach to develop conductive poly(methyl methacrylate)-reduced graphene oxide composite with segregated network," *Polymer Bulletin*, **81**(10), pp. 8917–8931, Jul. 2024,

https://doi.org/10.1007/s00289-024-05151-x

[19] G. Sauerbrey. Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. Zeitschrift für Physik 1959; 155, p. 206-22.

[20] T. L. Hsieh, P. S. Hung, C. J. Wang, Y. S. Chou, and P. W. Wu, "Controlled synthesis of uniform hollow polypyrrole microcapsules by a cosolvent approach," *Springer Nature Applied Sciences*, **1**(4), Apr. 2019, https://doi.org/10.1007/s42452-019-0332-8

[21] A. O. Triqadafi, T. N. Zafirah, H. A. Dharmawan, and S. P. Sakti, "Four-Channels High-Resolution Frequency Counter for QCM Sensor Array Using Generic FPGA XC6SLX9 Board," *Journal of Electrical and Computer Engineering*, **2023**, 2023, https://doi.org/10.1155/2023/5182455

[22] X. Qiao, X. Zhang, Y. Tian, and Y. Meng, "Progresses on the theory and application of quartz crystal microbalance,", *Applied Physics Reviews*, Sep. 01, 2016, doi: https://doi.org/10.1063/1.4963312

[23] L. Sartore, M. Barbaglio, L. Borgese, and E. Bontempi, "Polymer-grafted QCM chemical sensor and application to heavy metal ions real time detection," *Sensors and Actuators B: Chemical*, **155**(2), pp. 538–544, Jul. 2011, https://doi.org/10.1016/j.snb.2011.01.003

[24] F. Fauzi, A. Rianjanu, I. Santoso, and K. Triyana, "Gas and humidity sensing with quartz crystal microbalance (QCM) coated with graphene-based materials – A mini review," *Sensors Actuators B: Chemical*, Oct. 15, 2021, https://doi.org/10.1016/j.sna.2021.112837

[25] D. Ayci *et al.*, "The influence of the surface morphologies of Langmuir Blodgett (LB) thin films of porphyrins on their gas sensing properties," *Sensors Actuators B: Chemical*, **158**(1), pp. 62–68, Nov. 2011, https://doi.org/10.1016/j.snb.2011.05.033