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Nourwanda M. Serour
Alexandria University

Ahmed S.E. Hammad
Egypt-Japan University of Science and Technology

Ahmed H. El-Shazly
Alexandria University

Dina A. El-Gayar
Alexandria University

Shaaban A. Nosier
Alexandria University

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Novel Green Micro-Synthesis of Graphene-Titanium Dioxide Nano-Composites with Photo-Electrochemical Properties

1) **Nourwanda Mohamed Serour[1*], Ahmed Salah Eldin Hammad[2,3], Ahmed Hassan El-Shazly[1,2], Dina Ahmed El-Gayar[1], Shaaban Attia Nosier[1]**

1 Department of Chemical Engineering, Faculty of Engineering, Alexandria University, Alexandria, Egypt

2 Department of Chemical and Petrochemicals Engineering, Egypt-Japan University of Science and Technology, EJUST, Alexandria, Egypt

3 Department of Chemical Engineering, Faculty of Engineering, Port Said University, Port Said, Egypt

Corresponding Author: Nourwanda Serour.

E-mail: eng-nourwanda.sourour@alexu.edu.eg

Phone: +20-122 127 6464.

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Abstract

Background: Graphene-Titanium dioxide nano-composite forms a very promising material in the field of photo-electrochemical research. **Methods**: In this study, a novel environment-friendly synthesis method was developed to produce well-distributed anatase nano-titanium dioxide spherical particles on the surfaces of graphene sheets, this novel method has great advantages over previously developed methods of producing graphene-titanium dioxide nanocomposites (GTNCs). High calcination temperature 650°C was used in the preparation nano titanium dioxide, chemical exfoliation for graphene synthesis and GTNC was produced by our novel method by depositing titanium dioxide nanoparticles on graphene sheets using a Y-shaped micro-reactor under a controlled pumping rate with minimal use of chemicals. **Results**: The physiochemical and crystallographic properties of the GTNC were confirmed by TEM, XRD, FTIR and EDX measurements, confirmed process repeatability. Spherical nano-titanium dioxide was produced in the anatase phase with very high crystallinity and small particle diameters ranging from 9 nm to 25 nm, also the as prepared graphene (RGO) exhibited minimal flake folding and a high carbon content of 81.28% with a low oxygen-to-carbon atomic ratio of 0.172 and GTNCs produced by our novel method had a superior loading content, a homogeneous distribution and a 96.6% higher content of titanium dioxide particles on the graphene sheets compared with GTNCs prepared with the one-pot method. For its photoelectrochemical properties, chronoamperometry showed that GTNC sample (2) had a higher peak current of 60 μA compared with that of GTNC sample (1), which indicates that the separation and transfer of electron-hole pairs are better in the case of GTNC sample (2) and according to the LSV results, the generation of photocurrent in the samples can be observed through multiple on-off cycles, which indicates that the electrodes are stable and that the photocurrent is quite reversible.

1. Introduction

Graphene loaded with titanium dioxide nanoparticles forms a very promising nanocomposite with superior physical, chemical and thermal properties. Such nanocomposites have made remarkable contributions in many industrial applications, such as those requiring the enhancement of photocatalytic activity, electrical conductivity, and heat transfer.

Graphene, which consists of a two-dimensional hexagonal crystal lattice of carbon atoms, was discovered in 2004 by Geim and Nocoselov [1]. Graphene proved to have a large specific surface area of approximately 2630 m^2/gram, an excellent thermal conductivity of 5000 W/m.K, a band gap of zero and high photocatalytic activity due to its ability to absorb up to 2.3% of white light and due to the relaxation and recombination of photo-induced electron-hole pairs in graphene, which depends mainly on the carrier concentration [2]. The primary methods used to produce graphene are micromechanical exfoliation [3], liquid-phase exfoliation [4], chemical exfoliation [5-8] and chemical vapour deposition (CVD) [9, 10]. On the other hand, nano-titanium dioxide is a non-metallic compound that is found in three main crystal forms: rutile, anatase and brookite. Titanium dioxide has many distinguishing properties, such as its chemical stability, non-toxicity, highly efficient photocatalytic effect, high refractive index and heat resistance, and it is used to enhance heat transfer in many applications, such as pigments, photocatalysis and nanofluidic. There are several synthesis methods for nano-titanium dioxide, such as the sol-gel technique [11, 12], the sol technique [13], the hydrothermal technique [14], the solvothermal technique [15], thermal coprecipitation [16-19], sono-chemical synthesis [20], CVD [21] and physical vapour deposition. Other methods include the direct oxidation of titanium metal into titanium dioxide using either an oxidizing agent or anodization, electrodeposition or microwave methods [22]. Recently, graphene sheets tailored with nano-titanium dioxide nanoparticles have become an attractive material, especially for use in photocatalysis applications, due to the distinctive properties of both components. Such composites are favourable for photocatalytic applications due to the ease of photogeneration through the graphene material, which enhances the photocatalytic properties of the composites over those of titania nanoparticles alone due to the excellent electron trapping and transportation properties of graphene, resulting in the suppression of the photogenerated electron-hole recombination in titania [23]. The most common methods used to produce graphene-titanium dioxide nanocomposites (GTNCs) are the hydrothermal and solvothermal methods [24, 25]. However, they are very complicated, time consuming, and costly and require high chemical consumption. In 2015, Arun Kanti *et al*. [26] developed a cheap and eco-friendly method of producing GTNCs. Unfortunately, the produced composite had a very low loading content of nano-titanium dioxide on the graphene sheets, which is not desirable in photocatalysis applications [27]. Therefore, we developed a new modification to this process to enable the production of GTNCs with a homogeneous distribution and a higher loading content of nano-titanium dioxide on the graphene sheets.

In this study, GTNCs were produced using two methods: the original green one-pot synthesis process, which results in a low content of titanium dioxide in the composite and a non-uniform distribution, and our new approach, in which the composite is produced using a micro-reactor. The new approach yields composites shows a higher loading and a uniform, homogeneous distribution of titania particles on the surfaces of the graphene sheets. Photo-electrochemical measurements, including linear scan voltammetry (LSV) and chronoamperometry (CAM), were performed on GTNC samples that were produced using both our novel modified system and the original method [26], and the results were evaluated to test the effects of our novel green micro-synthesis method on the photo-electrochemical properties of the produced composites.

2. Materials and Methods

2.1 Materials and Equipment

All reagents used were purchased from Sigma-Aldrich and of very high grade: titanium tetrachloride of 99.5% purity, sulfuric acid (98%), ammonium hydroxide solution (33% concentration), absolute ethanol (99.9% concentration), graphite powder, nitric acid, hydrazine hydrate, methanol, hydrogen peroxide and potassium permanganate. Deionized water was freshly produced and directly used.

The equipment used was as follows: a heater and magnetic stirrer, a fuming hose, an ice bath, a pH meter, a vacuum dryer, a muffle furnace, a centrifuge, an ultrasonic probe (power, 500 W; amplitude, 40%; frequency, 20 kHz, Hielscher, Germany), an ultrasonic bath (power, 160 W; frequency, 40 kHz), a drying oven, an agate mortar and pestle, a microwave irradiation reactor (power, 1000 W), a syringe pump, a Y-shaped micro-reactor, field-emission transmission electron microscope (JEOL JEM-2100F,USA), X-ray diffractor (XRD-6100 Shimadzu, Japan) and Vertex 70 IR spectrometer (Bruker Scientific Instruments, Germany). All glassware used was rinsed thoroughly with soap and tap water and was then washed with deionized water immediately before use.

2.2 Nano Particles Synthesis

2.2.1 Anatase Nano-Titanium Dioxide Synthesis *via* the Sol-Gel Method

Spherical anatase nano-titanium dioxide was prepared *via* the sol-gel method with the hydrolysis of titanium tetrachloride as a precursor in the presence of sulfuric acid, as reported by Li *et al*. [28]. First, 150 ml of deionized water was mixed with a solution of 10% diluted sulfuric acid. The mixture was placed in a beaker surrounded by an ice bath; then, magnetic stirring at speeds ranging from 1200 to 1500 rpm was applied until the temperature of the solution reached 0°C. Next, titanium tetrachloride was added in a dropwise manner under continuous stirring while the temperature was maintained at 0°C, using a 1:0.4 molar ratio of $TiCl_4$ to 10% H_2SO_4 and a 1:15 volume ratio of $TiCl_4$ to H_2O. After half an hour, the solution turned greyish white in colour as titanium oxy-sulphate formed, as described by the hydrolysis reaction in equation (1), and white fumes of HCl emerged. The solution was then heated at a hydrolysis temperature of 45°C until the solution became transparent again. Then, ammonium hydroxide solution was added in a dropwise manner until the pH became slightly higher than 7, and a white precipitate started to form as nanoparticle formation was stimulated by the presence of an alkaline medium. The mixture was left to gel overnight. Then, the mixture was filtered, and the precipitate was washed with ethanol and distilled water using centrifugation at 6000 rpm to remove any impurities, followed by drying in a vacuum oven to prevent contamination of the sample. The final step was calcination of the powder in a muffle furnace at 650°C for 90 min, after which the sample was ground. The hydrolysis and calcination temperatures were increased to promote the formation of spherical anatase nano-titanium dioxide. The chemical reaction sequence occurred as follows:

Hydrolysis of $TiCl_4$ to produce titanium oxy-sulphate:

$$\mathbf{TiCl_4 + H_2O + H_2SO_4 \rightarrow Ti\text{-}O\text{-}SO_4\ (Grey\ sol.) + 4\ HCl\uparrow\ (white\ fumes)} \tag{1}$$

Addition of ammonium hydroxide to neutralize the mixture, leading to the formation of a white precipitate:

$$\mathbf{Ti\text{-}O\text{-}SO_4 + 2\ NH_4OH \rightarrow H_2TiO_3\downarrow + (NH_4)_2SO_4} \tag{2}$$

Formation of titanium dioxide after washing, drying and heating:

$$\mathbf{H_2TiO_3 \xrightarrow{\blacktriangle} TiO_2\downarrow\ (white\ ppt.) + H_2O} \tag{3}$$

2.2.2 Graphene (Reduced Graphene Oxide) Synthesis *via* Chemical Exfoliation

The chemical exfoliation process consisted of two main steps. In the first step, the modified Hummers' method was used to produce graphene oxide (GO) from graphite flakes, and the second step was the reduction of the GO using hydrazine hydrate to obtain graphene (reduced graphene oxide, RGO). This modified synthesis process involves both the oxidation and exfoliation of graphite sheets due to the thermal treatment of the solution. The synthesis method is described in detail as follows. First, graphite flakes were added to 500 ml of H_2SO_4 (98%) and 160 ml of HNO_3 in a 1000 ml volumetric flask kept in an ice bath under continuous stirring. The mixture was then stirred for 1 hour at 0°C, and potassium permanganate was added to the suspension very slowly at a rate of 1 gm/min. The rate of addition was carefully controlled to keep the reaction temperature lower than 15°C. The mixture was maintained under stirring for four days and subjected to ultrasonication for 20 min every day while adding ice cubes; the solution was finally treated with 40 ml of H_2O_2, causing the colour to change to bright yellow. It was then left to sit without stirring for 3-4 hours to allow the particles to settle to the bottom, after which the remaining liquid was poured off, leaving the precipitate at the bottom. The resulting mixture was repeatedly washed using a centrifuge, first with 10% HCl and then with deionized (DI) water, several times until it formed a gel-like substance (of neutral pH). After centrifugation, the gel-like substance was vacuum dried at 60°C for more than 6 hours to obtain GO powder. In the reduction step, 2 ml of hydrazine hydrate was added to the suspension (GO powder in distilled water) and heated at 80°C using microwaves. A kind of black flocculent substance gradually precipitated out of the solution. The product was filtered using qualitative filter paper. Finally, the resulting black product was washed with methanol and water and dried at 80°C for one day to obtain sheets of graphene, also known as RGO.

2.2.3 Graphene-Titanium Dioxide Nanocomposite (GTNC) Synthesis

In this study, two GTNC samples were prepared using two different methods, and the effect on the resulting nanocomposite of using a Y-shaped micro-reactor in the green one-pot synthesis method [26] was studied. First, graphene sheets and spherical nano-titanium dioxide particles were ground using an agate mortar and pestle to avoid specimen contamination. Then, the same amount of each powder (*i.e.*, the mass ratio of graphene (RGO) to titanium dioxide was 1:1) was separately dissolved in 50 ml of absolute ethanol using an ultrasonic probe with 500 W of power, a frequency of 20 kHz and an amplitude of 40% to achieve a homogeneous dispersion of each powder in solution. The two resulting solutions were then mixed and placed in an ultrasonic bath operating at 160 W of power and a frequency 40 of kHz for approximately 90 min. In this step, titanium dioxide molecules adhered to the surfaces of the graphene sheets due to the presence of active sites formed by hydroxyl functional groups on the graphene surface. The resulting solution, which was dark black in colour, as shown in Fig. (**1**), and was then dried under ambient conditions overnight. The resulting powder was then subjected to microwave irradiation to achieve better exfoliation. The nanocomposite produced using this method was dark black in colour and is referred to as GTNC sample (1).

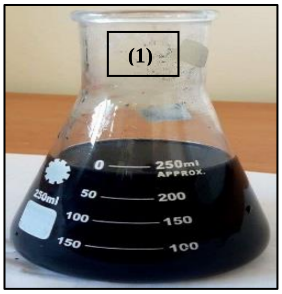


Fig. (1) *Black GTNC sample (1) in ethanol solution, produced without the use of a micro-reactor.*

GTNC sample (2) was prepared by grinding graphene and titanium dioxide powders and then placing the same amount of each in 50 ml of absolute ethanol and sonicating with an ultrasonic probe for 15 min. The two solutions were pumped at the same time at the optimal flow rate to give the solutions sufficient time to achieve close contact and to avoid any obstruction in the system due to particle accumulation. The solutions were pumped with a syringe pump into a Y-shaped micro-reactor with an estimated channel diameter of 706 μm which is the common diameter size used in micro-mixers, as shown in Fig. (**2**). The small channel diameter of the micro-reactor increased the surface contact between the two powders, maximizing the loading and achieving a homogeneous distribution of titanium dioxide nanoparticles on the surfaces of the graphene sheets. The resulting grey solution obtained from the micro-reactor, which is shown in Fig. (**3**), was then placed in an ultrasonic bath for 90 min. Then, the sample was dried overnight at ambient temperature. The resulting powder was then subjected to microwave irradiation for better exfoliation. The nanocomposite produced with this method was dark grey in colour and is referred to as GTNC sample (2). A schematic diagram of the new green micro-synthesis method that was used to produce GTNC sample (2) is presented in Fig. (**4**). To check the repeatability of our novel method, GTNC sample (3) was also prepared using the same process. TEM and EDX analyses of the sample were carried out to confirm the homogeneity of the distribution and the better loading of titanium dioxide nanoparticles on the graphene surfaces.

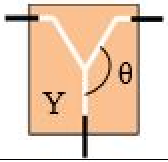
Micro-Reactor Type	**Microscopic Representation**	**Actual Image**	**Average Channel Diameter (μm)**
Y-shaped micro-reactor			706 μm

Fig. (2) *Microscopic representation and actual image of the Y-shaped micro-reactor used in this research.*

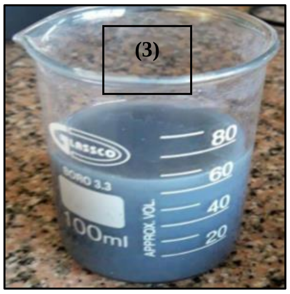


Fig. (3) *Grey GTNC sample (2) in ethanol solution, produced using our novel approach.*

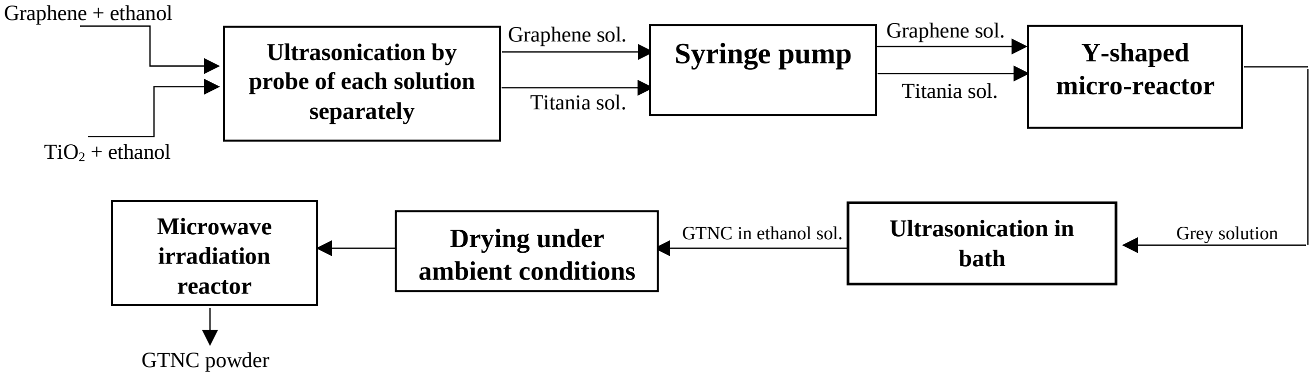


Fig. (4) *Schematic diagram of the proposed novel technique for the green micro-synthesis of GTNCs.*

2.3 Nanoparticles characterization

2.3.1 Transmission Electron Microscopy (TEM)

A field-emission transmission electron microscope (JEOL JEM-2100F) was used in this research. Ethanol was used to dilute the samples by ultrasonication, and the samples were then placed on a grid to dry overnight and were then investigated *via* TEM after drying. TEM is used to image specimen at a very high resolution using a small wave length electron beam to be able to identify the shape, distribution, size, surface morphology and degree of crystallinity of the nanoparticles.

2.3.2 Energy-Dispersive X-ray Spectroscopy (EDX)

EDX was performed using an energy-dispersive X-ray spectroscope (JEOL JEM-2100F) to provide an elemental analysis of the chemical compositions of the samples based on the interactions between excitation X-rays and each sample as each element has specific atomic structure that gives a unique set of peaks on the electromagnetic emission spectrum, it represents a quantitative analysis of high accuracy. The Cliff Lorimer ratio method for thin specimens was used as the quantitation method.

2.3.3 X-ray Diffraction Spectroscopy (XRD)

The XRD technique was used to identify the material and determine the crystallinity, unit cell dimensions and chemical properties of the materials. This technique depends on the angles of diffraction of X-ray emissions. The sample must be ground very hard into fine powder before examination. An X-ray diffractor (XRD-6100 Shimadzu, Japan) equipped with a Cu-Kα radiation source with a wavelength of $\lambda = 1.5418$ Å was used to perform a 2theta scan ranging from 5° to 80° at a scanning pitch of 0.02°.

2.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to determine and specify the functional groups present in each specimen. Technique depends on infrared spectrum of absorption or emission of the sample, the FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range and analyse it. A Vertex 70 IR spectrometer (Bruker Scientific Instruments, Germany) was used.

2.4 Photo-Electrochemical Measurements of Graphene-Titanium Dioxide Nano-Composite

Photo-electrochemical characterization was conducted in a single-compartment cell with a Pyrex window using a three-electrode configuration in the presence of 0.5 M Na_2SO_4 electrolyte, we used the same set up that was used before in our previous research [29]. GTNC sample (1) and GTNC sample (2) were deposited on fluorine-doped tin oxide (FTO) substrates *via* electrophoretic deposition (EPD) to obtain sample electrodes. In each measurement, one of these sample electrodes was used as the working electrode, a Pt rod was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. LSV and chronoamperometry (CAM) were performed using a potentiostat (Princeton Applied Research PARSTAT 4000A). The light irradiation source was a 365 nm Suruga Seiki UV-LED with an intensity of up to 50 mW/cm^2. The powders of GTNC samples (1) and (2) were deposited on FTO conducting glass via EPD for thin film fabrication. The EPD process was performed using 1 mg of GTNC powder suspended in 50 ml of acetone in the presence of 10 mg of iodine by means of ultrasonication for 15 min. Two parallel FTO electrodes (2.5 × 2 cm^2) were immersed in the solution, and a bias of 50 V was applied between the electrodes for 20 min by a DC power supply (Takasago ZX-400LA). The coated area was controlled to be 4 cm^2, and the fabricated electrodes were dried in air without any further treatment.

3. Results and Discussion

3.1 Transmission Electron Microscopy (TEM)

TEM images were used to identify the shape, distribution, size and degree of crystallinity of the nanoparticles. TEM images of the titanium dioxide indicate the formation of perfectly sphere-shaped particles with a high degree of crystallinity, as shown by the image in Fig. (**5a**), which was acquired at 1 nm magnification scale. Additionally, the crystallites shown are perfectly stacked, forming a crystalline arrangement. The particle size, as indicated in Fig. (**5b**) at a magnification scale of 10 nm, ranges from 9 nm to 25 nm, meaning that the minimal particle size was achieved by this method; this was accomplished by raising the hydrolysis and calcination temperatures. Graphene (RGO) is shown in Figs. (**5c**) and (**5d**) at a magnification scale of 100 nm. It is observed that exfoliated graphene sheets formed with a few wrinkles at the edges and that the RGO surfaces have more defects than typical graphene does, causing the RGO sheets to have more reactive sites due to the presence of functional groups on their surfaces. As seen from Figs. (**5e**) and (**5f**), the GTNC prepared *via* the green one-pot synthesis method is not homogeneous, and the titania nanoparticles are not uniformly distributed. Moreover, the loading of titania particles on the graphene sheets is very low, indicating that a significant number of titanium dioxide nanoparticles were wasted, as few dark particles, which correspond to the titanium dioxide particles, are present on the light sheets, which correspond to the graphene sheets. On the other hand, Figs. (**5g**) and (**5h**) show that in GTNC sample (2), which was prepared with the aid of the Y-shaped micro-reactor, the titania nanoparticles are homogeneously and uniformly distributed on the graphene surfaces. Indeed, in some areas, the graphene sheet is not visible due to the dense packing of titania on its surface, indicating high loading of titania on the graphene surfaces. Additionally, the TEM images of GTNC sample (3) in Figs. (**5i**) and (**5j**) show good repeatability of our novel synthesis method because GTNC sample (3) also has a very uniform and homogenous distribution of titania particles, similar to that observed in sample (2). GTNC samples (2) and (3), which were prepared with our method, show improved crystallographic properties compared with those of GTNC sample (1), which was prepared with the original green one-pot synthesis method. The main cause of the homogenous distribution and high titania content of GTNC sample (2) as shown in the TEM images is that the adherence of the nano-titania particles on the graphene surfaces depends on two types of bonds: chemical bonds with the trace oxygen functionalized groups resulting from the GO preparation step and van der Waals attraction forces. The use of the small-diameter micro-reactor in our novel method considerably enhances the contact between the titania nanoparticles and the graphene sheets by increasing the contact time and contact surface area, which gives the particles sufficient time to diffuse from the solution to the solid surfaces and to form more van der Waals attraction bonds between the titania and graphene and more strong chemical bonds with the remaining

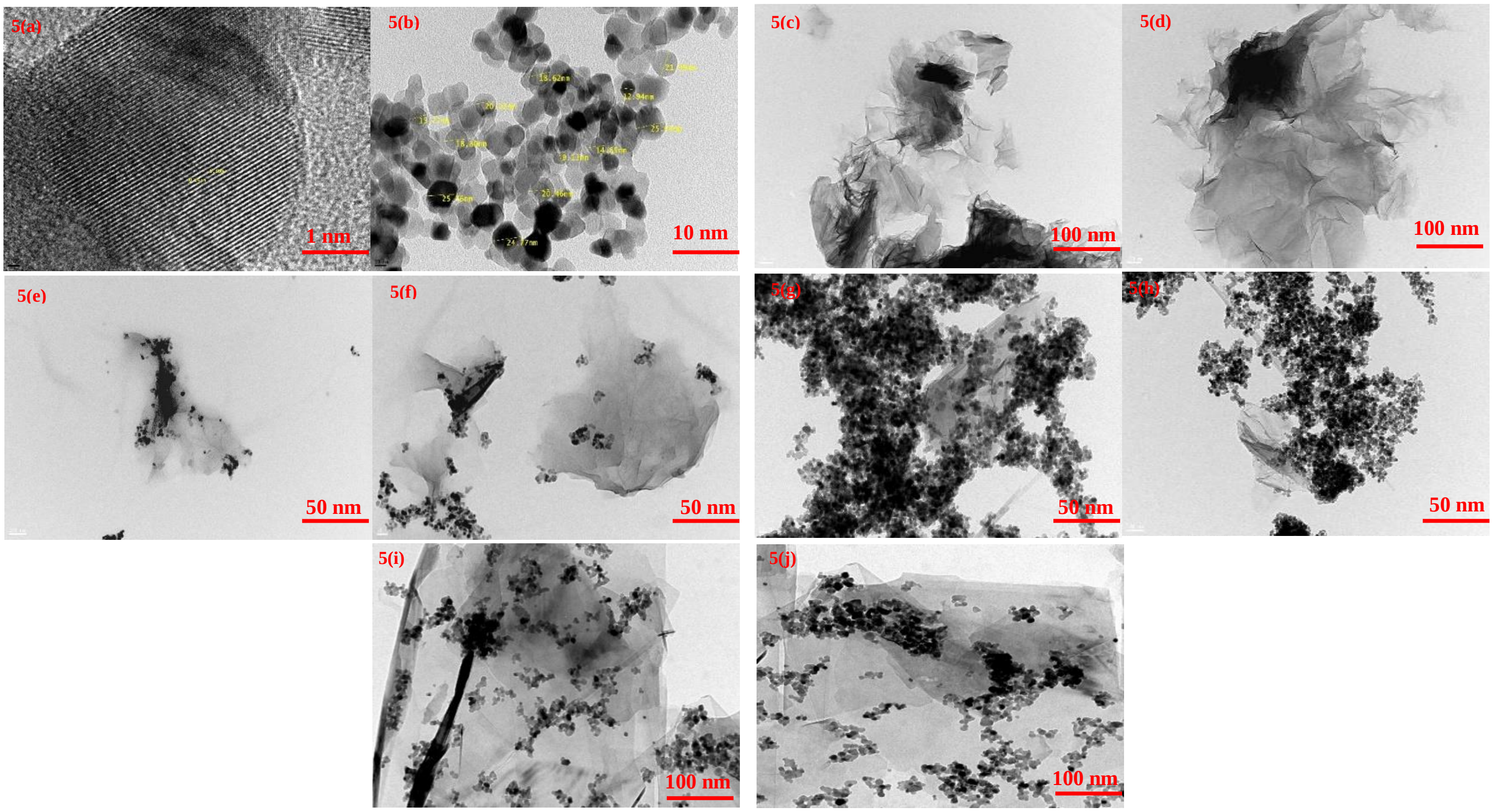


Fig. (5) *TEM images of nanoparticles. (a) & (b) Anatase nano-titanium dioxide at magnification scales of 10 nm and 1 nm, respectively. (c) & (d) Graphene (RGO) at a magnification scale of 100 nm. (e) & (f) GTNC sample (1) at a magnification scale of 50 nm. (g) & (h) GTNC sample (2) at a magnification scale of 50 nm. (i) & (j) GTNC sample (3) at a magnification scale of 100 nm.*

3.2 Energy-Dispersive X-ray Spectroscopy (EDX)

Figs. (**6**) and (**7**) show the EDX spectra and the studied areas for nano-titanium dioxide, graphene (RGO), GTNC sample (1), GTNC sample (2) and GTNC sample (3). In Fig. (**8**), the EDX results for anatase nano-titanium dioxide indicate that the composition of the formed material is 35.4% titanium and 64.6% oxygen by weight. For graphene (RGO), the EDX results indicate that 81.3% of the RGO prepared *via* chemical exfoliation in this study consists of carbon, with a relatively low oxygen-to-carbon atomic ratio of 0.172. The oxygen-to-carbon atomic ratio of synthesized graphene typically ranges from 0.041 to 0.18, as mentioned in previous studies by Mumuera *et al.* [30], and the remaining functionalized oxygen groups will contribute to the formation of bonds with titania in the nanocomposite. According to the EDX results, GTNC sample (2) has a higher elemental content of titanium than GTNC sample (1) does; the elemental mass fraction of titanium in sample (1) is 0.4%, whereas that in sample (2) is 13.1%. These findings indicate that the titanium dioxide content of GTNC sample (2) is higher than that of GTNC sample (1) by 96.6%, which can be explained by the better nucleation and growth of the titania particles on the graphene that was achieved with the use of the Y-shaped micro-reactor. Finally, the repeatability of our novel method is again confirmed by the EDX results for GTNC sample (3), which is found to contain 79.8% C, 16.7% Ti and 12.5% O; these values are very close to those obtained for GTNC sample (2), confirming the repeatability of our process.

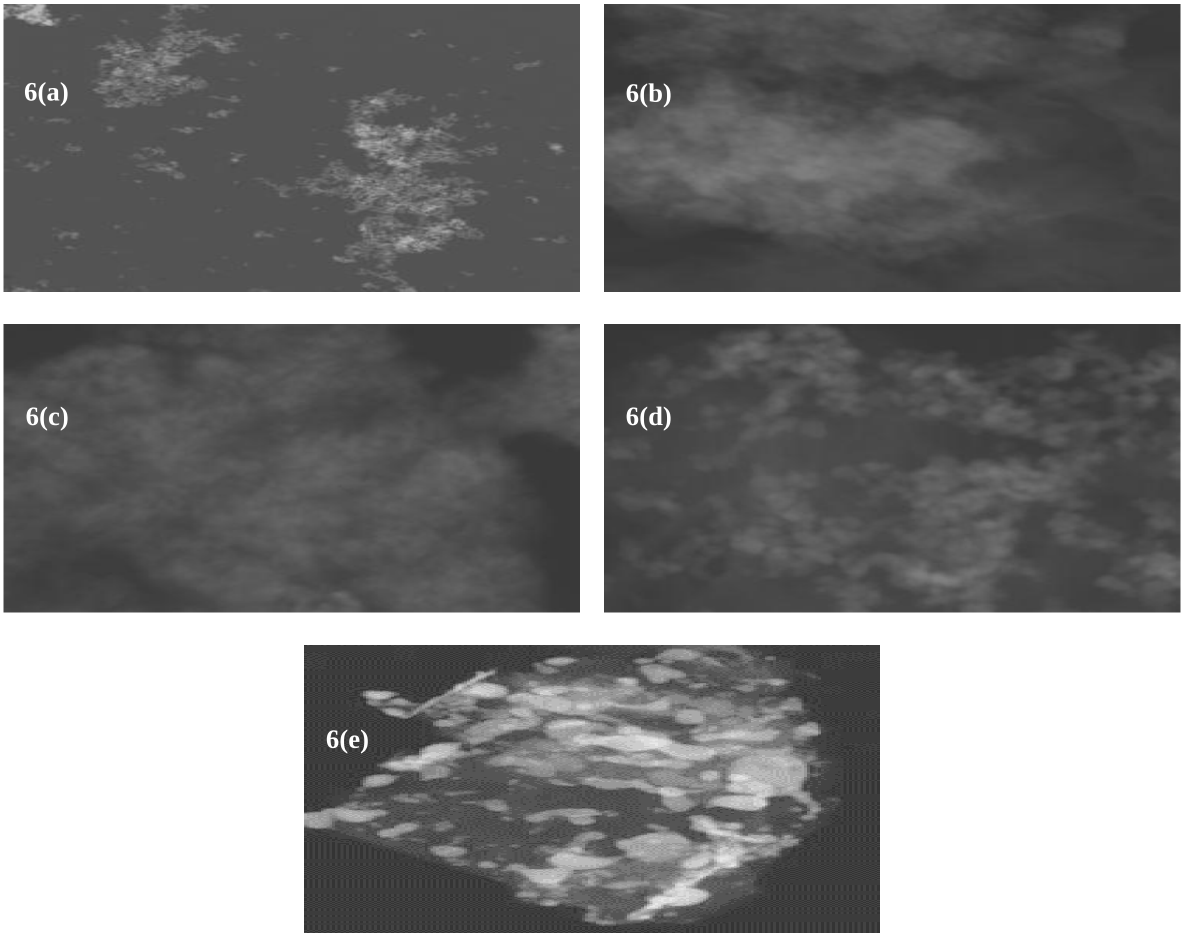


Fig. (6) *Areas studied (Electron Image) with EDX for the nanomaterials at 300 nm scale. (a) Anatase nano-titanium dioxide. (b) Graphene (RGO). (c) GTNC sample (1). (d) GTNC sample (2). (e) GTNC sample (3).*

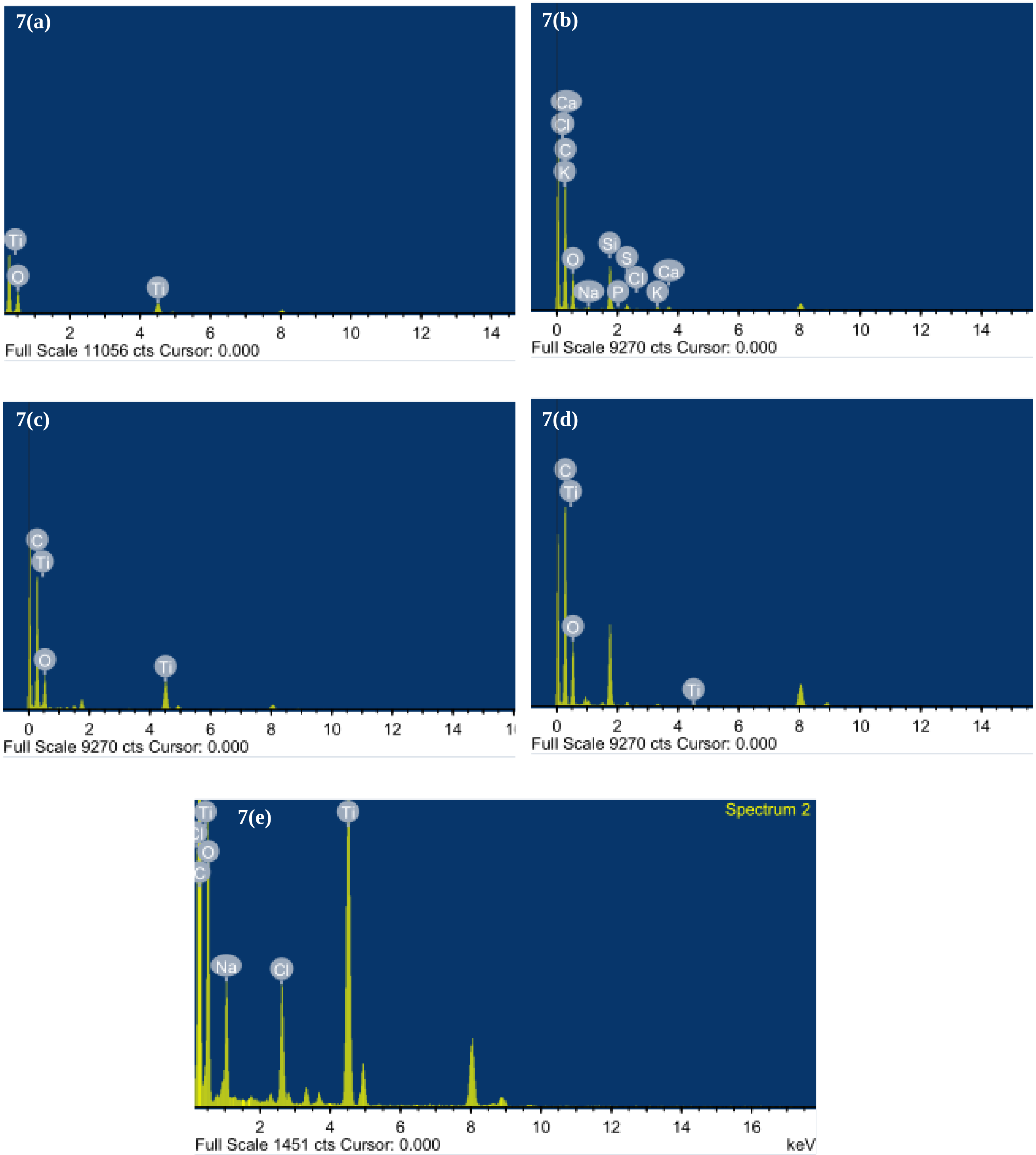


Fig. (7) *EDX spectra of the nanomaterials. (a) Anatase nano-titanium dioxide. (b) Graphene (RGO). (c) GTNC sample (1). (d) GTNC sample (2). (e) GTNC sample (3).*

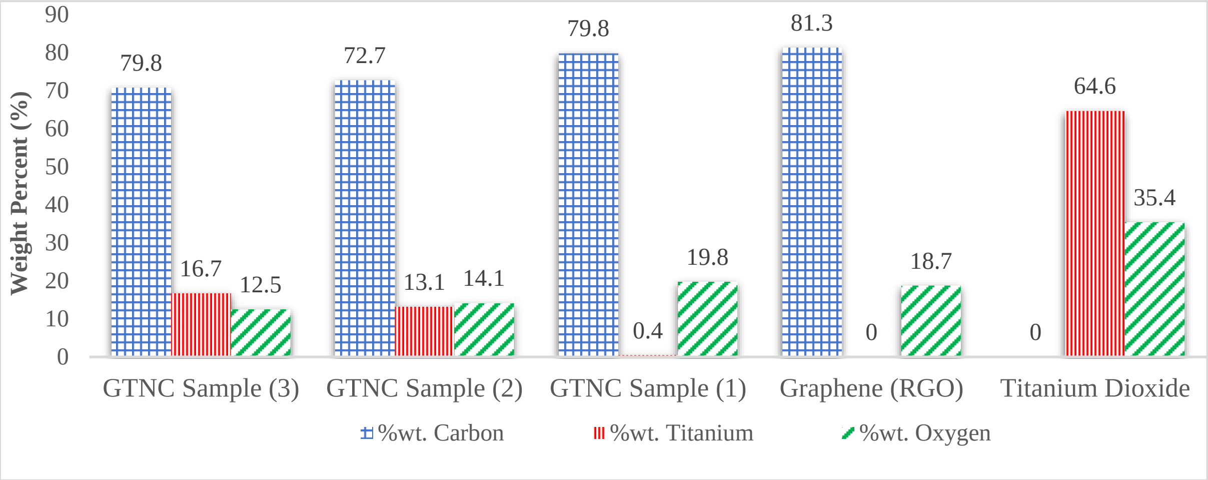


Fig. (8) *Elemental weight percentages for anatase nano-titanium dioxide, graphene (RGO), GTNC sample (1), GTNC sample (2) and GTNC sample (3).*

3.3 X-ray Diffraction Spectroscopy (XRD)

Fig. (**9a**) indicates that the XRD spectrum of the titania sample matches those of JCPDS card no. 21-1272 and reference [31], confirming the formation of spherical anatase titanium dioxide. Additionally, the highest peak is found at a 2theta value of 25.29°, indicating the formation of titanium dioxide. The peaks at 2theta values of 25.29°, 37.79° and 48.02° correspond to the (101), (004) and (200) planes, respectively, and prove the formation of the anatase phase of titanium dioxide with no evidence of the presence of the rutile or brookite phases. The high intensity of the peaks in Fig. (**9a**) indicates the formation of highly crystalline spherical nano-titania particles. In Fig. (**9b**), the highest peaks at 2theta values of 24.38° and 23.66° suggest the formation of RGO with relative d-spacings of 0.364 nm and 0.375 nm, respectively. The d-spacing values corresponding to the highest peaks indicate the formation of a two-dimensional structural layer of graphene (RGO), and the peak at a 2theta value of 43.3°, corresponding to the (100) plane, reveals the configuration of the hexagonal crystal structure of carbon in the lattice. As seen in Figs. (**9c**) and (**9d**), the spectra of both GTNC samples (2) and (1) contain a peak at 25°, which indicates the formation of RGO, and two sharp peaks at 37° and 48°, which suggest the presence of spherical anatase titanium dioxide. The XRD results show that GTNC samples (1) and (2) have similar diffraction patterns, although with a small difference in the width of the peak at 25°. Table **1** shows the numerical XRD results for the samples along with the corresponding d-spacing, lattice parameters and full width at half maximum (FWHM) for each peak.

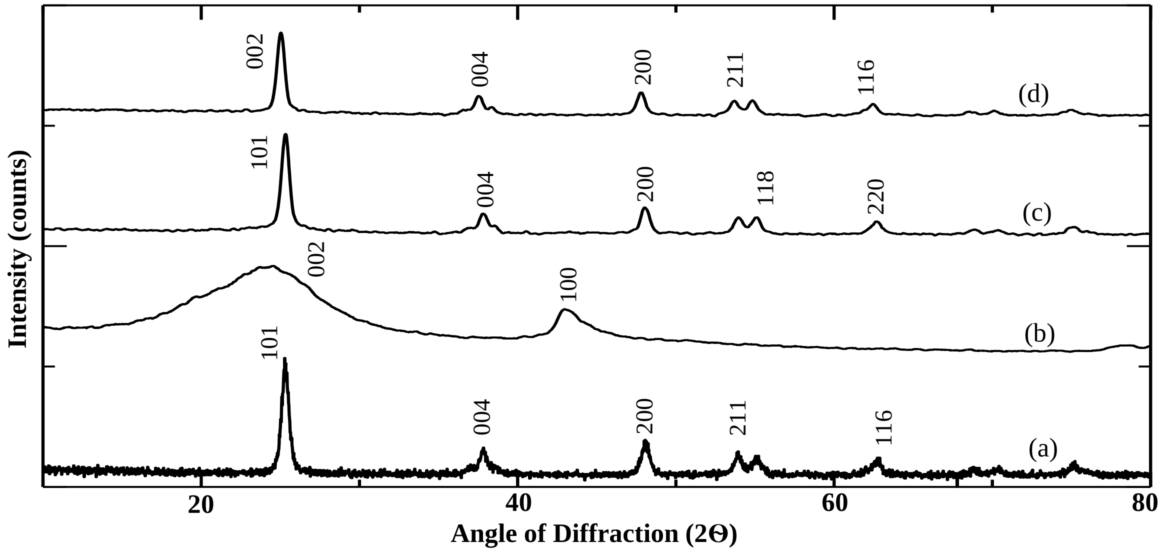


Figure (9) XRD representations. (a) Miller Indices of TiO_2. (b) Miller Indices of Graphene (RGO). (c) Miller Indices of GTNC sample (2). (d) Miller Indices of GTNC sample (1).

Table 1 Diffraction peak analysis for anatase nano-titanium dioxide, graphene sheets, GTNC sample (1) and GTNC sample (2)

GTNC Sample (1)				**GTNC Sample (2)**			
2Theta (°)	**d-Spacing (A)**	**FWHM (°)**	**Miller Indices**	**2Theta (°)**	**d-Spacing (A)**	**FWHM (°)**	**Miller Indices**
24.38	3.648	0.4	(002)	25.01	3.557	0.56	(101)
25.29	3.517	0.57	(101)	37.51	2.395	0.58	(004)
37.81	2.377	0.62	(004)	47.75	1.902	0.57	(200)
48.01	1.893	0.62	(200)	53.64	1.707	0.57	(211)
53.93	1.698	0.64	(211)	62.38	1.487	0.59	(118)
62.64	1.481	0.64	(118)	70.02	1.342	0.4	(116)
70.31	1.337	0.46	(116)	75.22	1.262	0.42	(220)
75.92	1.252	0.28	(220)				
Anatase Nano-Titanium Dioxide				**Graphene Sheets (RGO)**			
2Theta (°)	**d-Spacing (A)**	**FWHM (°)**	**Miller Indices**	**2Theta (°)**	**d-Spacing (A)**	**FWHM (°)**	**Miller Indices**
25.29	3.518	0.5621	(101)	24.38	3.648	0	(002)
37.79	2.378	0.5367	(004)	41.34	2.182	0.32	(100)
48.02	1.892	0.616	(200)				
53.89	1.699	0.56	(211)				
62.65	1.481	0.66	(118)				
70	1.342	0.38	(116)				
75.09	1.264	0.52	(220)				

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

As indicated in Fig. (**10a**), the functional groups observed in the titanium dioxide sample at a wavelength of 732 cm^{-1} indicate the presence of O-Ti-O anatase bonding. In addition, the peak at 1630.22 cm^{-1} is associated with water adsorbed on the particle surfaces, whereas the peak at 3444.24 cm^{-1} shows the presence of hydroxyl groups which matches with peaks indicated in previous research Samira *et al.* [32], and the peak at 2922 cm^{-1} indicates the presence of trace amounts of organic

C-H bonds. Figs. (**10b**) and (**10c**) present the FTIR spectra of GTNC samples (2) and (1). Both samples have peaks at almost the same wavelengths corresponding to vibrating bonds, with the peak at 3441.45 cm^{-1} indicating water adsorbed on the surface, the peak at 2923 cm^{-1} corresponding to carbon-hydrogen single bonds, the peak at 1633 cm^{-1} corresponding to hydroxyl group bonds, and the peaks at 1284 cm^{-1}, 1121 cm^{-1} and 1137 cm^{-1} corresponding to carbon-oxygen single bonds. The FTIR results show that GTNC samples (1) and (2) have the same functional groups adsorbed on their surfaces, namely, C-O, C-H, O-H and H_2O. Fig. (**10d**) shows the FTIR spectrum of the graphene (RGO), in which the peak at 3453 cm^{-1} is related to the vibrations of hydroxyl groups, the peak at 1636.7 cm^{-1} suggests the vibrations of carbon-carbon double bonds, and those at 1384.3 cm^{-1} and 1116 cm^{-1} indicate the vibrations of carbon-oxygen single bonds.

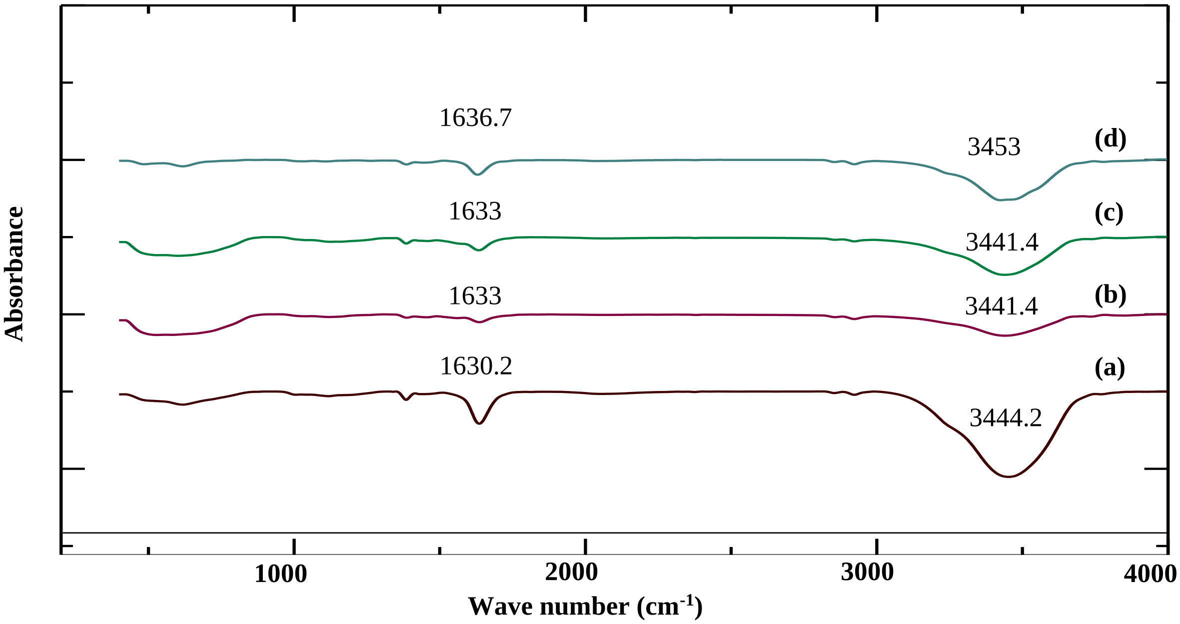


Fig. (10) *FTIR representations. (a) TiO_2. (b) GTNC sample (2). (c) GTNC sample (1). (d) Graphene (RGO).*

3.5 Photo-Electrochemical Measurements

CAM was conducted to determine the photocurrent stability of GTNC samples (1) and (2), and the results are displayed in Fig. (**11**). The tests were performed by applying a bias of 1.17 V for 800 s to each sample. Fig. (**11**) shows the CAM curve for 800 s at the desired electrochemical potential. Initially, the sample was left for 60 s in the dark until a steady current was attained. Then, UV-LED light (365 nm) with a maximum intensity of 50 mW cm^{-2} was applied for 600 s and then turned off. The findings show that the two electrodes have different curves, which indicate that the electrode prepared with GTNC sample (2) is more stable than that prepared with GTNC sample (1). Moreover, GTNC sample (2) has a higher peak current of 60 μA compared with that of GTNC sample (1), which indicates that the separation and transfer of electron-hole pairs are better in the case of GTNC sample (2) (the sample prepared with our novel method) because this sample has a higher loading content of titania particles, as shown by the TEM and EDX results; the combination of titania with a carbonaceous material forms a heterojunction nanostructure that restricts the electron-hole pair recombination rate in titania, leading to higher quantum activity and better photocatalytic activity, consistent with previous research Melian *et al*. [33].

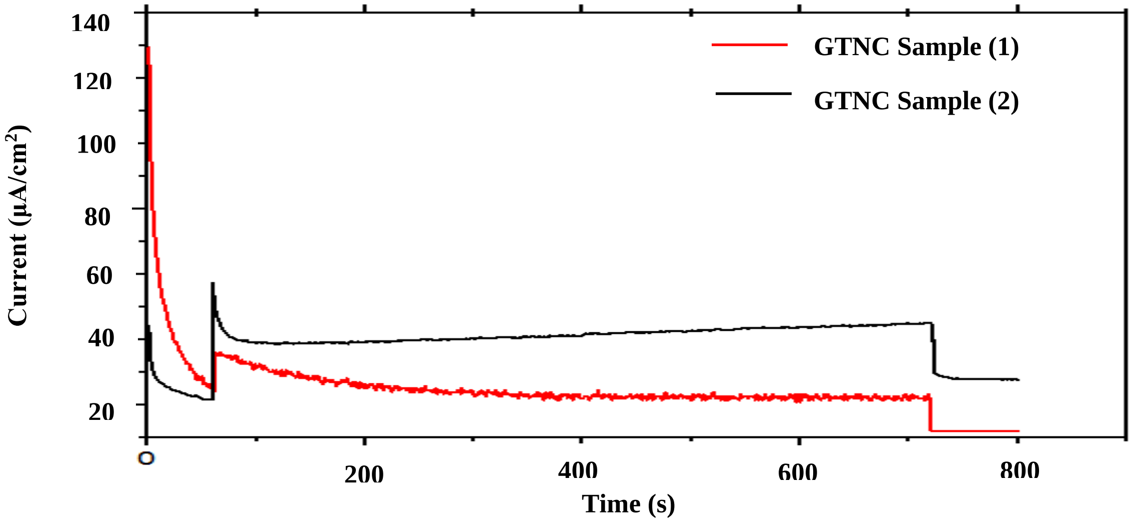


Fig. (11) *CAM measurements of GTNC sample (1) and GTNC sample (2) over 800 s (60 s in the dark, then 600 s under UV-LED light (365 nm) with a maximum intensity of 50 mW cm^{-2}, then dark again) at 1.17 V vs. Ag/AgCl.*

LSV was used to investigate the capabilities of the electrodes prepared with GTNC samples (1) and (2). The LSV sweep was conducted from -1 V to +1 V *vs.* Ag/AgCl at a scan rate of 0.05 V/s under chopped light irradiation (UV-LED, 365 nm). The photocatalytic activity of a semiconductor material depends on the amount of current generated due to the transfer of electrons from the photoanode electrode to the counter electrode under light irradiation. The photocurrent measurements of the GTNC sample (1) and (2) electrodes are shown in Fig. (**12**). The generation of photocurrent in the samples through multiple on-off cycles is observed, which indicates that the electrodes are stable and that the photocurrent is quite reversible.

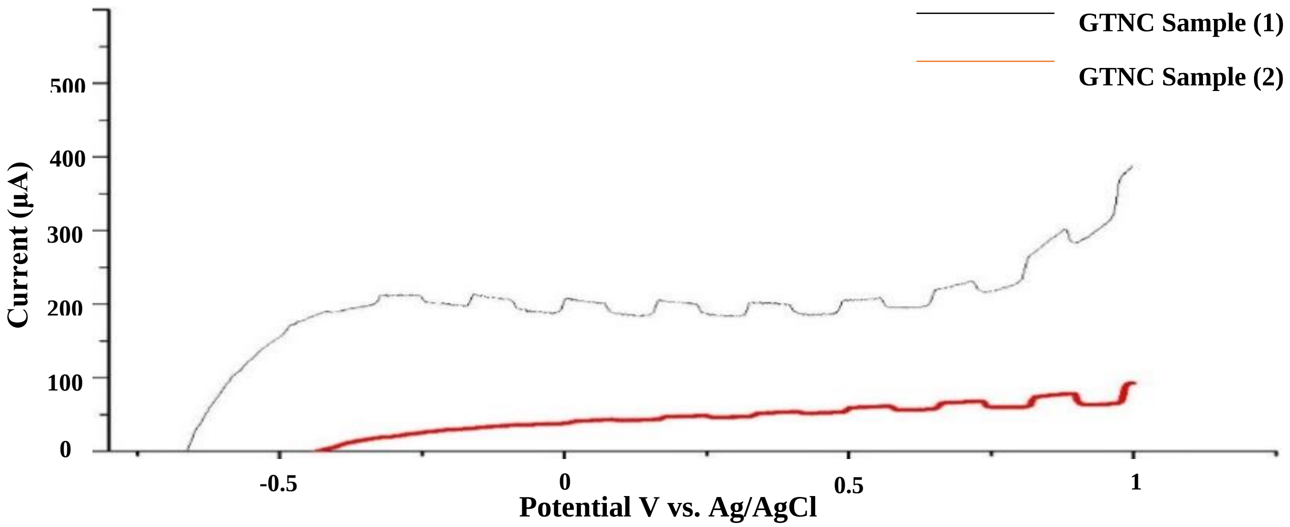


Fig. (12) *Linear scan voltammograms of GTNC samples (1) and (2) under dark-light cycles. Measurements were performed in a three-electrode configuration in 0.5 M* Na_2SO_4 *from -1 V to +1 V vs. Ag/AgCl at a scan rate of 0.05 V/s under UV-LED (365 nm) irradiation.*

4. Conclusion

- A new methodology has been established for producing graphene-titanium dioxide nanocomposites (GTNCs) with an excellent distribution and a high loading content of titanium dioxide on the graphene sheets.
- High calcination temperature 650°C resulted in promoting the formation of spherical nano-titanium dioxide in the anatase phase with very high crystallinity with small particle diameters ranging from 9 nm to 25 nm.
- The as prepared graphene (RGO) exhibited minimal flake folding and a high carbon content of 81.28% with a low oxygen-to-carbon atomic ratio of 0.172.
- GTNC sample (2) produced with this novel approach, shows a 96.6% increase in titania content over that of GTNC sample (1) and a more homogeneous distribution of spherical anatase titanium dioxide nanoparticles on the graphene (RGO) sheets, which provide it with superior crystallographic and physiochemical properties due to the better nucleation and growth of the titania particles.
- The FTIR results show that GTNC samples (1) and (2) have functional groups of C-O, C-H, O-H and H_2O adsorbed on their surfaces.
- The XRD results show that GTNC samples (1) and (2) have similar diffraction patterns, with a small difference in the width of the peak at a 2theta value of 25°.
- The repeatability of our novel process is confirmed by the TEM and EDX analysis of GTNC sample (3).

- Chronoamperometry measurements indicate the electrode prepared with GTNC sample (2) is more stable than that prepared with GTNC sample (1). Moreover, GTNC sample (2) has a higher peak current of 60 μA compared with that of GTNC sample (1), which indicates that the separation and transfer of electron-hole pairs are better in the case of GTNC sample (2). According to the LSV results, the generation of photocurrent in the samples can be observed through multiple on-off cycles, which indicates that the electrodes are stable and that the photocurrent is quite reversible.

List of Abbreviations

GTNC	Graphene Titanium Dioxide Nano Composite
TEM	Transmission Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray Diffraction Spectroscopy
UV	Ultra-Violet
PEC	Photo Electro-Chemical
EPD	Electrophoretic deposition
FTO	Fluorine doped tin oxide
LSV	Linear Sweep Voltammetry
CAM	Chronoamperometry

Conflict of Interest

The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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