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Graphene, GO, and Borophene: Innovations in QCM-Based Humidity Sensors for Enhanced Sensitivity

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Abstract - Humidity measurements are crucial in daily life as they influence human comfort, health, safety, and product quality. Quartz Crystal Microbalance (QCM) sensors, known for their fast response times and high sensitivity, offer a significant advantage in humidity sensing due to their ability to provide highly linear and accurate measurements. These sensors are particularly valuable because they enable real-time, precise humidity detection with minimal calibration, making them ideal for various applications. This mini-review highlights the significance of QCM sensors, focusing on the sensing layers made from nanomaterial fillers integrated into composite matrices. Typical QCM sensor surfaces are could be coated with highly conductive materials such as graphene, graphene oxide (GO), and borophene, which offer excellent humidity-sensing capabilities due to their two-dimensional allotrope structure and unique properties of carbon and boron. This review begins with a brief overview of humidity measurement principles and QCM sensor characteristics. It then explores a variety of materials used for preparing QCM sensing layers, discussing their advantages and disadvantages for humidity sensor applications. Finally, the review presents future perspectives on the development of layer-by-layer self-assembled conductive polymeric films, novel GO-based composite QCM humidity sensors, and borophene-based humidity sensors, illustrating their potential for multifunctional composites.

Keywords: Quartz Crystal Microbalance (QCM), Quick-response, Highly sensitive, Graphene oxide (GO)-based humidity sensors, borophene-based humidity sensing platforms.

Grafen, GO ve Borofen: QCM Tabanlı Nem Sensörlerinde Artırılmış Hassasiyet için Yaklaşımlar

Öz - Ortam neminin belirlenmesi, insan konforu, sağlığı, güvenliği ve ürün kalitesini doğrudan etkilediği için günlük yaşamda büyük bir öneme sahiptir. Hızlı yanıt süreleri ve yüksek hassasiyetleri ile bilinen Quartz Kristal Mikroteraziler (QCM), nem algılama konusunda yüksek doğrulukla doğrusal ölçümler sağlayabilme yetenekleri sayesinde önemli bir avantaj sunar. Bu sensörler, gerçek zamanlı, hassas nem tespiti yapabilmeleri ve minimum kalibrasyon gerektirmeleri nedeniyle özellikle değerlidir, bu da onları çeşitli uygulamalar için ideal kılar. Bu mini derleme, QCM sensörlerinin önemini vurgulamakta olup, kompozit matrislere entegre edilmiş katkı malzemelerinden karbon ve bor bazlı nanomalzemelerden hazırlanan algılama katmanlarına odaklanmaktadır. Derlemede, grafen, grafen oksit (GO) ve borofen tabanlı malzemelere ağırlık verilecektir. Bu malzemeler, karbon ve borun benzersiz özellikleri ve iki boyutlu allotrop yapıları sayesinde mükemmel nem algılama yetenekleri sunar. Bu derleme, nem ölçüm ilkeleri ve QCM sensör özellikleri hakkında kısa bir genel bakışla başlamakta, ardından QCM algılama katmanlarını hazırlamak için kullanılan çeşitli malzemeleri incelemekte ve bu malzemelerin nem sensörü uygulamalarındaki avantajlarını ve dezavantajlarını tartışmaktadır. Son olarak, derleme, katmanlar arası kendiliğinden montaj edilen iletken polimerik filmler, yenilikçi GO tabanlı kompozit QCM nem sensörleri ve borofen tabanlı nem sensörlerinin geliştirilmesine yönelik gelecekteki perspektifleri sunarak, bunların çok fonksiyonlu kompozitler için potansiyelini ortaya koymaktadır.

Anahtar kelimeler: Quartz Kristal Mikrodengeleme (QCM), Hızlı Yanıtlı, Yüksek Hassasiyetli, Grafen Oksit (GO) Tabanlı Nem Sensörleri, Borofen Tabanlı Nem Algılama Platformları.

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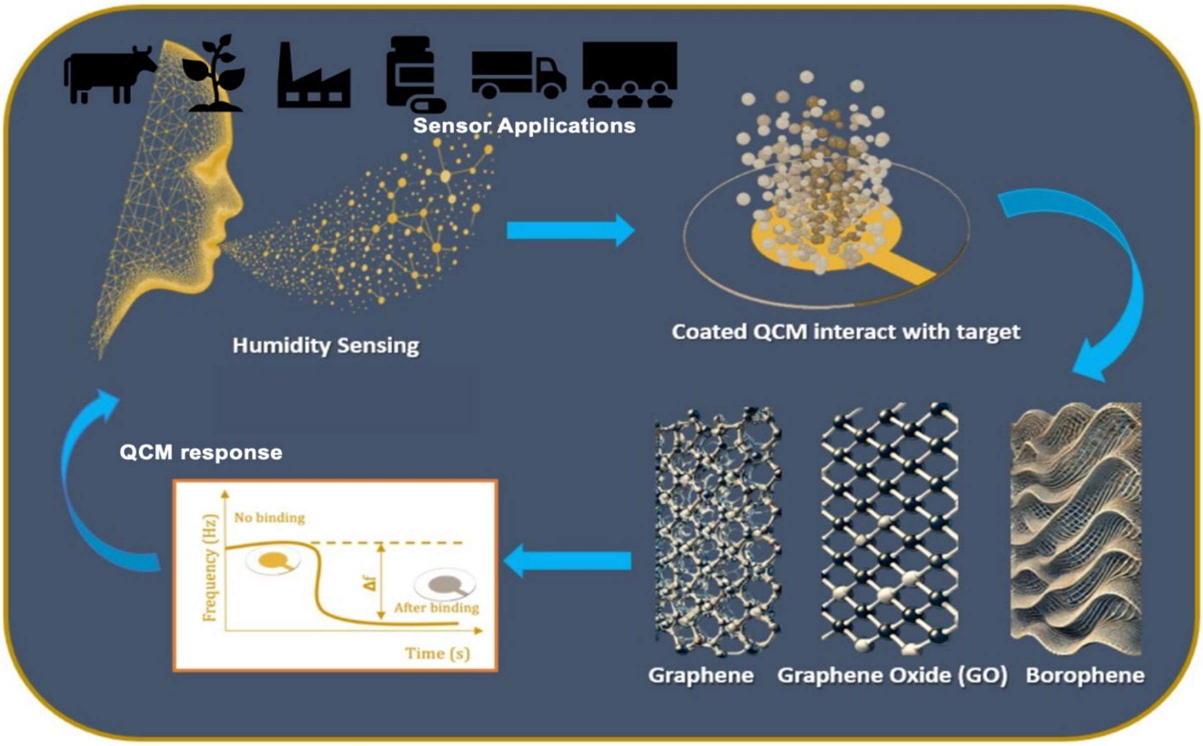
GRAPHICAL ABSTRACT



1. Introduction

Humidity and its control is crucial in many areas of our daily lives [1, 2], and therefore, humidity measurement has attracted significant attention since the 1900s [3]. Humidity measurement plays a vital role in various industries, such as weather forecasting [4], food safety [5,6], human comfort [7, 8], agricultural process control [9], and mining (for gas leakage monitoring) [10], among others. As a result, there has been an increasing demand for the development of rapid, cost-effective, and highly sensitive humidity sensors. Although a variety of methods have been developed, the quartz crystal microbalance (QCM) stands out as a leading candidate due to its outstanding advantages. QCM sensors offer excellent sensitivity to mass changes at the nanogram level, a wide measurement range, stability, and reliability under mild operational conditions. Additionally, they are compact and can be developed at a low cost [11]. These features make QCM sensors particularly attractive compared to other traditional methods, which may struggle with sensitivity or operational stability in certain conditions.

The schematic representation of QCM is shown in Figure 1. A quartz disk is positioned between two gold electrodes, and when a voltage is applied, oscillation at a specific frequency occurs. This oscillation results in a shift in the resonance frequency [12]. The mass change on the QCM surface is directly related to this shift in frequency, which can be accurately quantified using the Sauerbrey equation [13]. The resonance frequency shift (Δf) is typically measured over time, as the mass change on the quartz surface occurs due to the adsorption or desorption of materials.

$$\Delta f = -2.26x10^{-6} f_0^2 \frac{\Delta m}{A} \quad (1)$$

Here, the equation specifies that the mass change is represented by Δm (in grams), and the resonance frequency shift by Δf (in MHz). The original frequency of the quartz crystal is f_0 (in MHz), and A (in cm^2) is the surface area of the quartz electrode. Importantly, the shift in frequency is not directly dependent on the applied voltage. However, the QCM's performance can be affected by voltage if it's part of a system designed for electromechanical resonance, but this is generally outside

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the scope of the Sauerbrey equation. As shown in the Eq.1, there is a proportional relationship between Δm and Δf, indicating that as the mass on the quartz surface increases or decreases, the resonance frequency shifts accordingly. This relationship is fundamental for many piezoelectric sensing applications, as the frequency shift provides a sensitive and accurate method to quantify mass changes at the surface. For instance, Favrat et al. developed a QCM sensor for real-time measurement of fatty acid removal in a cleaning mechanism, which involved an aqueous solution containing anionic and non-ionic detergents [14]. The real-time measurement was performed by observing the frequency change in the quartz crystal during the cleaning process. In another study, Susilo et al. (2019) used spray coating to deposit reduced graphene oxide on the QCM surface to develop a piezoelectric biosensor [15]. Mass deposition on the QCM surface results in a decline in its resonant frequency. The crystal's thickness affects both the resonant frequency and the mass sensitivity, as a thinner crystal typically has a higher resonant frequency and greater sensitivity to mass changes.

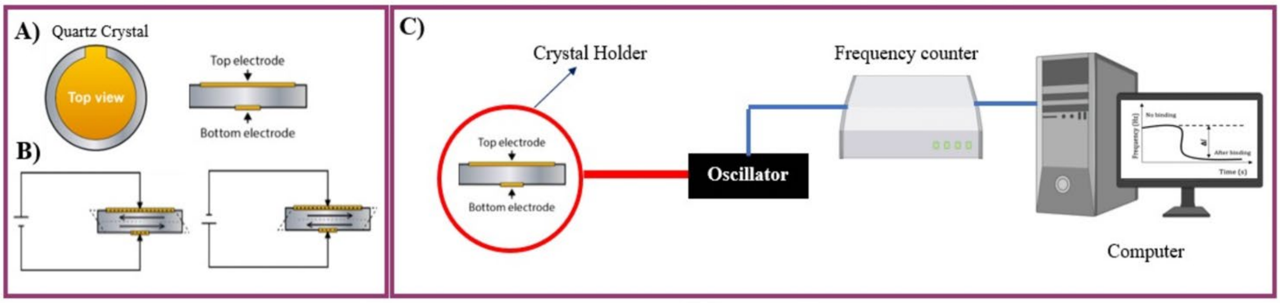

Figure 1. Schematic illustration of a QCM setup.

On the other hand, QCM is not functional by itself for humidity detection, and an additional sensing layer is necessary. Li et al. (2021) demonstrated that an uncoated QCM has a minimal response to humidity, whereas a coated QCM exhibited a high response to relative humidity [16]. Kosuru et al. (2016) investigated PVP and metal-organic framework coatings on the QCM surface for humidity sensing. They tested the sensitivity of uncoated QCM sensors alongside these coated sensors and found that uncoated QCM showed the lowest sensitivity [17].

The selection of materials and development methods for the sensing layer is of great importance [18], as the sensing layer also determines the characteristics of the QCM sensor. The sensing material is coated on the electrode of the QCM (as shown in Figure 1); note that the uncoated quartz is shown in Figure 1, as it represents the unmodified QCM setup. Therefore, in addition to the chemical structure and physical properties of the sensing layer, the mass and viscoelastic properties of the material used for the sensing layer also influence the QCM sensor response [19]. To ensure the humidity sensitivity of the QCM, the electrode surface is covered with various water-adsorbing materials, including polymers [20], ceramics [21], different chemical incorporations [11], nanostructures [22], and composites [23, 24]. For instance, molecularly imprinted polymers (MIPs) can offer good selectivity and sensitivity as a coating material on QCM sensors, but they are not suitable for relative humidity levels around 50%, and their structural and morphological instability is another issue that needs to be addressed [25]. On the other hand, ZnO, as an example of metal oxides, has the advantage of morphology-dependent sensing and has garnered significant attention for this reason [26]. Due to their high surface area for interactions, 1-dimensional ZnO nanomaterials are among the most promising candidates for applications [27]. Unfortunately, these materials lack hydrophilicity, which is an important parameter for humidity sensing [28, 29, 30].

For most humidity sensing applications, fast response/recovery times are essential to ensure real-time measurement. The key parameters affecting QCM (Quartz Crystal Microbalance) measurements include several factors related to both the crystal itself and the experimental conditions. The QCM crystal plays a fundamental role in the sensor's performance, as its properties directly influence the frequency response. The electrode surface also impacts the measurement by determining

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the interaction between the crystal and the adsorbed material. The sensing material deposited on the electrode surface is another critical factor, as its physical and chemical properties influence the mass changes detected by the QCM. In addition, the thickness of the sensing material is important, as it determines the magnitude of the frequency shift for a given mass change. The electrode area also affects the sensitivity of the QCM, with larger areas generally providing higher sensitivity. Environmental factors, such as temperature and humidity, can further influence QCM measurements by affecting both the crystal's behavior and the properties of the sensing material. Together, these factors must be carefully controlled to ensure accurate and reliable QCM measurements. In such cases, surface properties play a crucial role [31]. For example, Qi et al. (2018) synthesized acidized multiwalled carbon nanotubes as a sensing layer on QCM surfaces and achieved relatively fast response and recovery times (49s / 6s) [32], while Gao et al. (2019) achieved even better results in terms of response and recovery times (10s / 3s) by fabricating colloidal tin oxide nanowires [33]. Furthermore, Horzum et al. (2011) demonstrated that the use of ZnO-based fibers can provide very fast response (0.5 s) and recovery (1.5 s) times when produced via electrospinning [34]. On the other hand, hydrophilic organic polymers are unable to meet these criteria, as recovery times after adsorption typically range from 25 to 75 s [35]. Dai et al. (2017) studied the humidity sensing properties of organic hybrid polymers and observed a 40 s recovery time [36]. These types of materials are not effective enough for enhanced humidity sensing in critical applications. Moreover, it has been shown that nanostructured materials offer better properties than their bulk counterparts for QCM sensors [37], as they have a larger surface area to volume ratio, higher mechanical modulus, and better chemical stability [38].

To achieve specific improvements, such as enhanced sensitivity for QCM humidity sensors, hybrid composite materials can be used, which combine two or more different materials. Essentially, two approaches can be applied: (1) using an additional nanostructured/porous material to enhance the specific surface area and increase interactions with water molecules and the surface, or (2) using another humidity-sensitive material to improve overall humidity sensitivity [11]. Composite materials for humidity sensors exhibit low hysteresis, excellent sensitivity, fast response/recovery times, enhanced selectivity, stability, and linearity [39]. Nanostructured innovative composites, also known as nanocomposites, with large surface areas and oxygen-rich functional groups, ensure excellent humidity sensing performance [40, 41].

Superior physicochemical features that make them commonly used materials in sensing, energy and biomedicine applications in addition to other utilizations. Carbon nanomaterials are taking attention because of their low weight, and high strength and conductivity [39]. The significant attention on carbon nanomaterials because of their chemical, mechanical, optical, electrical and thermal properties has provided enhancement in fundamental and applied science.

2. Graphene and Graphene Oxide (GO) nanomaterials

Graphene is one of the 2D structures of carbon that has various derivatives containing graphene oxide (GO) and reduced graphene oxide (rGO). Due to its superior properties such as mechanical strength, flexibility, high surface to volume ratio, good conductivity, different electrical and optical properties, simply modifiable, and thermal stability, graphene-based nanomaterials are the most popular nanomaterials for a while [42, 43, 44].

Graphene was discovered in 2004, but its history is not that new, as it represents a two-dimensional structure derived from the three-dimensional material graphite [45]. The most outstanding feature of graphene is that it is the thinnest and strongest material which is composed of 2D sheets less than 10 nm in thickness [45]. Even though graphene and its derivatives have basically the same 2D structure, there are slight differences which give various physicochemical properties to every one of them.

Graphene Oxide (GO), one of the main derivatives of graphene, can be obtained as result of chemical exfoliation and oxidizing of graphite powder and has hydrophilic functional groups on its carbon plane surface [46]. As it can be seen in Figure 2, GO is the oxidized state of graphene.

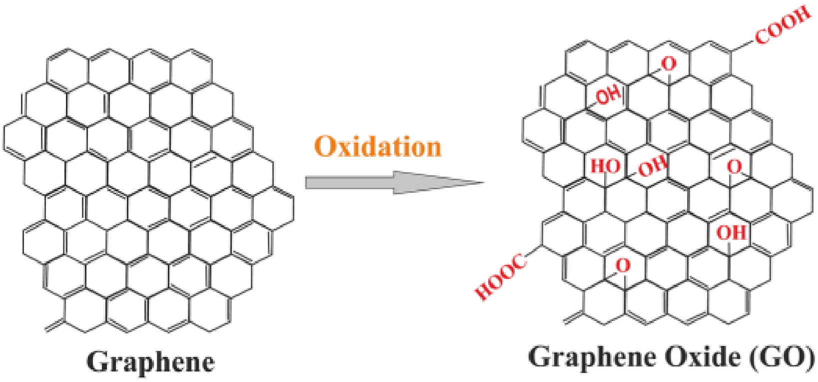

Figure 2. Conversion of graphene into GO [33].

GO has a cost effective and large-scale production, also the processing of GO is easier compared to graphene. Both graphene and GO demonstrate good mechanical, thermal and electrical properties thanks to their morphology. On the other hand, the most important difference between graphene and GO is their structure. While graphene is in a crystalline form, GO has both crystalline and amorphous regions. GO has oxygen-containing groups such as epoxy, hydroxyl, carboxylic and carbonyl which make GO hydrophilic and give an opportunity to use it in many fields from drug delivery to healthcare, solar cells to energy storage, etc [47]. In addition to mechanical, electrical and optical properties that GO has thanks to its oxygen-containing functional groups on the surface, it also gives the opportunity to be used in biotechnology by providing a large surface area and biocompatibility [48]. Therefore, GO is one of the most interesting carbon-based materials for biotechnological and nanotechnological applications.

3. Borophene Structures

Borophene is a newly developed material, designed as an alternative to graphene, which is one of the most extensively studied carbon-based 2D materials in recent years [49]. Borophene emerged initially through theoretical calculations and simulations, making it the first material to be conceptually predicted and later successfully synthesized. The first experimental synthesis of borophene was achieved in 2019, marking a significant breakthrough in materials science [50]. Since its synthesis, borophene has attracted widespread attention due to its exceptional chemical, electronic, mechanical, and thermal properties, which surpass those of graphene in several aspects. These remarkable properties suggest a vast potential for borophene in various advanced applications such as supercapacitors, batteries, hydrogen storage, and biomedical technologies [51].

Figure 3a shows the borophene structure which is obtained by extracting a slice from the bulk boron crystal. This slice forms a single-layer, two-dimensional sheet of boron, with different configurations that can be tailored depending on the specific synthesis conditions. Historically, the development of borophene has followed a theoretical path, starting with early predictions about its possible structures and properties. The theoretical models and their evolution are illustrated in Figure 3b, showing how the material was initially proposed and later refined through various simulations and experimental advancements [52].

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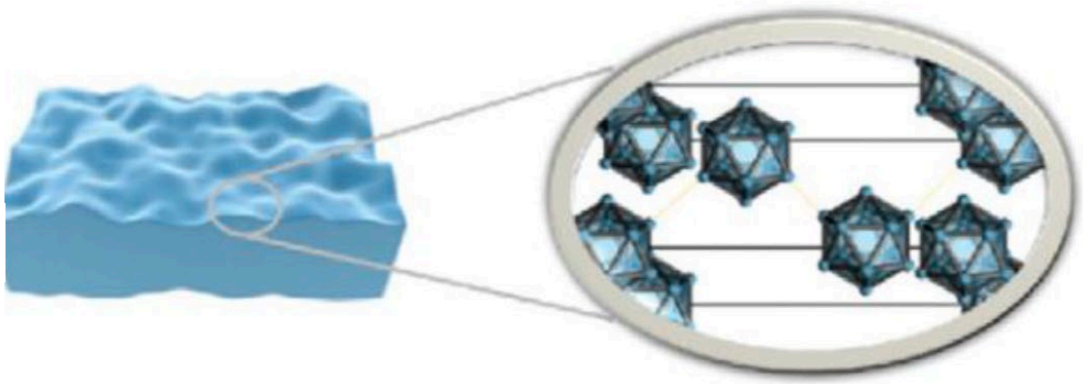
(a)



(b)

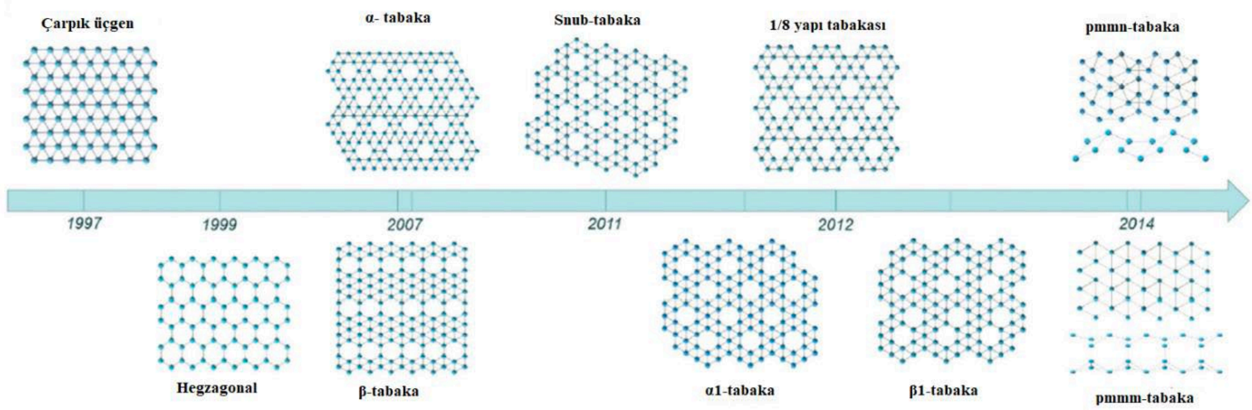


Figure 3. Boron structure (a) and Developments of Borophene in history (b).

4. QCM humidity sensing applications

Three key factors that significantly influence the sensitivity and stability of QCM humidity sensors have been identified: flexibility, surface-to-volume ratio, and hydrophilicity [38]. To enhance these properties, researchers have been focusing on the development of novel materials and the combination of existing materials to create composites with improved performance characteristics [53]. Composites, which are materials made by combining two or more substances to achieve enhanced properties, have become a popular approach in the field.

For instance, Chen et al. (2020) introduced a composite-based QCM humidity sensor incorporating MOF-SnO_2/Chitosan, which demonstrated significant improvements in sensitivity, selectivity, response/recovery times, and stability [54]. Metal-organic frameworks (MOFs) are a class of novel functional materials with a porous structure and a high specific surface area, making them ideal for creating templates that facilitate the preparation of metal oxides like SnO_2. Chitosan, a biopolymer, also plays a crucial role in improving the sensor's performance due to its film-forming ability and hydrophilic nature, which are attributed to the presence of NH_3^+ and OH^- groups in its structure.

SnO_2 is recognized for its excellent humidity sensing capabilities, its high stability, and its ease of fabrication, making it a favorable choice for the core component of the humidity sensor. When SnO_2 is combined with chitosan, the composite benefits from enhanced hydrophilicity, which aids in the adsorption of water molecules, ultimately improving humidity sensitivity. As a result, the QCM sensor coated with the MOF-SnO_2/Chitosan composite exhibits superior humidity sensing performance when compared to sensors based on MOF-SnO_2 or chitosan alone, as confirmed by various characterization methods [54].

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Materials and surface coatings used to enhance the performance of sensors play a critical role. In recent years, two-dimensional materials such as graphene oxide (GO) and borophene have been increasingly favored for improving the humidity sensing capabilities of QCM sensors. In the following sections, we will explore the potential applications of these materials in QCM-based humidity sensing and discuss the advantages they offer in detail.

4.1. Graphene and Graphene Oxide in QCM humidity sensing applications

Similar to the examples mentioned above, various composite materials are being developed to functionalize the QCM by coating them on its electrode surface. Among these, graphene and its derivatives stand out due to their exceptional properties. Graphene is an extremely thin (about 34 nm) two-dimensional material that exhibits excellent physical properties such as high flexibility, intrinsic mobility, thermal and electrical conductivity, and high transmittance. In addition, graphene derivatives also possess unique mechanical, chemical, and electrical properties, making them highly attractive for use in composites for sensing applications. For example, graphene oxide (GO), a major derivative of graphene, is an excellent candidate for humidity sensing applications. On the other hand, reduced graphene oxide (rGO), a derivative and oxidized form of graphene, exhibits numerous chemical defects and good conductivity, but lacks significant water adsorption activity [55]. Humidity sensors developed using GO have enhanced sensitivity, short response/recovery times, and are suitable for flexible electronics, as GO possesses hydrophilic functional groups such as carboxyl, hydroxyl, epoxy, etc., on its surface [56, 57]. Table 1 shows the typical GO-based composite materials used in QCM sensing layer preparation method, and sensing properties with response time and humidity range. On the other hand, a typical humidity sensing application involves detecting the humidity in breath. The schematic illustration (Figure 4) for an ultrafast QCM humidity sensor demonstrates the goal of sensing humidity from exhaled breath [58].

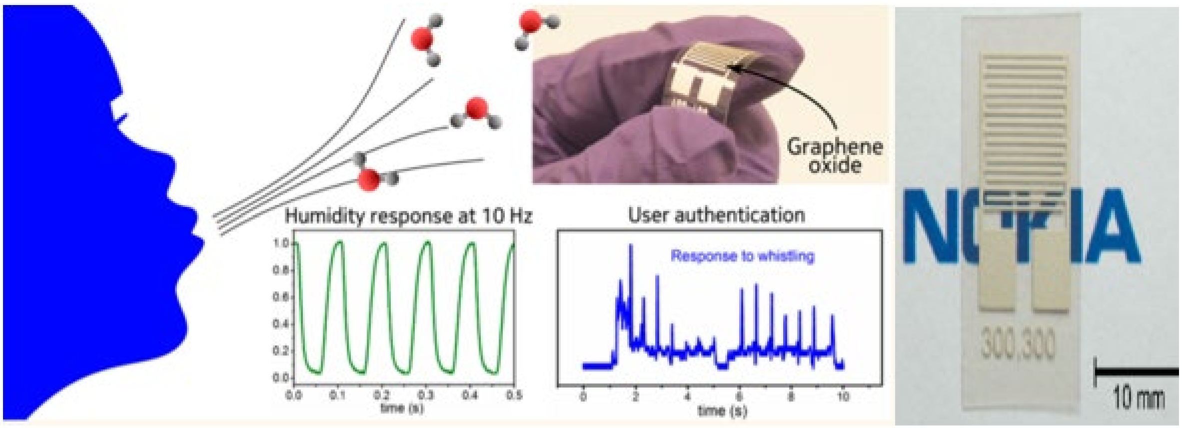

Figure 4. Schematic illustration for ultrafast QCM humidity sensor goal of sensing the humidity by breath, GO flexibility and graphical abstract of response time (left) and a photograph of GO sensing element (right) [58].

Table 1. GO-based composite materials for QCM humidity sensing applications.

Sensing layer	Method	Response Recovery time (s)	Humidity Range (%)	References
GO/ZnO composite thin film	Spray coating	9 s / 5 s	11.3%-97.3%	[59]
PANI/GO	Layer by layer self-assembly	8 s / 5 s	11%-97%	[57]
GO/SnO_2/PANI film	In-situ oxidative polymerization	7s / 2 s	0%-97%	[57]
GO/$Cu(OH)_2$ nanowires film	Drop-casting	1.9 s / 7.6 s	0%-80%	[60]
MoS_2/Graphene Oxide/C_{60}-OH	Drop-coating	1.3 s / 1.2 s	2%-97%	[61]

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GO/PEI	Spray coating	53 s / 18 s	11.3%-97.3%	[62]
GO/Nafion nanocomposite film	Spin coating	23 s / 5 s	11.3%-84.3%	[63]
C_{60}/GO	Drop-casting	4 s / 5 s	11%-97%	[64]

The figure includes a graphical abstract showing the sensor's response time on the left, highlighting its quick detection capabilities, and a photograph of the GO (Graphene Oxide) sensing element on the right, which is used to measure humidity levels. The GO material's flexibility contributes to the sensor's sensitivity and performance in detecting variations in humidity [58]. Borini et al. (2013) utilized the super-permeability property of GO to develop a fast humidity sensor [58]. They experimented with different thicknesses and preparation methods for the GO coating to achieve faster response/recovery times. Although they were able to obtain an ultrafast response/recovery time, a hysteresis effect occurred, and sensitivity was affected under certain conditions [58]. In another study, Yao et al. (2014) attempted to leverage the mechanical properties of GO, such as its high flexibility, to enhance the QCM sensor's performance at high relative humidity values [65]. They compared a GO-coated QCM humidity sensor with a PEG-coated one and demonstrated that the GO-based QCM humidity sensor outperformed the PEG-based one. However, they also found that the GO-based sensor exhibited poor selectivity at lower relative humidity values due to cross-sensitivity with the presence of certain gases. The humidity-sensing property of GO may decrease as a result of physical interactions between GO carboxyl groups and water molecules [65]. These drawbacks can be addressed by incorporating other materials, turning the GO coating into a GO-based composite for QCM humidity sensing applications.

As mentioned earlier, graphene oxide is a two-dimensional material with a large surface area and hydrophilicity due to its structural defects. This strong adsorption capacity of GO can lead to cross-sensitivity, but the incorporation of different polymers, such as polyaniline (PANI), can address this issue by improving the sensitivity of the QCM humidity sensor. Zhang et al. (2018) investigated a GO/SnO_2/PANI nanocomposite for coating the QCM surface to enhance humidity sensing. In their study, SnO_2 was in nanoparticle form, while PANI was in nanofiber form. PANI surrounded both GO and SnO_2, bringing them all into contact to form a nanocomposite film [57]. The materials in the nanocomposite provided different properties to the structure. For example, PANI ensured stability and ease of fabrication for repeatability, while SnO_2 contributed hydrophilicity for sensitive and rapid response/recovery times, and GO provided functional groups that enhance water adsorption onto the surface [66, 67].

In another study, Fang et al. (2020) used $Cu(OH)_2$ nanowires in combination with GO to create a composite film for real-time respiration monitoring by sensing humidity. The study showed fast response/recovery times, high sensitivity, and high linearity, with potential applications being investigated by measuring various breathing patterns such as normal breathing, speaking, etc. $Cu(OH)_2$ nanowires, with their large surface area-to-volume ratio and hydrogen groups, enhanced interactions between water molecules and the coating material. The addition of $Cu(OH)_2$ nanowires to the GO composite also helped overcome the limitations of GO, such as agglomeration and swelling. This is significant, as homogenization of composites remains an unresolved issue and is a major challenge in nanofiller-added hybrid composite structures. Fang et al. (2020) studied the change in sensing performance for GO-coated, $Cu(OH)_2$-coated, and $Cu(OH)_2$/GO composite-coated QCM layers, with the best results coming from the $Cu(OH)_2$/GO composite-coated QCM [60]. The findings from this study are promising for future medical monitoring applications of QCM humidity sensors.

Carboxyl graphene (G-COOH) specifically chosen for its high surface area and porosity added polystrene electrospun nanofibers directly deposited onto the QCM [68, 69]. In recent years, Hydroxylated graphene quantum dots (OH-GQDs), a novel class of nanomaterials, have emerged as an effective solution for increasing the number of active sites on the GO surface. This approach offers

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a promising way to further enhance sensor sensitivity. Ding et al. (2024) was introducing OH-GQDs could provide additional active sites, potentially offering a more significant improvement in sensor performance [70]. Clay/GO/chitosan multilayer nanocoatings at high humidity suggested as high gas barrier to enhance the barrier properties of bio-based polymers for food packaging applications [71]. Two types of anionic nanoplatelets, graphene oxide (GO) and montmorillonite (MMT), with large aspect ratios (300–1000 and 200–1000, respectively), were compared for bilayered systems. The 23 nm thick CH/MMT/CH/GO hybrid coating also demonstrates good nanoplatelet exfoliation. While different mechanical properties were observed, the stiffer MMT exhibited distinct characteristics, whereas GO, due to its flexibility, resulted in the formation of wrinkles. The higher content of highly oriented and tightly packed nanoplatelets in the multilayer assembly contributed to this effect, as well as to enhanced transparency, low oxygen permeability, and minimal variation in oxygen permeability with increasing humidity [72].

4.2. Borophene in QCM humidity sensing applications

Borophene is another two-dimensional material consisting of a single layer of boron atoms. Similar to graphene, borophene possesses unique chemical and physical properties [73]. Although its features make borophene a remarkable candidate for sensor applications, the instability arising from its reactivity results in several drawbacks in real-world applications [74]. Therefore, borophene has been investigated in various heterostructure forms in the literature. However, as a new two-dimensional material, borophene cannot be easily fabricated into heterostructures using simple methods.

In recent years, researchers have achieved remarkable results in terms of response/recovery time, sensitivity, detection range, and limit of detection for gas sensing applications using borophene-based sensors [75, 76]. Typically, different hybrid composite materials like SnO2 have been used to obtain stable heterostructures. Shen et al. (2020) indicated that borophene's sensitivity to CO2 is weak when compared with other gases, such as NO, NH3, or CO [75]. This is of great importance for carbon monoxide detection and CO detectors.

Hou et al. (2021) produced a borophene-graphene heterostructure in a hydrogen-rich environment for sensitive and fast humidity sensing by growing borophene on graphene surfaces [76]. They emphasized that the sensitivity of the sensor, which is 4,200%, is the highest among 2D material-based chemiresistive sensors, with a relatively short response (10.5 s) / recovery time (8.3 s). To prevent instability, the sensor was fabricated using the drop-coating method, and it remained stable over a wide RH range, from 0% to 85%. In another study, Hou et al. (2021) fabricated a special innovative borophene heterostructure that contains both borophene and MoS2 [77]. This sensor showed even more enhanced sensitivity, reaching 15,500% at 97% RH. This study once again highlights that borophene-based sensors are promising candidates for future human health care and wearable electronic sensing devices.

5. Conclusion and Future Perspectives

Quartz Crystal Microbalance (QCM) sensors have emerged as a powerful tool for humidity sensing, offering high sensitivity, fast response times, and real-time monitoring capabilities. The integration of nanomaterials such as graphene, graphene oxide (GO), and borophene has significantly enhanced the performance of QCM humidity sensors. Graphene's exceptional surface area, flexibility, and electrical conductivity make it an ideal candidate for improving sensor sensitivity, while GO's tunable surface chemistry offers additional advantages in terms of functionality. However, challenges such as GO agglomeration and cross-sensitivity still need to be addressed, and these can be mitigated by incorporating complementary materials that provide greater mechanical stability and hydrophilicity.

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Borophene, with its promising electrical and mechanical properties, represents an exciting frontier for humidity sensing. Nevertheless, its instability and limited application in real-world conditions present significant challenges. Exploring borophene-based composites, particularly with stabilizing agents like MoS_2 or other nanomaterials, could lead to breakthroughs in overcoming these limitations and creating highly efficient humidity sensors.

Despite the advances made in QCM-based humidity sensors, several critical areas require further research and development. One of the main challenges remains improving the long-term stability and resistance to environmental factors such as temperature variations, pH changes, and exposure to chemicals. Additionally, understanding the exact sensing mechanisms at the molecular level will be crucial for optimizing the materials used in QCM sensors, thereby enhancing their performance and accuracy.

Several promising directions for future research can be identified. First, further optimization of the nanocomposites used in QCM sensors is necessary, particularly by combining GO with other materials that enhance its mechanical stiffness and hydrophilicity. The design of hybrid nanomaterials could address current issues like swelling, agglomeration, and cross-sensitivity, resulting in more stable and reliable sensors. Additionally, stabilizing borophene through composite materials is an exciting avenue, with potential applications in humidity sensors that require higher performance and durability.

Another promising approach is the development of layer-by-layer self-assembled conductive polymeric films, which could offer enhanced tunability, flexibility, and sensor functionality. These films would allow for precise control over the properties of QCM sensors, potentially enabling multifunctional devices capable of detecting a range of environmental factors beyond humidity. Furthermore, the integration of QCM humidity sensors into wearable and portable electronics offers significant potential for real-time monitoring in fields such as healthcare, industrial safety, and environmental monitoring.

To fully realize the potential of QCM-based humidity sensors, it is also essential to address challenges related to large-scale fabrication and cost-effective production. Refining manufacturing techniques such as electrospinning and wet-spinning will be crucial to ensuring the consistent, high-quality production of QCM sensors. Additionally, sustainability efforts in material production, particularly for graphene and other nanomaterials, will play a key role in making these sensors more environmentally friendly and cost-efficient.

In conclusion, the development of advanced QCM humidity sensors is at the forefront of sensing technology, with promising advances in nanocomposites and sensor design. However, overcoming challenges such as material stability, scalability, and long-term reliability will require continued research and innovation. As the demand for real-time, highly sensitive, and durable humidity sensors grows across various industries, the collaboration between materials science, sensor engineering, and manufacturing techniques will be essential to drive the next generation of QCM-based humidity sensing technologies.

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