ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

GRAPHENE OXIDE/CALCIUM TITANATE COMPOSITE PREPARATION FOR HUMIDITY SENSING BY QUARTZ CRYSTAL MICROBALANCE

M.Sc. THESIS

Zeynep DEMİRTAŞ

Department of Nanoscience and Nanoengineering

Nanoscience and Nanoengineering Programme

AUGUST 2022

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Zeynep DEMİRTAŞ
(513201037)

Department of Nanoscience and Nanoengineering

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Thesis Advisor: Assoc. Prof. Dr Birgül BENLİ

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KUVARS KRİSTAL MİKROBALANS İLE NEM TAYİNİNE YÖNELİK GRAFEN OKSİT/KALSİYUM TİTANAT KOMPOZİTLERİN ÜRETİMİ

YÜKSEK LİSANS TEZİ

Zeynep DEMİRTAŞ

(513201037)

Nanobilim ve Nanomühendislik Anabilim Dalı

Nanobilim ve Nanomühendislik Programı

Tez Danışmanı: Doç.Dr. Birgül BENLİ

AĞUSTOS 2022

Zeynep DEMİRTAŞ, a M.Sc. student of İTU Graduate School student ID 513201037, successfully defended the thesis/dissertation entitled "GRAPHENE OXIDE/CALCIUM TITANATE COMPOSITE PREPARATION FOR HUMIDITY SENSING BY QUARTZ CRYSTAL MICROBALANCE", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Assoc. Prof. Dr. Birgül BENLİ** İstanbul Technical University	**.....**
Jury Members :	**Assoc. Prof. Dr. Caner ÜNLÜ** Istanbul Technical University	.....
	Assoc. Prof. Dr. Cem Bülent ÜSTÜNDAĞ Yildiz Technical University	.....
	Assoc. Prof. Dr. Birgül BENLİ Istanbul Technical University	.....

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To my family,

FOREWORD

As a Bioengineer, I have learned lots of new information during my master's degree programme in Nano Science and Nano Engineering at Istanbul Technical University. First of all, I would like to thank Birgül BENLİ for accepting to be my advisor and giving me a chance to be part of the Bee The Surface family. I would like to thank Prof. Dr. Feridun BOYLU, the Head of Mineral Processing Engineering, who provides the opportunity to use the laboratories and facilities of the department.

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Zeynep DEMİRTAŞ
(Bioengineer)

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ABBREVIATIONS

AuNMs	**:** Gold nanomaterials
FT-IR	**:** Fouirer Transform Infrared Spectrophotometer
GO	**:** Graphene Oxide
GO/CaTiO3	**:** Graphene Oxide/Calcium Titanate composite
SEM	**:** Scanning Electron Microscope
XRD	**:** X-ray Diffraction
UV-Vis	**:** UV-visible spectrophotometer
QCM	**:** Quartz Crystal Microbalance

SYMBOLS

0D	**:** Zero-dimensional
1D	**:** One-dimensional
2D	**:** Two-dimensional
3D	**:** Three-dimensional
CaO	**:** Calcıum Oxide
$CaTiO_3$	**:** Calcium Titanate

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GRAPHENE OXIDE/CALCIUM TITANATE COMPOSITE PREPARATION FOR HUMIDITY SENSING BY QUARTZ CRYSTAL MICROBALANCE

SUMMARY

Humidity measurement has been taking attention since 1900s because of the fact that it is used in various aspects from weather forecasts to food and human safety, agricultural processes to mineral processing facilities. Therefore, there has been a growing requirement and extensive research on designing humidity sensors that are rapid, cost-effective, and highly sensitive. Although various methods have been developed, the Quartz Crystal Microbalance (QCM) is a very promising candidate, as it has excellent sensitivity to changes in mass with a nanogram level of detection and, an extensive measuring range. In addition, QCM sensors are stable and reliable in mild operation conditions and can be developed with low-cost. However, the quality and the properties of sensors are highly dependent on the additional sensitive layer. Thus, an additional sensing layer on the surface of QCM electrodes is required to improve the sensor performance including selectivity, sensitivity, response/recovery time and stability.

The sensing layer is one of the most important parameters that affects sensing properties of QCM. In literature, there are numerous studies for using different single component containing materials as sensing layer for humidity measurement. On the other hand, the combination of two or more materials, composites, is necessary to obtain improved sensing properties. For humidity sensing, the composite material can be made either with an additional porous material to enhance the interactions with water molecules or with an additional humidity sensitive material to increase the overall humidity sensitivity.

Graphene oxide, a two-dimensional material with excellent physical properties, is an excellent candidate for humidity measurement because of the hydrophilic groups on its surface that ensure the adsorption of water molecules. In addition, the use of an additional nanostructured material as calcium titanate can improve the sensitivity by increasing the surface area to volume ratio.

In this thesis, the preparation and coating properties of graphene oxide/calcium titanate composite-based material was investigated for the first time in literature. GO was obtained from graphite powder by using a modified Hummer's method. Calcium titanate particles were synthesized by sol-gel method. After the production of two different materials separately, they blended to obtain the composite material. Characterization analyses were performed for optical, structural, and morphological properties of graphene oxide, calcium titanate and graphene oxide/calcium titanate composite materials. The obtained results confirm that a successful production of the composite material was achieved.

KUVARS KRİSTAL MİKROBALANS İLE NEM TAYİNİNE YÖNELİK GRAFEN OKSİT/KALSİYUM TİTANAT KOMPOZİTLERİN ÜRETİMİ

ÖZET

Gelişen teknoloji ve insanların artan ihtiyaçları göz önünde bulundurulduğunda giyilebilen sensörler gibi küçük boyutlarda sensörlerin üretilmesi her geçen gün daha fazla dikkat çekmektedir. Sensörler, hedef bir parametrenin saptanması veya ısı, ışık ve hareket gibi belirli bir uyarana karşın cevap verilmesi ve bu parametre/uyaranların hesaplanabilir bir çıktıya dönüştürülmesi için kullanılan cihazlardır. Günümüzde pek çok alanda kullanılan ve artık insan hayatı kaçınılmaz bir parça olan sensörler gaz ve nem algılanması uygulamaları için de araştırılmakta, kullanılmaktadır. Sensör uygulamaları sırasında akustik, kapasitif, elektromanyetik, elektromekanik, termistör, ultrasonik, piezoelektrik etki vb. gibi çeşitli teknolojiler kullanılmaktadır.

Nem ölçümü ise, hava tahminlerinden gıda ve insan güvenliğine, tarımsal proseslerden maden işleme tesislerine kadar pek çok alanda kullanılması nedeniyle 1900'lü yıllardan itibaren ilgi görmeye başlamıştır. Bu nedenle, hızlı, uygun maliyetli ve son derece hassas nem sensörleri tasarlama konusunda artan bir gereksinim ve kapsamlı araştırmalar olmuştur. Çeşitli yöntemler geliştirilmiş olmasına rağmen, Kuvars Kristal Mikroterazisi (QCM), nanogram düzeyinde bir algılama ve geniş bir ölçüm aralığı ile kütledeki değişikliklere karşı mükemmel bir duyarlılığa sahip olduğu için çok umut verici bir adaydır. Ayrıca QCM sensörleri, hafif çalışma koşullarında kararlı ve güvenilirdir ve düşük maliyetle geliştirilebilir. Ancak QCM yüzeyi tek başına neme karşı yeterince duyarlı olmadığı için elektrot yüzeyinin bir algılama yüzeyi ile kaplanması gerekir. Literatürde QCM yüzey kaplaması için geliştirilmiş farklı özelliklere sahip birçok malzeme hakkında çalışmalar mevcuttur. Bununla birlikte, sensörlerin kalitesi ve özellikleri, büyük ölçüde ekstra bir duyarlı algılama katmanına bağlıdır. Bu nedenle, seçicilik, hassasiyet, yanıt/geri kazanım süresi ve kararlılık dahil olmak üzere sensör performansını iyileştirmek için QCM elektrotlarının yüzeyinde ek bir algılama katmanı gereklidir.

Algılama katmanı, QCM'nin algılama özelliklerini etkileyen en önemli parametrelerden biridir. Literatürde, nem ölçümü için algılama katmanı olarak farklı tek bileşenli malzemeleri içeren çok sayıda çalışma bulunmaktadır. Öte yandan, gelişmiş algılama özellikleri elde etmek için iki veya daha fazla malzemenin, yani kompozitlerin, kombinasyonu gereklidir. Nem algılama için, kompozit malzeme ya su molekülleri ile etkileşimleri geliştirmek için gözenekli malzemenin eklenmesi ile ya da genel nem duyarlılığını artırmak için neme duyarlı ekstra bir malzeme kullanılması ile yapılabilir. Yapılan çalışmada nem tutucu özellikli bir malzemeye ek olarak su moleküllerinin tutulmasını artırarak aradaki etkileşimi geliştirmek amacıyla ikinci bir malzeme kompozit oluşumu için kullanılmıştır.

Ek olarak, bilindiği üzere boyutları 1-100 nm arasında değişkenlik gösteren nanomalzemeler yukarıdan aşağıya (top-down) ve aşağıdan yukarıya (bottom-up) şeklinde iki farklı yaklaşım ile üretilirler ve bulk (dökme) formlarına göre daha farklı ve gelişmiş özellikler göstererek günümüzde araştırmacıların daha iyi özelliklere sahip yeni malzemeler geliştirmelerine de olanak sağlamıştır. Malzemelerin nano boyutlarda farklı fizikokimyasal özellikler göstermesindeki iki ana faktör boyut küçültmeyle ortaya çıkan yüzey etkileri ve kuantum etkileridir. Kompozisyon ve morfoloji gibi farklı kriterlere göre sınıflandırılabilen nanomalzemeler boyutlarına göre de sınıflandırılabilirler. İki boyutlu (2-D) yapısıyla grafen, çeşitli ilgi çekici özelliklere sahip bir nanomalzeme olmakla birlikte grafen oksit veya indirgenmiş grafen oksit gibi türevler içermektedir ve bu özellikleri sayesinde ilaç dağıtımı, doku mühendisliği, biyosensör uygulamaları gibi çeşitli alanlarda kullanılmaktadır. Grafen-temelli malzemelerin türevleri farklı özelliklere sahip olup bunlardan grafen oksit, grafenin kristal yapısından farklı olarak kendi yapısında karbon yüzeyi üzerinde hidrofilik fonksiyonel gruplara sahip olması sebebiyle hem kristal hem de amorf bir yapı sergilemektedir. Grafen oksit sahip olduğu oksijen içeren grupları sayesinde pek çok biyoteknolojik ve nanoteknolojik uygulamalarda kullanılması arzu edilen bir malzeme haline gelmiştir.

Mükemmel fiziksel özelliklere sahip iki boyutlu bir malzeme olan grafen oksit, yüzeyindeki su moleküllerinin adsorpsiyonunu sağlayan hidrofilik gruplar nedeniyle nem ölçümü için mükemmel bir adaydır. Ayrıca, kalsiyum titanat olarak ek bir nanoyapılı malzemenin kullanılması, yüzey alanı/hacim oranını artırarak duyarlılığı iyileştirebilir. Bu sebeple kalsiyum titanat partikülleri hem çevreci bir yaklaşıma sahip olup, yüksek dielektrik geçirgenliği ile küçük boyutlarda etkili performans sürdürebilmek hem de su moleküllerinin adsorpsiyonu sırasında porlu bir yüzey sağlayarak etkileşimin gerçekleşeceği yüzey alanını artırmak amacıyla kullanılmıştır.

Bu tezde, literatürde ilk kez grafen oksit/kalsiyum titanat kompozit esaslı malzemenin hazırlanma ve kaplama özellikleri araştırılmıştır.

Grafen oksit, modifiye edilmiş bir Hummer yöntemi kullanılarak grafit tozundan elde edilmiştir. Hummers metodu grafen oksit sentezi için kullanılan en yaygın metot olmakla birlikte yapılan çalışmalar sırasında metot üzerinde bazı modifikasyonlar gerçekleştirilmiştir. Diğer üretim yöntemlerine göre görece daha hızlı ve güvenli olması bu metotu öne çıkaran özelliklerindendir.

Kalsiyum titanat nanopartikülleri başlangıç malzemesi olarak Kalsiyum oksit ve Titanyum (IV) izopropoksit kullanılmasıyla bir sol-jel yöntemi ile sentezlenmiştir. Sentez sonrasında havan kullanılarak partiküller mekanik bir yöntem ile toz haline getirilmiştir.

İki farklı malzeme ayrı ayrı üretildikten sonra karıştırılarak kompozit malzeme elde edilmiştir. Grafen oksit, kalsiyum titanat ve grafen oksit/kalsiyum titanat kompozit malzemelerin optik, yapısal ve morfolojik özellikleri için karakterizasyon analizleri yapılmıştır.

Karakterizasyon sırasında optik özellikler, UV-Vis spektrofotometre kullanılarak belirli dalga boylarındaki piklerin tespiti ile incelenmiştir. Ayrıca, üretilen malzemenin iletkenliği hakkında bilgi veren bant aralığı enerjileri de bu aşamada hesaplanmıştır.

Yapısal özellikler için ise FT-IR ve XRD analizleri gerçekleştirilmiştir. FT-IR'da tespit edilen karakteristik fonksiyonel grupların varlığı her üç malzemenin de yapısı hakkında hakkında bilgi vermektedir. Özellikle grafen oksitin yapısında bulunan oksijen içeren hidrofilik grupların varlığına dair bulgular FT-IR analizi ile teyit edilmiştir.

Malzemelerin morfolojik analizi için SEM görüntüleri alınmış ve literatür ile benzer sonuçlar elde edilmiştir. Elde edilen sonuçlar, kompozit malzemenin başarılı bir şekilde üretildiğini doğrulamaktadır.

1. INTRODUCTION

1.1 Purpose of Thesis

Considering the developing technology and the increasing needs of people, the production of sensors in small sizes such as wearable sensors attract more and more attention day by day. Humidity, on the other hand, is desired to be accurate and measurable in a short time, as it exists in almost every part of human life, packaging of food and drugs, detection of gas leakage, detection of respiratory disorders in humans and more, because it exists and causes important results.

In this thesis, graphene oxide and calcium titanate perovskite particles were synthesized separately for the purpose of combining calcium titanate perovskite particles, which was synthesized by a cost effective and simple method, and graphene oxide, which was synthesized by Hummers method, to obtain a more advanced composite film for humidity detection and to use this composite as a sensing layer for coating on the QCM electrode for the first time in the literature.

For the purpose of developing a humidity sensor that is faster, more sensitive, longer lasting and more accurate than its counterparts in the literature, the synthesized GO/$CaTiO_3$ composite materials was aimed improve the properties of quartz crystal microbalance electrodes (QCM, area = 0.22 cm^2) when it is coated on the electrode surface.

1.2 Literature Review

In December 1959, Richard Feynman gave a speech entitled “There is plenty of room at the bottom, an invitation to enter a new field of physics”. After this speech, nanotechnology term was firstly used by Norio Taniguchi in the title of a paper as “On the basic concept of nano-technology” [1,2]. Nanotechnology does not only contain the usage of various materials, structures, devices and systems with distinctive features due to their small size but also covers the technologies which ensure the usage of

controlled and manipulated materials at this scale. Producing useful materials and devices by using nanotechnology is considered between 1 to 100 nm at length scales [3]. Various characteristics of a material physically, chemically and biologically can be obtained by nano-scale technology compared to the corresponding bulk material's properties [4]. To understand where nanotechnology stands now, nanoscience and nanomaterial developments need to be addressed.

Different types of nanomaterials such as nanoparticles, nanowires, nanorods or dots are used for different applications in nanotechnology, for instance, food, agriculture, medicine, pharmacy [5]. In general, there are two distinct approaches to produce materials in nanotechnology that are called top-down and bottom-up [6]. In the top-down approach, nanomaterials are produced from larger construction toward nano-scale structures without any change in original bulk material properties and any control in atomic levels. In other words, the top-down approach contains an elementary bulk material that includes nano scale details, and the process of deconstruction of elementary material [7]. Considering that the surface structure has a significant effect on surface chemistry and physical features of nanomaterials, the top-down method is not convenient to obtain very tiny nanoparticles with proper shape, since it is not possible even under high energy use [8]. The bottom-up approach, also called molecular manufacturing, in which the material is produced by the assembly or self-assembly processes of atoms or molecular components [9]. The bottom-up approach is more appropriate for the production of the vast majority of nanomaterials since it ensures the production of well-distributed nanomaterials with even shape and size. In addition, morphology of the materials are well controlled with economical processes in the bottom-up approach [8].

1.2.1 Nanomaterials

Materials are called nanomaterials if they consist of at least one dimension smaller than 1000 nm while 100 nm is considered the upper limit of nanoscale by some authors without any scientific evidence to support this limit [15]. Materials demonstrate different physicochemical features at nanoscale in comparison with their bulk form (Figure 1.1). Two major factors affect this situation; surface effects and quantum effects which come in sight by the reduction in size [13]. Because of the raising fraction of surface atoms to interior atoms, surface effects ensure a more proper scaling

of physical properties, an enhanced chemical reactivity, and a lower melting temperature to nanomaterials. Moreover, electron confinement within tiny nanoparticles has become possible with the help of quantum effects in nanoscales. This property makes the quantized energy spectrum clear, as a result, magnetic momentum appears that is important for nonmagnetic materials [14]. Thus, physical properties can be size and shape dependent in the case of nanomaterials. There are various classifications for nanomaterials according to different criteria such as dimension, composition and morphology [10]. Based on dimension, they can be zero- (0D), one- (1D), two- (2D) or three- (3D) dimensional [11]. The dimensional classification which depends on the number of nanoscale dimensions of materials was introduced in 2007 [16]. In zero dimensional materials, electron motion is confined for all directions. Nanoparticles, quantum dots, nanoclusters, filaments etc. are all classified as 0D materials that are 1-100 nm in length for all spatial dimensions [17]. The nanomaterials that have two characteristic dimensions in 1-100 nm scale and one non-nanometre size are called one dimensional nanomaterials. The electrons of these materials are confined in two dimensions which allow the motion only in 1D. Unlike 0D materials, length is larger than width in 1D. Apart from the most common examples to 1D such as nanofibers, nanowires and nanotubes; nanocables, nanorods, nanoribbons are in 1D nanomaterials [18]. Nanomaterials that have many surface atoms and large aspect ratio are called two dimensional materials. Electrons of these materials are confined in one dimension which means they can freely move in other two dimensions. Nanosheets, nanofilms, nanocoatings and nanolayers are common examples of these plate-like shape materials. Thanks to their high mechanical flexibility and optical properties, they can be utilized in various applications. Graphene, as the first discovered 2D material, and its derivatives are the well-known examples of this class [17, 19]. The nanomaterials in which electrons can freely move any dimension are called three dimensional materials. They are also called bulk material since all dimensions are greater than 100 nm. 3D nanomaterials are generally found in complex formations such as nanoflowers, nanopillars and nanoballs [20].

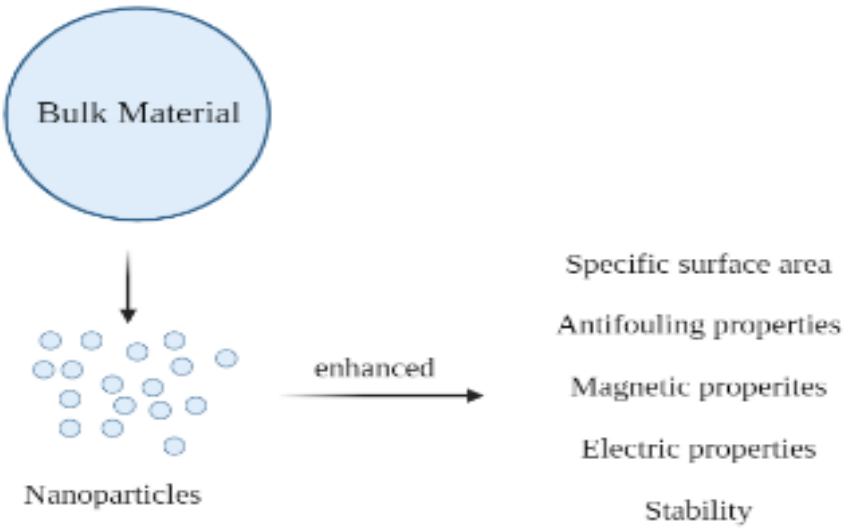

Figure 1.1: Illustration showing improvements of some properties from bulk material to nanomaterial.

In addition, nanomaterial's chemical composition about if they are made of a single element such as gold and carbon or multiple elements such as composites and metal oxides is another classification [12].

1.2.1.1 Single component nanomaterials

In literature, there are various examples for single component nanomaterials from gold nanomaterials to polymeric nanomaterials or carbon nanomaterials to ceramic nanomaterials. Each of them has unique properties due to the material they have made of. For instance, gold nanomaterials (AuNMs) have been getting attention because of their potential to be used in clinical studies thanks to the adjustable size, shape and surface characteristics they have. They have excellent optical and catalytic properties to be used in biosensing applications. Also, they can be used in bioimaging applications thanks to their high brightness and photo-stability. Additionally, AuNMs have potential to be used in targeted drug delivery. Apart from these properties, being relatively nontoxic and being able to make direct conjugates with functional moieties, can be easily synthesized with desired shapes, which can be seen in Figure 1.2, make them attractive [21].

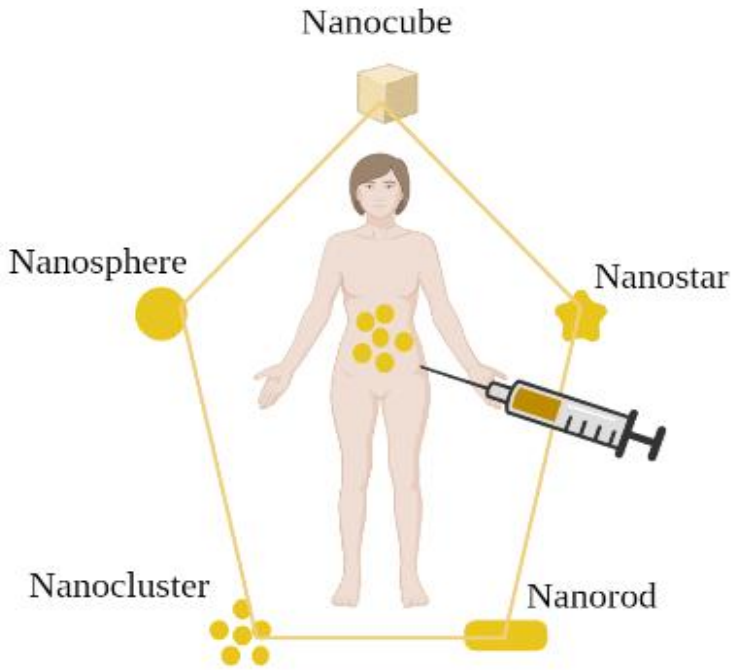

Figure 1.2: Schematic representation of nanostructure in biomedical applications. Modified from [22].

On the other hand, polymeric materials stand out by representing high biological safety and good biodegradability and therefore can be used in drug delivery and controlled release of active substances. In addition, stability, chemically controllable structure and size are the general advantages which are some but not only properties of natural and synthetic polymeric nanomaterials [23].

Carbon nanomaterials that are shown in Figure 1.3 consist of carbon elements mainly in the form of fullerene, carbon nanotubes or graphene, and have at least one dimension at nanoscale [24]. While fullerenes are 0D carbon materials, carbon nanotubes are 1D and graphene is 2D. They have 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 [25]. The significant attention on carbon nanomaterials because of their chemical, mechanical, optical, electrical and thermal properties has provided enhancement in fundamental and applied science.

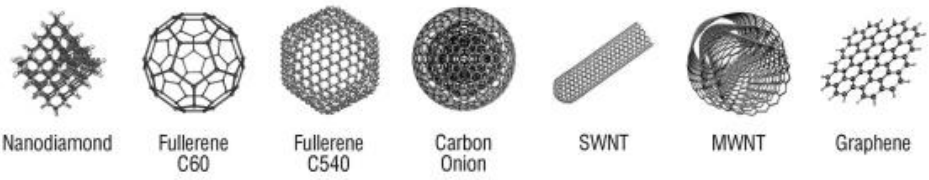

Figure 1.3: Different types of carbon-based nanomaterials. Copied from [26].

Fullerene has a hollow-like structure that contains only hexagonal and pentagonal faces [26]. On the other hand, carbon nanotubes are in the cylindrical shape of graphene sheets. Carbon nanotubes can be single- or multiple-walled that are the strongest and stiffest materials according to tensile strength and elastic modulus they have. In addition to these, they have high thermal and electrical conductivity [27]. Despite attracting properties of carbon nanotubes, graphene is more attractive in terms of fabrication and application. Thus, a considerable amount of progress has been made for the technological advance of graphene during past years and still continues to progress with an increasing number of articles and patents. The potential applications of graphene in batteries, capacitors, semiconductors, sensors, and semiconductors devices are being considered in addition to its mechanical and electrical properties, nowadays [28].

Graphene 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 [29, 30, 32].

Although graphene was discovered in 2004, its history is not that new since graphene can be considered a small part of graphite [31]. Hence, the history of graphene materials can be represented as in Figure 1.4 below.

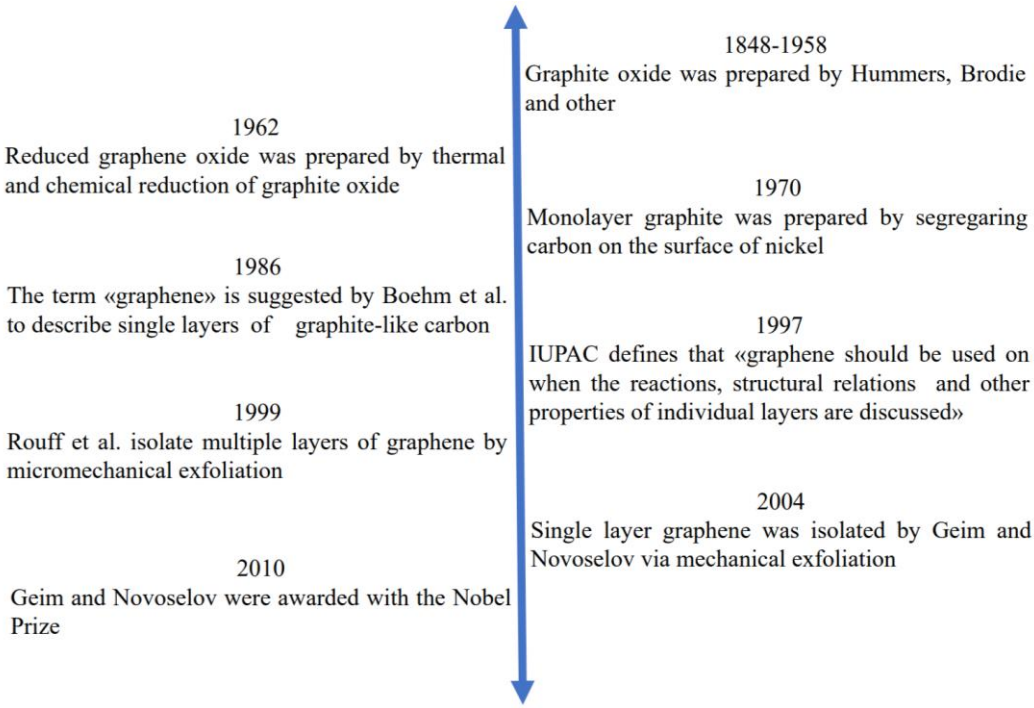

Figure 1.4: Important dates on graphene development. Modified from [31].

As a result of their extensive properties, graphene-based nanomaterials have been studied for various applications. A few examples to study fields of graphene-based materials can be listed as energy storage, antibacterial compositions, cancer treatments, tissue engineering, drug/gene delivery, photothermal and photodynamic therapy, bioimaging, biosensing, antifouling applications, water disinfection, pollution adsorption and gas sensing as it can be seen in Figure 1.5 below [33, 34, 35, 37].

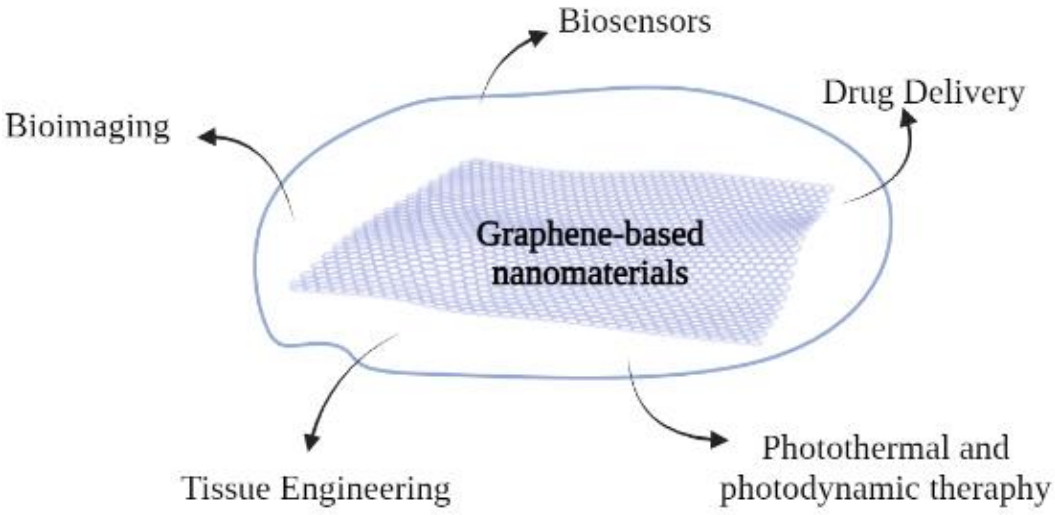

Figure 1.5: Applications of graphene-based nanomaterials. Modified from [36].

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 [31]. 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 [38]. As it can be seen in Figure 1.6, GO is the oxidized state of graphene.

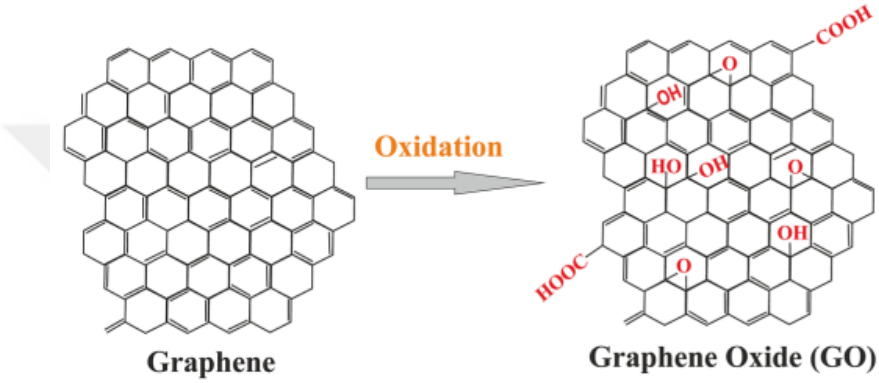

Figure 1.6: Conversion of graphene into GO. Copied from [33].

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 [39]. 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 [40]. Therefore, GO is one of the most interesting carbon-based materials for biotechnological and nanotechnological applications.

Ceramic nanomaterial

The term "ceramic" means inorganic non-metallic materials containing metal or non-metal ingredients that are formed with the help of high temperature to obtain robust mechanical properties [41]. In general, ceramics have attractive characteristic properties such as mechanical and corrosion resistance, good optical, electrical and magnetic properties, good refractory properties, chemical inertness and hardness which make them useful in a lot of applications especially where nanoscience and nanotechnology are involved [42]. Ceramics can be called nanoceramics or ceramic nanomaterials when they contain at least one substance within nano size [43]. Ceramic nanomaterials can be in the form of particles, fibres or sheets according to the application and have better properties such toughness and bioactivity compared to bulk ceramic materials [42].

Ceramic nanomaterials include perovskites. Perovskite structures exist in nature with a basic chemical formula: ABX_3. A and B are metallic cations while X is an anion, usually oxygen. This chemical formula results in marvellous possibilities of the formation of different crystalline structures with different properties [44, 46]. The name perovskite comes from a Russian mineralogist Lev Alexeevich Perovsky. The parameters that affect the physical and chemical features of perovskites can be listed as stoichiometry of anions and cations, oxidation states of cations, the crystalline structure and preparation methods, etc [45]. On the other hand, the stability depends on a variable factor called tolerance (*t*) factor which can differ according to size of cations, determines the symmetry of the compounds and has an effect on the dielectric properties [47]. The t value should be close to 1 for the formation of perovskite structure despite some perovskites that have *t* values between 0.90 and 1.10 [45].

Although cubic structure is the ideal structure at t=1 value, perovskite crystalline structures have various possibilities for symmetry such as cubic symmetry or orthorhombic symmetry [48]. In ideal $ATiO_3$ type perovskite oxides, the B site cation, Ti, is in the middle of an octahedral formation surrounded by six oxygen atoms and the A site cation is located in a cage of the twelve oxygen atoms which results good stability in a cubic crystal structure formation [49]. $CaTiO_3$, as a well-known member of this family, represents orthorhombic, tetragonal and cubic phases depending on production techniques. $CaTiO_3$ has recently become an interesting material thanks to its easy-preparation, excellent dielectric characteristics, excellent stability, and low-

cost [50, 51]. Especially because of its high dielectric permeability, $CaTiO_3$ has been studied in many applications. [52]. These applications include photocatalysis, electronics, gas sensors, gas separation, sorption [54].

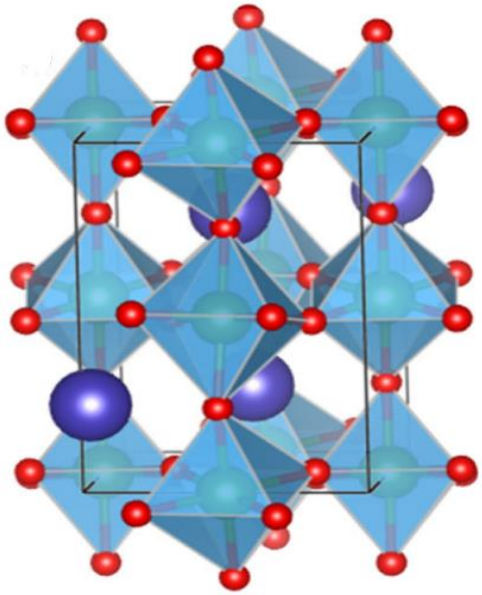

Figure 1.7: Structure of orthorhombic lattice of calcium titanate. Copied from [65].

To prevent large particle size and size distribution, different methods are studied in the production of $CaTiO_3$ nanoparticles. Some of them can be listed as mechanochemical, sol-gel, microemulsion, hydrothermal and solvothermal, etc [53].

1.2.1.2 Composite nanomaterials

Composite nanomaterials, also called nanocomposites, have unique physical properties which make them a special class of materials and thus have a wide range of applications. The attractive properties of nanocomposites are attributed to the combination of properties of at least two donor materials in a newly formed material [55]. Each nanocomposite material has unique properties based on the donor materials that are used for the production of nanocomposites such as metal oxides, polymers and ceramics [56]. They may have large specific surface area, porous structure, nanoscale size range, stability in extreme conditions [56, 57]. In addition, they have improved optical, electrical, mechanical and magnetic properties, can be produced in mild reaction conditions, and the interaction between matrix and reinforcement is high [58].

Nanocomposite materials should contain at least two components as it mentioned above; a continuous/matrix phase and a non-continuous/reinforcement material. The

properties of nanocomposite materials come from these two components and ensure that they are used in a wide range of applications [59]. Biomedical, membrane, packing, electronic, optic material, automotive, fire retardancy, drug delivery, tissue engineering, gene therapy, self-cleaning, antifouling, water purification, removal of contaminants, gas purification, and sensing applications are some of the areas that composite nanomaterials can be used [59, 60, 61]. It can be seen that composite nanomaterials have several applications due to their unique properties and have become an important key in our daily life. One of the most common uses of nanomaterials is in sensors and sensing applications such as environmental, healthcare, pharmaceuticals and drug delivery, food industry, and bioprocess. For instance, Zhu et al. reported a SnO_2-SiO_2 composite material with excellent sensing properties to humidity [62]. Zhang et al. fabricated GO/SnO_2/PANI composite for a high-performance humidity sensor in another study [63]. Each nanocomposite material improves the sensing process by the help of its unique properties. If an example is given, the advantages of ceramic-based composite nanomaterials are enhanced chemical, thermal and mechanical stability which occurs as a result of ABO3-type perovskite structure [55]. On the other hand, GO provides a flexible, large surface area, and hydrophilic functional groups to the GO-based composite nanomaterials [64].

1.2.2 Overview of sensors

A sensor is a device that is used for the detection of target parameters or responding to a physical stimuli (heat, light or motion etc.) and the conversion of that parameter/stimuli to a calculable output like digital signal [66]. Where the world is today, the need for the sensors is inevitable. Life as is known now, cannot be imagined without sensors since they have a vital role in all sectors. They are generally used in applications that include humidity and gas sensing by the help of various technologies such as acoustic, capacitive, doppler, electromagnetic, electro-mechanical, thermistor, inductance, fibre optic, microwave, laser, ultrasonic, piezoelectric effect etc [66]. Every one of these technologies uses different parameters and has unique advantages.

Acoustic sensors can detect the mass, which is an inherent feature for all analytes, and can be used with wireless systems easily. Acoustic technology provides rapid, sensitive, label-free and cheap detection. They can be divided according to the usage

of bulk or surface acoustic waves. The working procedure of these types of sensors is the detection and interconversion of acoustic waves [67].

The piezoelectric effect is a collective interaction between electrical, such as electrical field and charge, and mechanical, such as mechanical stress and strain, variables in the material. It is widely used in sensors by the principle of electromechanical transduction [69]. These types of sensors produce electrical signals as a response to the presence of mechanical stress. The inverse piezoelectric effect which results in a mechanical output because of the applied electrical field is also important for sensor applications [68]. The advantages of these sensors largely depend on the properties of the piezoelectric materials used.

Fibre optic sensors have attractive properties such as stability in harsh environments, long term monitoring, compact size, measurement in a wide range distance, immunity to electromagnetic interference. The most interesting property of fibre optic sensors is the opportunity of continuous physical quantity measurement through the fibre [70]. The working principle of fibre optic sensors depends on the properties of light transmitted throughout an optical fibre. Any change based on external factors in the fibre such as a change in temperature or stress state of the fibre causes variations in the transmitted light signal. Optical fibres can be divided to single-mode fibres and multi-mode fibres and, use distinct phenomena to modulate the transmitted light, thus, have different characteristics [71].

Capacitive sensors have simple structures however various advantages such as low-cost production, high sensitivity and selectivity, high reliability, thermal stability, low power need, wide linear response range, fast response time. In general, the performance of these types of sensors is based on capacitance that raises or reduces according to the dielectric properties of the sensing layer [72, 73].

In recent years, various kinds of sensors are used in diverse application areas by using distinct technologies. Sensors can be used for automotive and aerospace applications [78], medical diagnosis [79], food security [77], biotechnology [76], pharmaceutical [75], hazardous gasses and humidity detection [74].

1.2.3 Humidity sensing

Humidity is an important factor in our daily life that can be represented by absolute humidity or relative humidity. The total amount of water vapor in a certain volume is

called absolute humidity which is described by g/m3. There is a direct proportion between temperature and the ability of the air to hold moisture. On the other hand, relative humidity can be described as the amount of water vapor in the atmosphere at any temperature compared to the maximum amount of water vapor the atmosphere can hold at the same temperature [84].

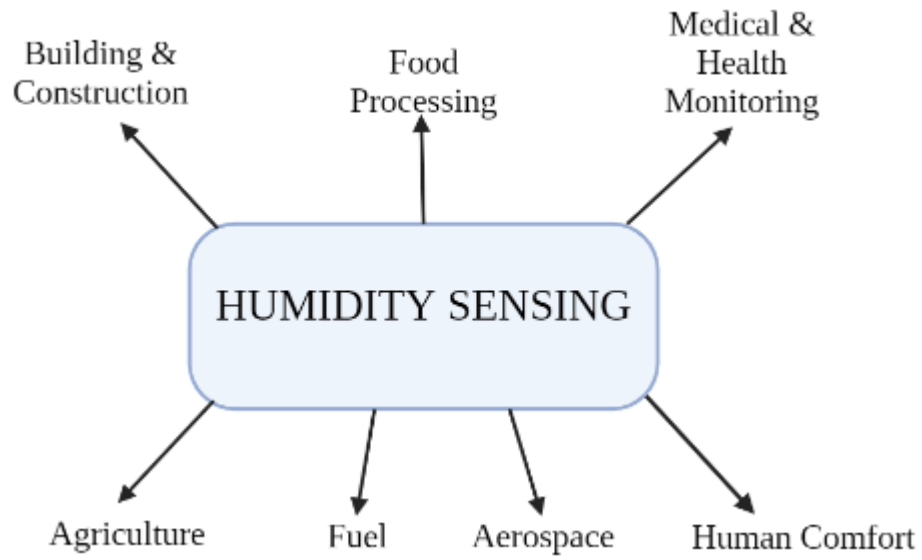

Figure 1.8: Different industries where humidity measurement is used.

Humidity measurement is a critical indication in diverse areas including food storage, weather forecast, agriculture, environmental monitoring, medical facilities, ventilation, air conditioning, process control and more (Figure 1.8) [80, 81, 82]. In this context, integrating sensors into humidity measurement applications enables real-time, reliable, repeatable and precise measurements. Therefore, humidity sensors can be used in many areas (Figure 1.9). Obviously, the humidity sensors determine the humidity by transforming the amount of water molecules in the environment into a measurable signal. The ideal properties for humidity sensors can be listed as high sensitivity, short response and recovery time, small hysteresis, long-term stability, negligible temperature dependence, resistance against contaminants and low manufacturing cost [85]. Humidity sensors can be classified based on the technology applied or the operation principle.

According to technology applied, humidity sensors can be capacitive or resistive. Basically, the capacitive humidity sensors rely on relative humidity. The dielectric constant value of the active layers and the crucial capacity of the film layer play an

important role for the sensing mechanism of capacitive-type sensors. The response time to humidity of these types of sensors are affected by the sensor design and the adsorption and desorption ability of materials [86]. Capacitive sensors have better stability than resistive sensors, especially in an intense water vapors environment. Also, they show better linearity in general [87]. On the other hand, resistive humidity sensors, also called impedance, transduce humidity to an impedance change which can be measured by a resistance, a current or a voltage [88].

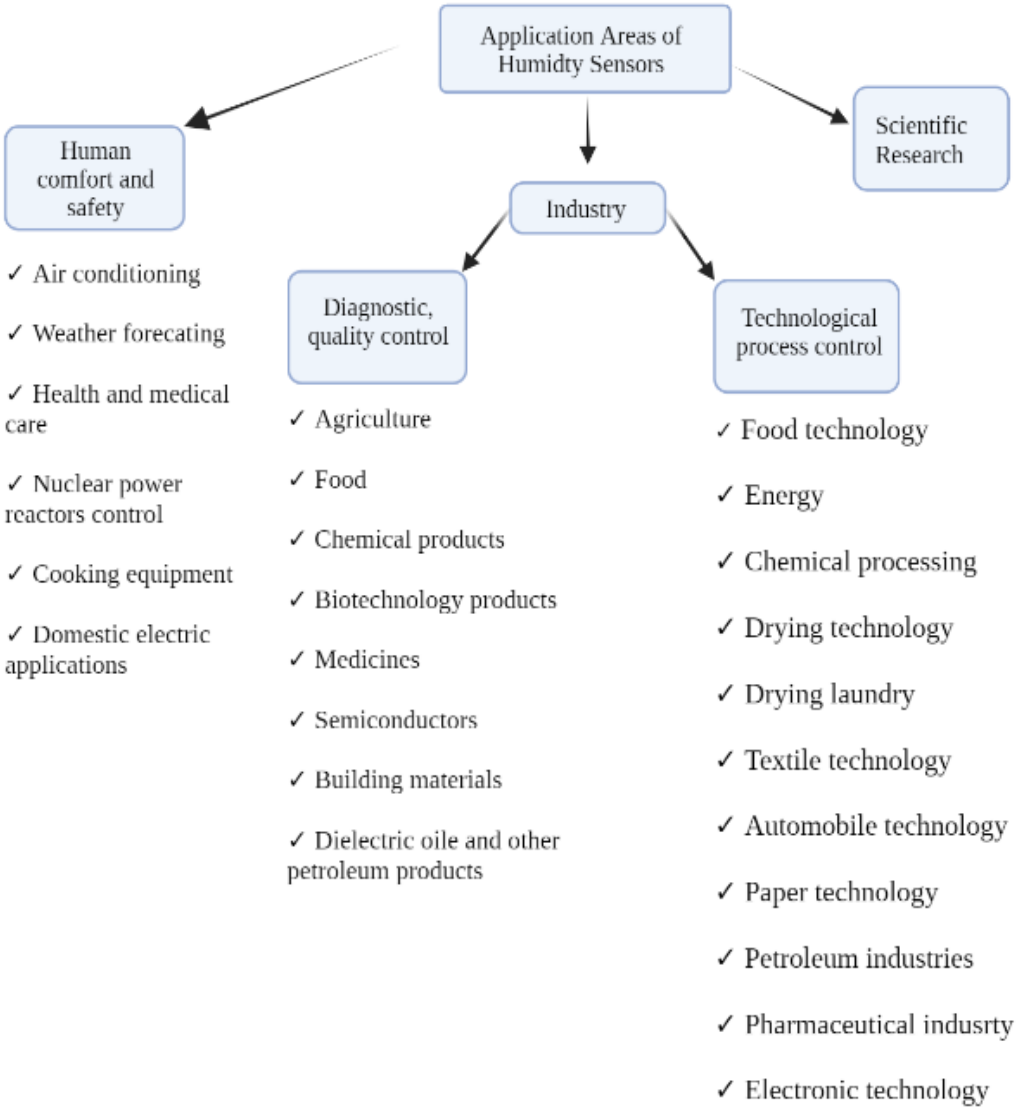

Figure 1.9: Application areas of humidity sensors. Modified from [83].

According to principle of operation, humidity sensors can be classified as (1) electrical humidity sensors, (2) optical humidity sensors, (3) mechanical humidity sensors and, (4) electrochemical humidity sensors. As an electrical sensor, the quartz crystal

microbalance is an important and well-studied candidate using the piezoelectric effect for humidity sensing.

1.2.4 Quartz crystal microbalance for humidity sensing

The detection of humidity by using sensors is one of the common desired applications in our daily life. This is why the production of cost-effective sensors with enhanced sensitivity is essential. Although various methods have been developed, the quartz crystal microbalance (QCM) is a very important candidate for humidity sensing issue due to its features which are having an excellent sensitivity to changes in mass with a nanogram level of detection level, having an extensive measuring range, stable and reliable in mild operation conditions, being small and can be developed with a low-cost [90]. The schematic representation of QCM is illustrated in Figure 1.10. The quartz disk is located between two gold electrodes. Throughout an applied voltage to the quartz crystal, an oscillation at a specific frequency occurs which determines a shift in resonance frequency [91].

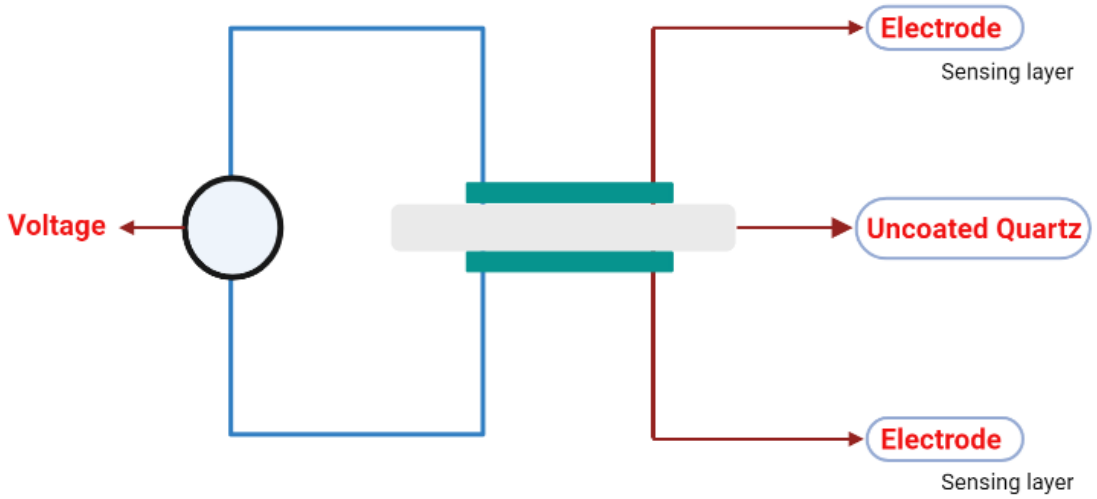

Figure 1.10: Schematic illustration of a QCM setup.

The mass change on the QCM surface is related with the shift in resonance frequency that is given by the Sauerbrey equation [92]:

$$\Delta f = -2.26x10^{-6} f_0^2 \frac{\Delta m}{A} \tag{1.1}$$

Here, the mass change is specified by Δm (g) while the resonance frequency shift is indicated by Δf (MHz). The original frequency of the quartz crystal is f_0 (MHz), and

A (cm^2) is the surface area of the quartz electrode. As it can be seen from the equation, there is a proportional relation between Δm and Δf values and this derivative is important because of its extensive use in piezoelectric analytical applications [92]. In addition, the parameters that affect the sensing properties of the QCM are shown in Figure 1.11.

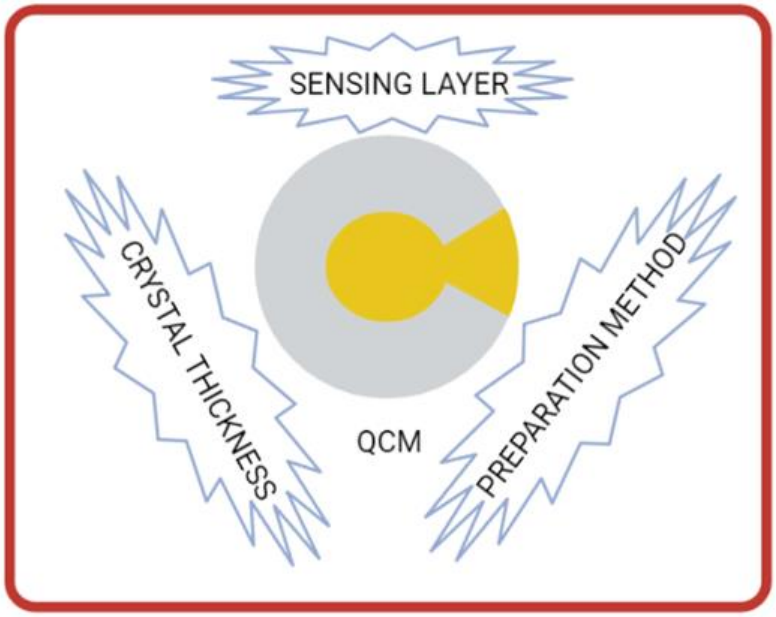

Figure 1.11: Parameters affecting the sensing properties of QCM. Modified from [91].

On the other hand, QCM is not functional alone for humidity detection and an additional sensing layer is necessary. Li et al. (2021) showed that uncoated QCM has little response to humidity while coated QCM showed high response to relative humidity [93]. In another study, Kosuru et al. (2016) investigated PVP and metal organic framework coatings on the QCM surface for humidity sensing. In this study, the uncoated QCM sensor sensitivity is tested in addition to these sensors and it is observed that uncoated QCM has the lowest sensitivity for humidity measurement [94]. To achieve certain improved or desired properties in the sensitivity of QCM humidity sensors, composite materials can be used which contain the combination of two or more different materials. Basically, two different approaches could be applied; (1) using an additional nanostructured/porous material to enhance the specific surface area for increasing the interactions with water molecules and the surface or (2) using another humidity sensitive material to enhance the overall humidity sensitivity [90].

There are a number of studies for QCM humidity sensing applications with GO-based composite materials. Table 1.1. indicates some of these studies. Table 1.1 is taken from our yet unpublished article which is "Recent Developments of Graphene/Borophene-based QCM Humidity Sensors" [101].

Table 1.1: QCM humidity sensing applications with GO-based composite materials

Composite Material	Method	Response Recovery time (s)	Humidity Range (%)	Ref.
GO/ZnO composite thin film	Spray coating	9 s / 5 s	11.3%-97.3%	[95]
GO/$Cu(OH)_2$ nanowires film	Drop-casting	1.9 s / 7.6 s	0%-80%	[64]
GO/Nafion nanocomposite film	Spin coating	23 s / 5 s	11.3%-84.3%	[96]
GO/SnO_2/PANI film	In-situ oxidative polymerizatio n	7s / 2 s	0%-97%	[63]
PANI/GO	Layer by layer self-assembly	8 s / 5 s	11%-97%	[97]
MoS_2/Graphene Oxide/C_{60}-OH	Drop-coating	1.3 s / 1.2 s	2%-97%	[98]
GO/PEI	Spray coating	53 s / 18 s	11.3%-97.3%	[99]
C_{60}/GO	Drop-casting	4 s / 5 s	11%-97%	[100]

In this study, graphene oxide, a two-dimensional material with excellent physical properties, was used because of the hydrophilic groups on its surface that increase the adsorption of water molecules. In addition, the use of an additional porous/ nanostructured material increases the surface area/volume ratio, the interaction of water molecules with the sensing surface increases, which enables the sensor to gain more advanced properties. Therefore, calcium titanate ($CaTiO_3$) perovskite was used in order to have a more environmentally friendly approach, to maintain effective performance in small sizes with high dielectric permeability, and to increase the

surface area where the interaction will occur by providing a porous surface during the adsorption of water molecules. The synthesized composite material was aimed to use for coating the surface of QCM electrodes.

1.3 Hypothesis

A fast, reliable and repeatable humidity measurement with cost effective methods is desired. The quartz crystal microbalance can meet most of the desired criteria but it is not sensitive enough for humidity on its own. Therefore, a sensing layer is essential for humidity measurement with QCM. Graphene oxide (GO) as a two-dimensional flexible material has hydrophilic functional groups such as carboxyl, hydroxyl, etc. on its surface which are useful for a sensitive humidity measurement. In addition to some drawbacks like hysteresis effect, GO humidity sensing property may decrease as a result of physical interaction between GO carboxyl groups and water molecules. These drawbacks can be overcome by addition of other materials which makes the coating material a GO-based composite for QCM humidity sensing application.

2. MATERIALS AND METHODS

2.1 Materials

The graphite powder and Titanium (IV) isopropoxide 97% were obtained from Sigma Aldrich. Calcium Oxide 99% was obtained from MERCK. Sulphuric acid 95-98%, Nitric acid 65%, and Hydrogen peroxide 35% were obtained from MERCK. Hydrochloric acid fuming 37% was obtained from ISOLAB chemicals. Potassium permanganate 98% was obtained from Alfa Aesar.

2.2 Synthesis of Graphene Oxide Nanofilms

A modified Hummers method was used for the synthesis of Graphene Oxide (GO) nanofilms (Figure 2.1). Hummers method is the most common method for GO synthesis which was brought to the world of science by Hummers and Offeman in 1958 [102]. This method has some significant developments such as being relatively fast, being more safe, preventing the formation of acid fog compared to other methods [103].

The modified Hummers method used during the experiment can be briefly explained as follows [104]; 25 ml of Sulphuric acid was added in a flask placed on a magnetic stirrer in an ice bath. While the stirring process continued at 20 °C and 600 rpm, 1 g of graphite powder was added, and a colour change to black was observed. 3 g of potassium permanganate was added after the temperature was fixed under 10 °C. The ice bath was removed, and the heater was activated to raise the temperature to 33 °C after 1 hour. Then the stirring at 33 °C continued for 2 more hours. 50 ml of distilled water was added to the solution to start the oxidation process which would lead to colour change from black to dark brown and the heater was deactivated. The solution was left to stir for 1 hour at room temperature. Another 100 ml of distilled water was added to the solution and waited for 1 hour. To remove waste potassium permanganate and stop the reaction, 5 ml of hydrogen peroxide was added to the solution and stirred

for about 30 minutes. The final solution was washed and filtered with %10 HCl and distilled water till pH was reached to 7. The graphite oxide powder was obtained after drying the final product at room temperature for 2 hours. Then, the sample was dispersed in distilled water to obtain graphene oxide by further processes. Finally, the exfoliation was achieved by ultrasonication for 45 minutes and centrifugation at 4000 rpm for 30 minutes and repeating this process one more time. After the last centrifugation process, the sample was collected and left to dry at 60 °C for 24 hours in the oven.

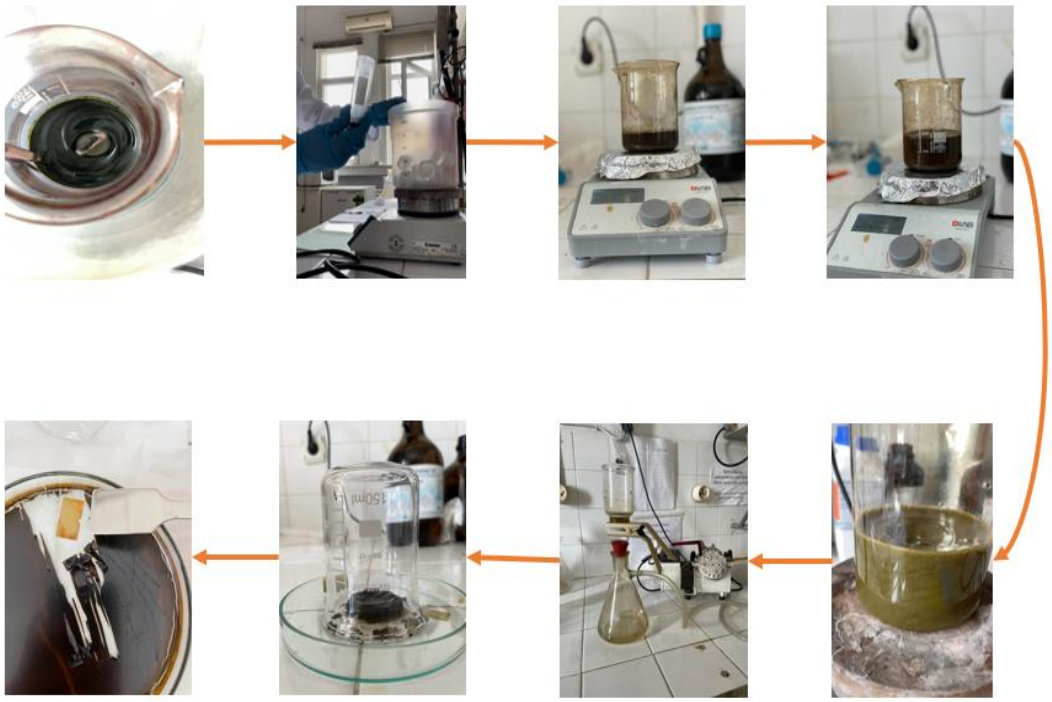

Figure 2.1: Experimental setup for GO synthesis.

2.3 Synthesis of Calcium Titanate, $CaTiO_3$, Nanoparticles

The sol-gel method was used for the synthesisation of $CaTiO_3$ perovskite nanoparticles. Calcium oxide (CaO) and Titanium (IV) isopropoxide ($Ti(OC_3H_7)_4$, ethanol, nitric acid (HNO_3) and distilled water were used for a simple process [105]. First of all, 5 gram of CaO was dispersed in 20 mL of ethanol at 60 °C with a magnetic stirrer (a). In another beaker, 2.5 gram of Titanium (IV) isopropoxide was dispersed in 10 mL of ethanol (b). After a while solution (b) was added drop wise to (a) and left to stir overnight. Another solution was prepared with 150 mL of distilled water and 3 mL of HNO_3 and added drop wise in the obtained solution. Finally, the heater and the

stirrer were closed, and the solution was left at room temperature to precipitate the product. The supernatant was removed, the product was left to dry at 100 °C for 24 hours in the oven. After drying, the powder form was achieved by using an agate mortar (Figure 2.2).

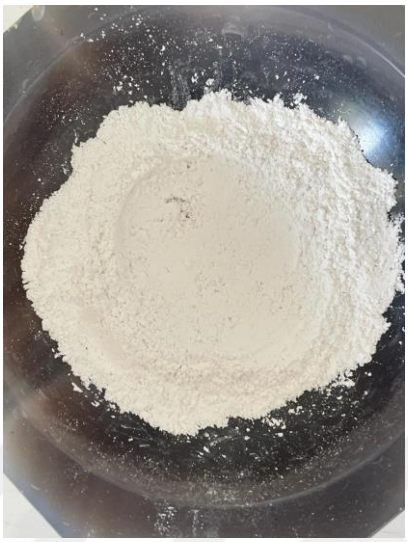

Figure 2.2: The powder form of $CaTiO_3$ particles.

2.4 Synthesis of GO/$CaTiO_3$ Nanocomposite

The composite nanomaterial was synthesized by a simple blending method [106,107]. Initially, 225 mg of graphene oxide was dispersed in 50 mL of distilled water by sonication for 1 hour. The same amount of perovskite nanoparticle was added into the solution and stirred at room temperature for 2 hours and sonicated for 1 hour. The product was filtered and dried at 50 °C for 24 hours to obtain GO/$CaTiO_3$ nanocomposite. It was expected to obtain a composite that is represented in Figure 2.3.

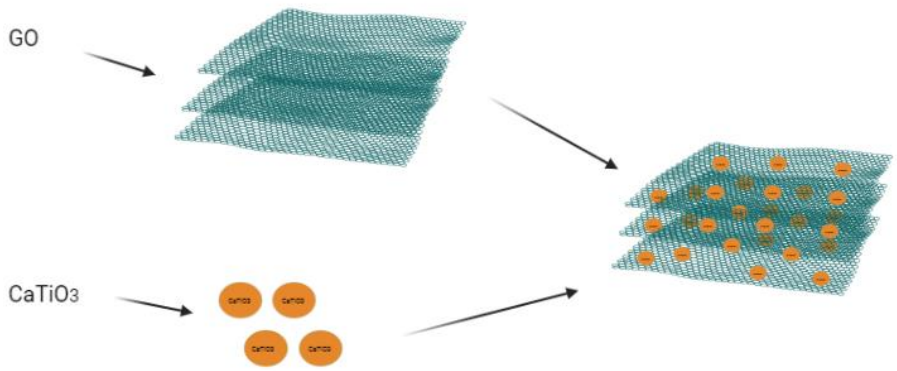

Figure 2.3: Theoretical model intended for the GO/$CaTiO_3$ nanocomposite film.

2.5 Characterization of $CaTiO_3$, GO and GO/$CaTiO_3$ materials

The characterization of synthesized materials involves; Uv-Vis Spectroscopy, FT-IR Spectroscopy, X-ray Diffraction and Scanning Electron Microscopy. The Uv-Vis absorption spectrums were observed in the range of 190-500 nm by using Shimatzu UV-1208 UV Spectrometer. The FT-IR spectrums were observed by using Spectrum 100 Optica FT-IR Spectrometer in the range of 650-4000 cm^{-1}. The XRD pattern was recorded using the Rigaku Smartlab X-Ray Diffractometer with CuKα radiation (λ = 1.54060 A). The XRD data was observed for $5° < 2\theta < 80°$. The morphological characterization was done by using SEM-QUANTA FEG 250. The SEM images were observed for 10 µm, 5 µm and 3 µm.

3. RESULTS AND DISCUSSION

The morphologies, structures, and optical absorption properties of synthesized materials were investigated, and the results of these analyses were discussed. After the production stage, graphene oxide was obtained in the film from while $CaTiO_3$ particles and GO/$CaTiO_3$ were obtained in powder form. To perform optical analyses, certain amount of each sample was redispersed.

3.1 The Optical Absorption Properties of the Materials

UV-Vis spectrophotometer was used for the analyses. In Figure 3.1, the UV-visible spectrum of the synthesized materials is shown. For GO sheets, the main absorption peak is about 230 nm and it demonstrates π to π^* transitions of aromatic C–C bonds. Apart from the main peak, there is a shoulder at about 300 nm which can be attributed to the π to π^* transitions of C=O bonds [108]. The band gap of the main GO sheets peak is 5.39 eV (Table 3.1). For $CaTiO_3$ particles which is shown by blue line, the main peak was at about 215 nm and defined π to π^* transitions taking place in $CaTiO_3$ [109]. The band gap of the main $CaTiO_3$ particles peak is 5.77 eV (Table 3.1). In addition, it can be seen that the composite material represents characteristics of both materials. For instance, the weak sharp peak at about 205 nm that belongs to GO sheets and the pit at about 380 nm that belongs to $CaTiO_3$ particles.

Table 3.1: Band gap energies of the produced materials.

Peak (λ)	Band gap energy (eV)
215	5.77
230	5.39
380	3.29

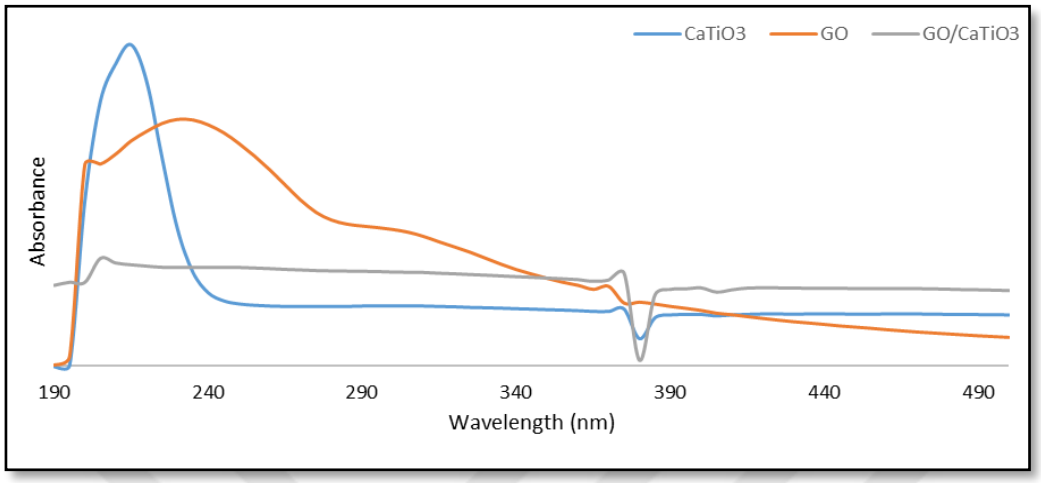

Figure 3.1: UV-Vis spectrum of $CaTiO_3$, GO and GO/$CaTiO_3$.

3.2 The Structures of the Materials

XRD and FT-IR analysis were used for the structural investigation. Figure 3.2 shows XRD patterns ($5° < 2\theta < 80°$) of $CaTiO_3$, GO and $CaTiO_3$/GO. Based on Figure 3.2 in the blue line, it can be said that there are some impurities in the CaTiO3 nanoparticles sample since there are some diffraction peaks which do not belong to the pure monoclinic phase of $CaTiO_3$ such as the peak at about $2\theta = 18°$. Apart from these, a monoclinic phase of $CaTiO_3$ nanoparticles was obtained [110]. According to the XRD data, the crystallite diameter (Dc) of $CaTiO_3$ nanoparticles was calculated as 15,78 nm by using the Scherer equation (Table 3.2). On the other hand, the highly intense peak in the orange line at about $2\theta = 10°$ is proof that the oxidation process of graphite powder was achieved successfully. There is no peak at this point for graphite powder [111]. The less intense peaks were observed at about $2\theta = 23°$ and $2\theta = 28°$, respectively.

Table 3.2: XRD crystallite size for the materials.

Peak Position (2θ)	FWHM (2θ)	Size (nm)
10	1.76	4.73
34	0.55	15.78

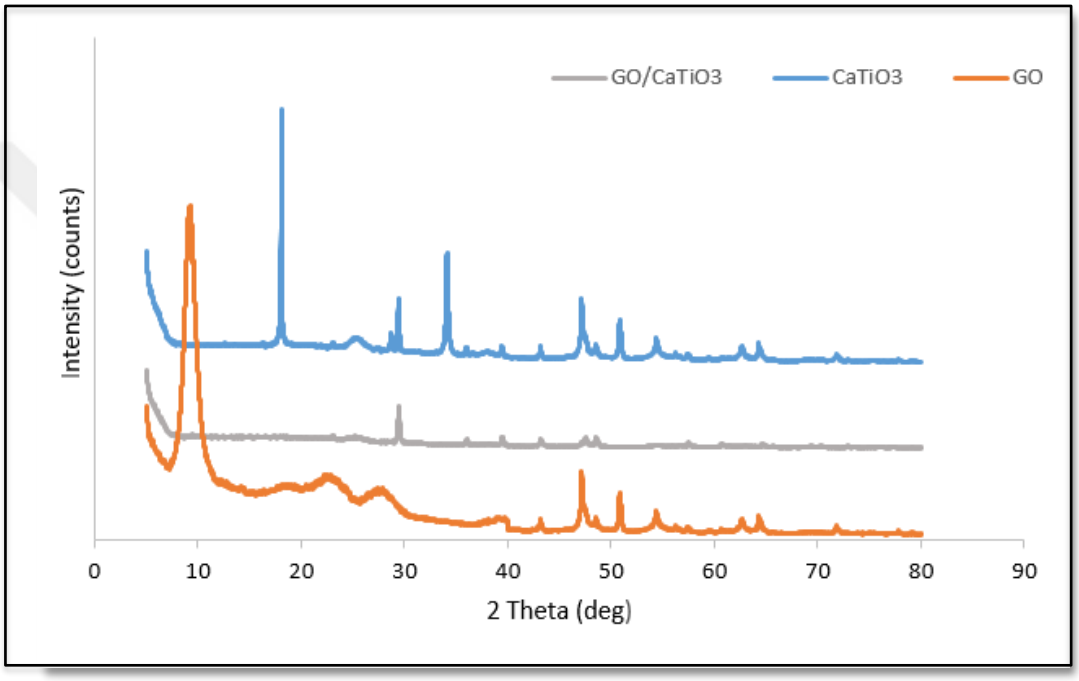

Figure 3.2: XRD patterns of GO/$CaTiO_3$, $CaTiO_3$ and GO.

Figure 3.3 illustrates the FT-IR spectra of $CaTiO_3$ particles and GO. As it can be seen, a number of characteristic bands for functional groups of GO were observed. Different oxygen containing functional groups were detected in GO. The broad peak between 2500 cm^{-1} to 3600 cm^{-1} can be attributed to O-H stretching vibrations [112]. The other peaks of GO at about 1713 cm^{-1}, 1146 cm^{-1} and 1039 cm^{-1} are the C=O, C-OH, and C-O, respectively while the peak at about 1621 cm^{-1} refers to C=C stretching [113]. In the FT-IR spectra of $CaTiO_3$, there are several peaks at 3642, 1415, 873 cm^{-1}. The small peak at about 3642 cm^{-1} is related to the hydroxyl group [114]. In addition, the peak at about 1415 cm^{-1} can be attributed to the stretching vibration of C-O groups. On the other hand, the composite material contains peaks of both materials (Figure

3.4). The broad peak at about 3254 cm^{-1} which belongs to GO and the other peaks at about 1419 and 874 cm^{-1} can be seen.

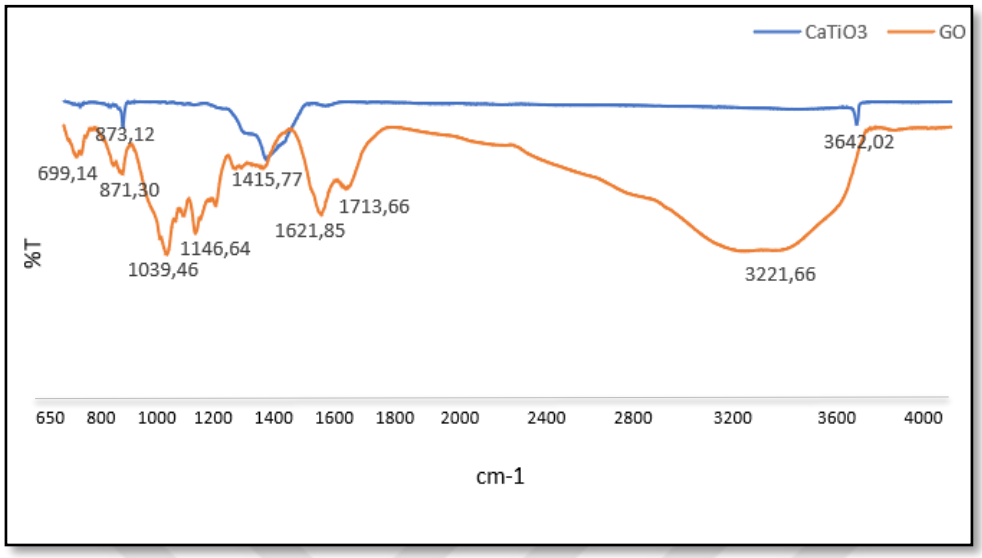

Figure 3.3: FT-IR spectra of $CaTiO_3$ particles and GO.

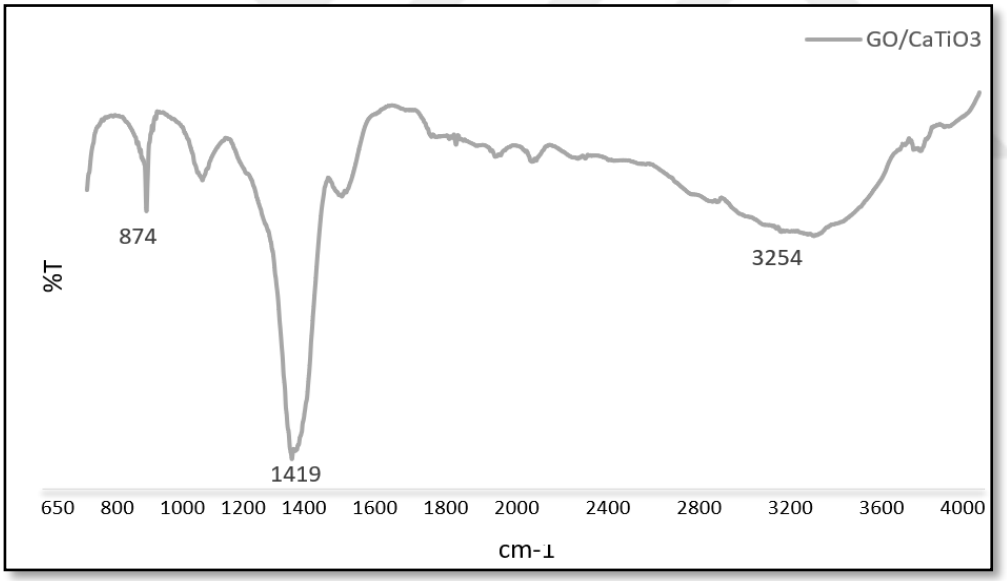

Figure 3.4: FT-IR spectra of GO/$CaTiO_3$ composite.

3.3 The Morphologies of the Materials

SEM images were used for the morphological analysis. In Figure 3.5, the morphology of $CaTiO_3$, GO and GO/$CaTiO_3$ composite materials can be seen. Figure 3.5 (a) exhibited the SEM images of $CaTiO_3$ perovskite particles. It can be said that particles are polydisperse. The images coincide appropriately with the literature. As it can be

seen in Figure 3.5 (b), GO nanosheets were positioned as randomly aggregated and the existence of crumpled thin sheet GO structure is caused by exfoliation. Also observed with wrinkles and folds on the surface of GO nanosheets were observed. It is approved from these results that GO nanosheets can be synthesized from graphite powder and exfoliated. From Figure 3.5 (c), the existence of composite material can be seen. GO nanosheets and $CaTiO_3$ particles are intertwined.

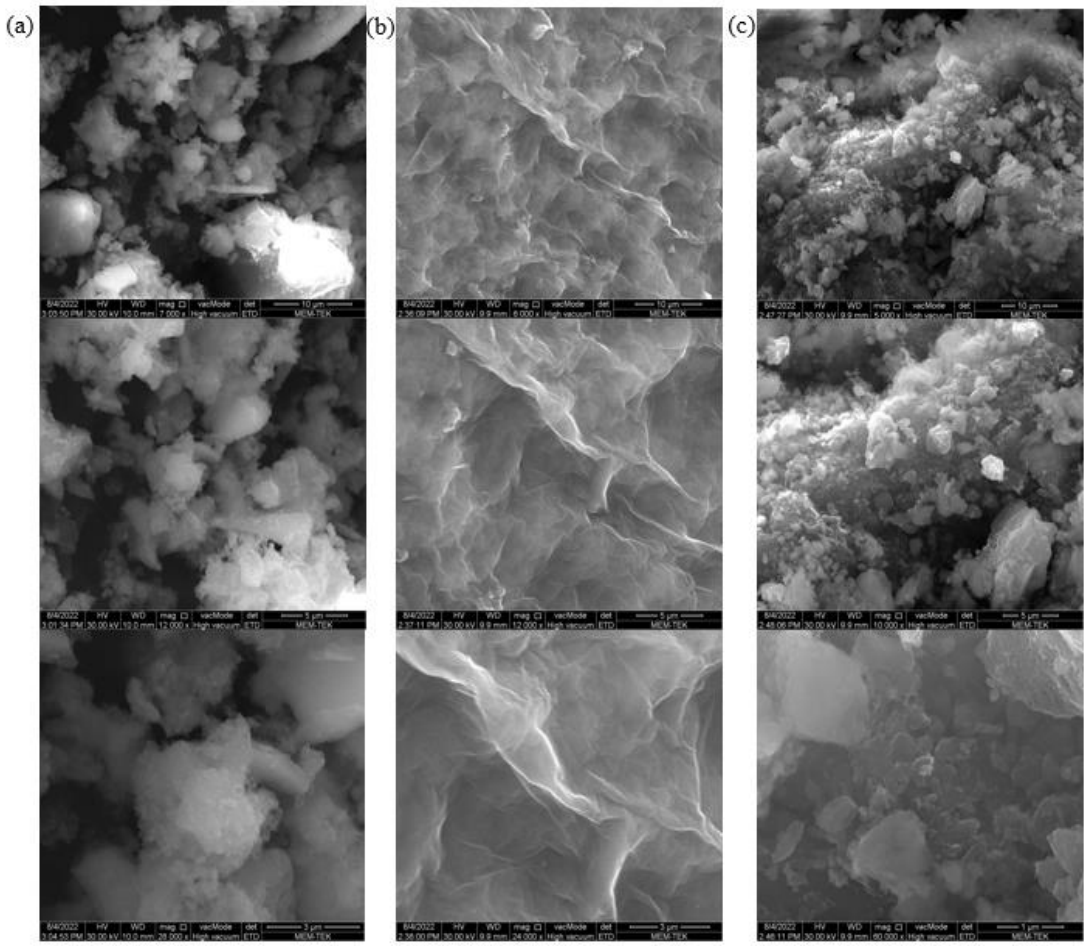

Figure 3.5: SEM images of $CaTiO_3$, GO and, GO/$CaTiO_3$, respectively.

4. CONCLUSION

Humidity measurement applications are desired to be done precisely and in a short time, as it exists in almost every part of human life, packaging of food and drugs, detection of gas leakage, detection of respiratory disorders in humans and more. Therefore, there has been a growing requirement and extensive research on designing humidity sensors that are rapid, cost-effective, and highly sensitive. Although various methods have been developed, QCM is a very promising candidate, as it has excellent sensitivity to changes in mass with a nanogram level of detection and, an extensive measuring range. In addition, QCM sensors are stable and reliable in mild operation conditions and can be developed with low-cost.

On the other hand, QCM is not functional for humidity and, an additional sensing layer is necessary. For this sensing layer, single component materials can be used. Graphene oxide, a derivative of graphene, has been used for humidity sensing applications thanks to its hydrophilicity. GO has hydrophilic functional groups on its surface. These groups can form hydrogen bonding with water molecules. Therefore, GO is more attractive for humidity sensing applications compared to graphene. A disadvantage of GO is its poor stability in various alkali solutions under certain conditions. Composite materials are made from two or more materials and have improved properties. In this study, calcium titanate particles were used with GO to form a composite material for the purpose of obtaining an improved material that is more sensitive to humidity.

In this thesis, GO nanofilms were synthesized with a modified Hummers method and $CaTiO_3$ particles were synthesized with a sol-gel method. After synthesizing the materials separately, they were simply blended and dried for 24 hours to obtain the composite material. The morphological, structural, and optical absorption properties of the synthesized materials were investigated. According to the comparisons with the

literature, the results of the characterization tests supported the successful synthesis of GO and $CaTiO_3$. Thus, a successful synthesis of GO/$CaTiO_3$ composite material was achieved for the first time in the literature. The synthesized composite could be used for coating the electrode of QCM to obtain an enhanced sensing layer for humidity sensing applications in future studies.

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APPENDICES

APPENDIX A: Nanoclay/ Graphene Oxide (GO) Composite-based Film Results.

APPENDIX A

Nanoclays also have humidity retention property. Therefore, two different nanoclays, sepiolite and halloysit, were used to prepare composite material with graphene oxide as preliminary experiment.

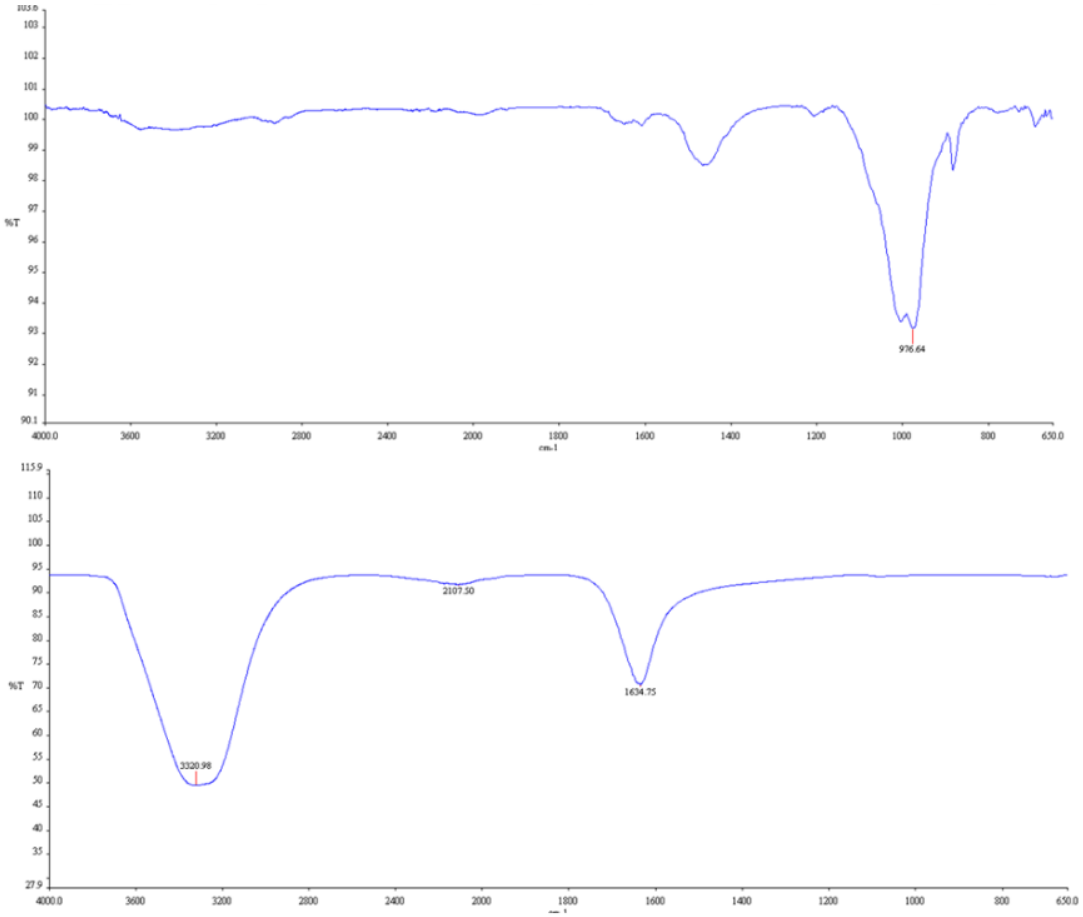

Figure A.1: The comparison of FTIR spectrums between Only S (Sepiolite) and Only S-GO.

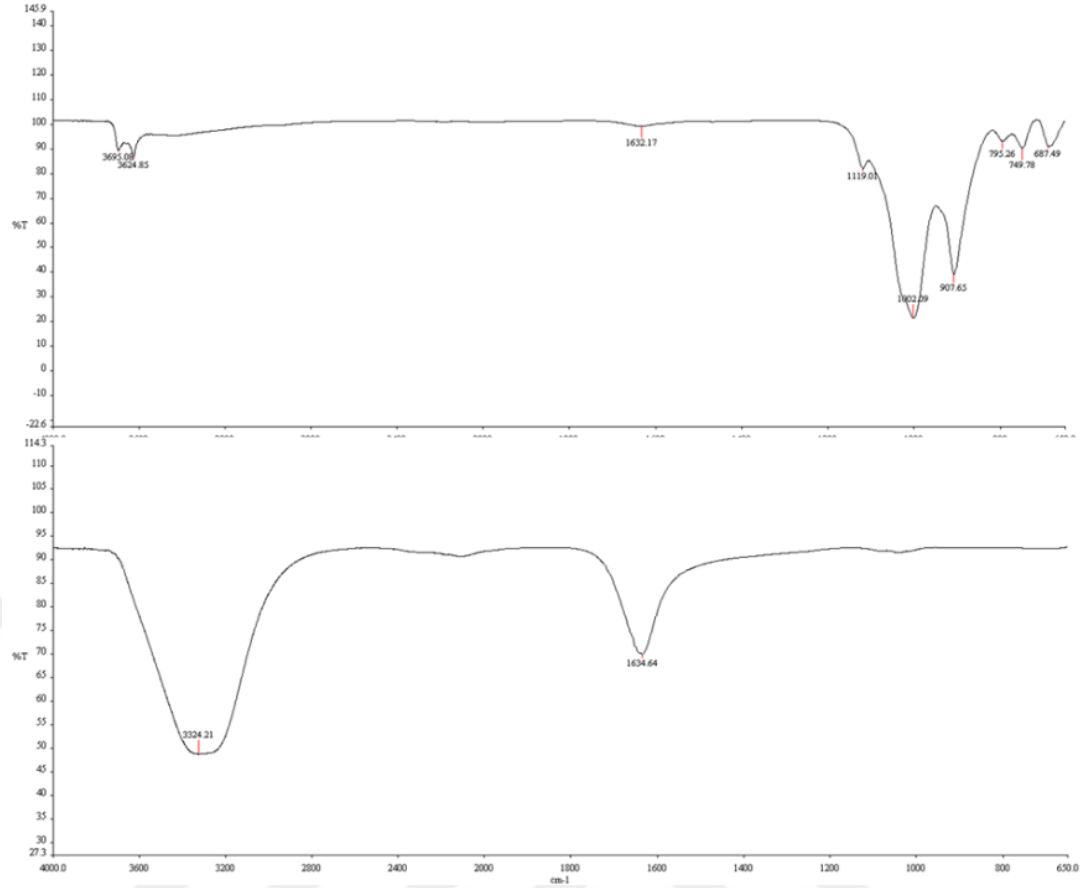

Figure A.2: The comparison of FTIR spectrums between Only H (Halloysit) and Only H-GO.

CURRICULUM VITAE

Name Surname: Zeynep Demirtaş

Education :

- **B.Sc. :** 2020, Yildiz Technical University, Faculty of Chemical and Metallurgical Engineering, Bioengineering