Journal of Materials and Environmental Science
ISSN : 2028-2508
CODEN : JMESCN

Copyright © 2021,
University of Mohammed Premier
Oujda Morocco

J. Mater. Environ. Sci., 2021, Volume 12, Issue 03, Page 483-496

http://www.jmaterenvironsci.com

Fabrication of a novel composite material used for thermo-cracking of Plastic Waste

Ameen Abdelrahman[1]*, A. Farghali[1], A.H. Zaki[2], Asmaa S. Hamouda[3]

[1]*Department of Renewable Energy Science & Engineering, Faculty of Postgraduate Studies for Advanced Science (PSAS), Beni-Suef University, P.O. Box 62511 Beni-Suef, Egypt*

[2]*Department of Materials Science and nanotechnology, Faculty of Postgraduate Studies for Advanced Sciences (PSAS), Beni-Suef University, P.O. Box 62511 Beni-Suef, Egypt*

[3]*Department of Environmental Sciences and Industrial Development, Faculty of Postgraduate Studies for Advanced Sciences (PSAS), Beni-Suef University, P.O. Box 62511 Beni-Suef, Egypt*

Received 25 Oct 2020,
Revised 25 Feb 2021,
Accepted 05 April 2021

Keywords:
Pyrolysis, AuNPs,TiO_2 : assembling : Graphene : Gas yields

Ameen Abderrahmana
chem.shaha@hotmail.com

Abstract

Today, everyone lives on that planet has observed a climate change, one of the biggest indirect impact causes on it, its plastic waste accumulated and ways of gets off. However, pyrolysis method is an old way to recycle biomass, and plastic waste, in that work we reached upgrade specific materials used as a Thermo –catalytic works on conversion plastic waste to renewable fuel, and benefit solids waste (char) .that techniques based on setting –up fixed bad reactor system with optimizing different parameter (temperature, loading catalyst and reaction time). Cracking industrial composite materials are consist of metals (Au and TiO_2) in Nano size assembled on thin layer graphene. Various spectroscopic measurements and analysis such as XRD, TEM, SEM, and Uv had been carried out to characterize novel composite and its applicable. Alongside, we get novel materials composite conducted at 600 ^{o}C, at loading ratio % 0. 1wt with high ratio of gas yield distribution Methane and syngas outcome.

1. Introduction

Recently, the world seeks to get effective solutions for climate change which build up on Green gases, increase temperature, and ecology plastic waste municipal. Hundreds of researchers worked on "how management solid plastic waste "throughout recyclable and reduce or even incineration and land filling .one of the best conventional method is pyrolysis and gasification process. Various studies have been investigated on industrial municipal solid wastes such as rubber tyres, styrene, TFE, PVC, PEHD and PELD, addition to many reporters recorded on upgrading and development pyrolysis technologies concern operation and process such as reactor sorts used (fixed, or plasma), reaction mechanism and product distribution characterization [1-4]. On the other side, chemicals engineers and materials science reviewers were interested studying ways to increase fuel production, tar reduce, gases ratio distribution. To applied pyrolysis reaction, it has to take in our consideration, different factors and premasters [5]. such as range of heating rate, catalyst used, pyrolysis products, time and kinetics modeling [6], from our knowledge, thermo gravimetric analysis (TGA) for some sort of plastic waste has been reported between t 410°C till 520°C [7]. For instance, high density polyethylene (HDPE) the thermal degradation is shown between 378 to 404°C and it completes at 517–539°C, [8] and Poly vinyl chloride (PVC) has two stages

260-385°C wherein ~62% weight loss and 385-520°C wherein ~22% of weight loss occurred Alongside, pyrolysis previous related to pyrolysis revealed the effecting different catalysts and adsorbents materials on improving the quality and deformation of the pyrolysis products. for examples, Brominat flame retarded (BFR) plastics, Silicates. [9,10] zeolites and clay rocks [11]. Fluid catalytic cracking (FCC) catalysts [12] metallic oxides [13,14], and ceramic materials.[15] Furthermore, using of catalytical materials is improved quality of oils, [16-20] and it allows a narrower range of hydrocarbons to be produced and created from municipal solid waste (MSW). Poly alkene plastics and heavy oil recyclable. particle size and metal oxide surface area (SiO_2, Al_2O_3, TiO_2 and CeO_2) had great effect on different types of degradation especially, free radical MMA polymerization [21,22].

Recently, one of the interested industrial applicable Metals is titanium. Due to its specific characterize, for instance, structure size of Titania nanoparticles and photocataltically sensitivity. that properties, it makes it used in different application such as optical devices, sensors, and photo catalysis [23,24]. As far the Performance of titian application is depending on particle size, crystallinity and the morphology. [25,26] Furthermore, TiO_2 is used as metal support interaction, chemical stability ,and acid–base property for different others metals oxides[27] .on the other side according our back information , since 2004, graphene is became a favorable materials in different application filed, especially in material engineering , due to its unique properties such two-dimensional (2D) structure, mechanicals electric and physical properties [28–30] one the other hand, worlds towards to discover materials have both environmental characteristic and low cost value , thus graphene is one of that materials .addition to , graphene is good supporter for others materials such as metals, ceramics and carbonaceous fibers materials. Integration of different materials together, will created Novel materials which has unique properties. carbon nanotube and graphen structure are used to promoted the efficiency of TiO transparent conductors [31–33] graphene-based [34, 35]. Recently, there are many methods used synthesize graphene by physical and chemical methods such as chemical vapor deposition (CVD), epitaxial growth, mechanical exfoliation, and reduction of graphite oxide [36, 37].also, direct convey of the graphene using CVD technique, vacuum filtration and Langmuir–Blodgett (LB) assembly .[38–40] Various studies and experiments are work on employ metals oxides and nanoparticles dissimilar base fluids e.g. graphene, [41, 42] Pd in water, [43] Pd/Ag in ethylene glycol and distilled water [44] and TiO_2 in ethylene glycol. [45] in that works we created a composite material composed of assembled Titanium and Gold in Nano size structure on a thin film of graphene, then it used as a thermos catalytically catalyst to convert plastic waste to fuel.

2. Methodology

2.1. Materials.

Samples preparation

Waste plastics samples were obtained from different sorts of caps and bottles. These were flushed and cleaned with several times water, dried, cut, and grinded into small portions. All chemicals used for nano-oxide metals were purchased from Loba Cheme (India). Without any purification.

2.2 *Experiments*

The nanoparticle of titanium oxide (TiO_2) powder was prepared by the physical grinding method. Amount of 50 g TiO_2 powder was put in a ball grinding machine (RETSCH Planetary Ball Mills Type PM 400) works at high-speed rotation. It was uniformly crushed and grinded for 5 hrs. collected material with utmost precaution to avoid any contamination. Finely, we got nano-size powder TiO_2.

Preparation of the gold nanoparticles.

To prepare Gold nanoparticles (AuNPs), it sizes around ~ 25-30 nm using reduction method of 2 ml of Tetrachloroauric acid (HAuCl4) (1 %) mixed with 2.5 ml of and tri-sodium citrate (1 %), with slightly adding and slowly stirring until the color has been changed to winy red [46].

Assembled of nanoparticles on thin graphene.

By dissolving 0.5 mg of Nano powder graphene in 20 ml hot distilled water for two days flocculated swelling addition to faculties spreading of NPs on its surface, then add 1 ml of Au –NPS string overnight, follow with adding 5 ml of TiO_2, leave it on ultrasonic string till 5 hrs, then filtrate, washed, and dried overnight. composite is ready to characterize and applicable as shown in figure [1].

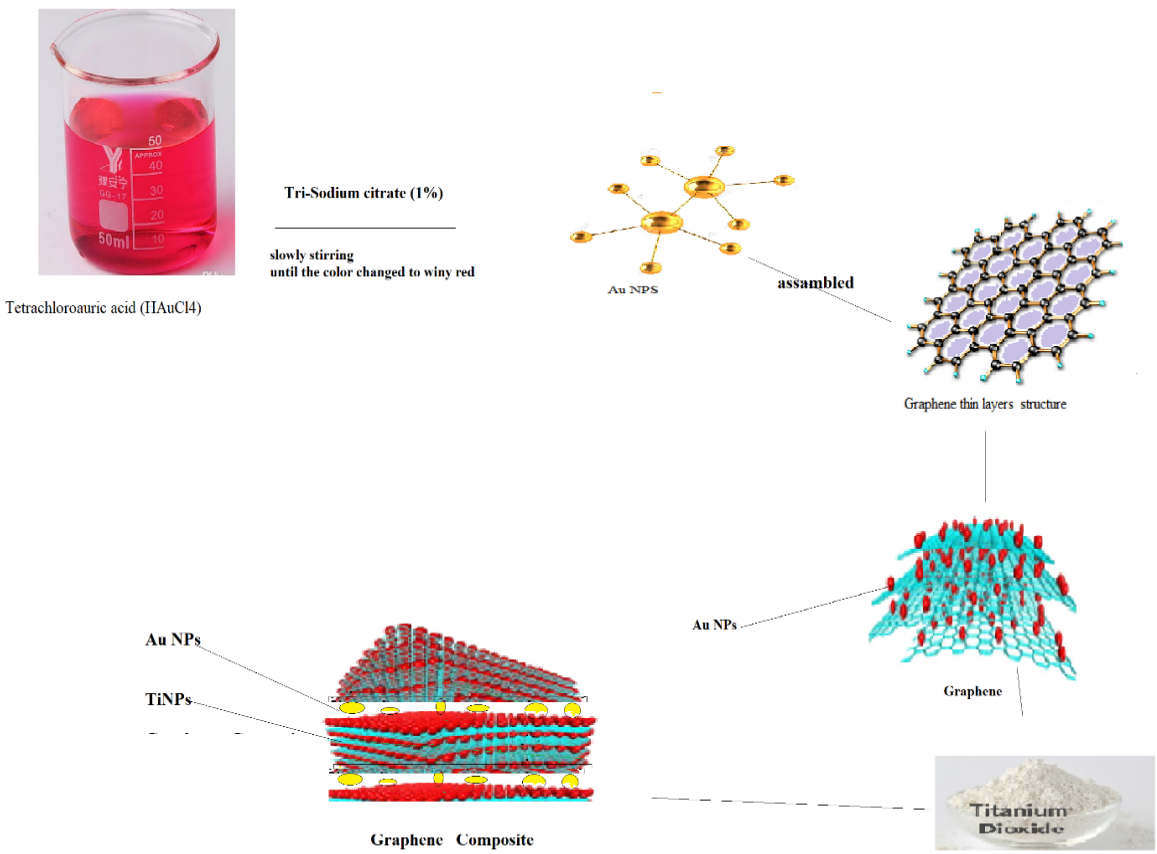

Figure 1. Illustrate the pathway thin-layers of graphene assembled NPs composite preparation method

2.3 Product characterisation

2.3.1 ***TEM*** characterize. All samples characterize were carried out utilize Transmission electron microscopy (TEM) Model: JEOL JEM-1230 operating at 120 kV associated specifically a CCD camera. All analysis has been done at National Research Centre. Measurements of samples conduct using a convenient method of prepared samples to get good results throughout the TEM image utilizing copper grids on an amorphous carbon film.

2.3.2 ***XRD*** analysis samples were carried out using X-ray diffraction patterns. It's a Pan Analytical Model X' Pert Pro, which was outfit with CuKα works at radiation (λ = 0.1542 nm), Ni-filter associated with the detector. The diffractograms were investigated at a 2θ range of 0.5°–90° and size of 0.02 Å. All measurements were conducted at Research Central Metallurgical Research and Development Institute.

2.3.3 All analysis has confirmed by ***Ultraviolet-visible*** (model UV-1800 Shimadzu UV spectrophotometer) spectral analysis around a wavelength of 150 e 1000 nm. All measurements have been done at Beni Suef University.

2.3.4 ***Pyrolysis and gasification*** processes were carried out using a fixed bed reactor which is heated utilizing an electrical furnace. Pyrolytic system is set up in environment department, Beni-Suef University.

2.3.5 Gaseous yield products were characterized using ***GC***, a VARIAN model CP-3800. All gases samples measurements have been carried out at the Egyptian Petroleum Research Institute (EPRI), Nasr city, Cairo.

3. Results and discussion

3.1 characterization

3.1 .1 Elemental analysis of Plastic waste (PW)

Table (1) point out the element analysis of plastic waste (PW) sample. The important reason to do that experiment to know how the main content of the plastic waste sample, add to the quality of gas yield produce after applied catalytic pyrolysis sample. The table illustrates the main element component like nitrogen, carbon, and hydrogen. The volatile matter is 100% in the proximate analysis. Due to the negligible percentage of ash in the sample, its degradation occurs with minimal formation of the residue. Thermal catalytic cracking was investigated using TGA Instrument modal SDTQ 600 simultaneous thermogravimetric analyzer. All measurements were carried out at the Egyptian Petroleum Research Institute. The samples were heated under nitrogen flow (100 ml min-1) from 500°C t0 800^{0}C at different flow rates 5, 10, and 20 min.

Table 1: element analysis of plastic waste.

Sample Code	N %	C %	S %	H %
Pw	1.028	64.05	Nil	3.77

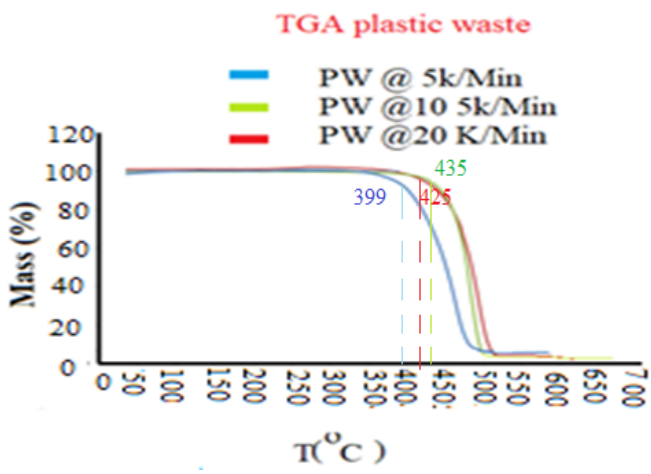

Figure 2. TDG curve for Plastic Waste characterization at different Heating flow rates.

Composite Thermal plastic waste analysis at different flow rates under N_2 atmosphere. thermal degradation is beginning from 100 to 530°C, passing different stage, solids, liquid, and gases associated with losing some molecules like CO_2 or water and small carbon chain and lights olefins .TGA enables us which the best conditions for pyrolysis reactions such as flow rate, and heating rate. Figure 2 illustrates

the plastic waste decomposition at a flow rate of 10°C/min. there are some changes in sample mass fraction related to raising the temperature. Degradation zone is approximately centralized on 425, 450, and 460 ºC for three different heating rates of 5, 10 and 20 °C/min.

3.2 2 material composite characterization.

TEM characterize.

All prepared samples were investigated utilize the Transmission electron microscopy (TEM) Model: JEOL JEM-1230 design at 120 kV with specifically a CCD camera. All measurements have been done at the National Research Centre. Using copper grids on an amorphous carbon film for samples measurement. Regard figure 3, we noticed numerous of TiO_2- and Au- nanoparticles are deposited on the graphene surface, with uniformly distributed and size around 15 to 25 nm. small size of NPs is created active sides both (Au – Au, and Ti- Ti) with metals based on metallic bond and metals with graphene throughout ππ bond TiO_2, and Au size diameter are promoted activation energy gaps of graphene structure, because both of two metals is characterized with photocatalytic phenomena.

XRD analysis. The TiO_2, AuNPs, and their composite were characterized using X-ray diffraction patterns. It's a Pan Analytical Model X' Pert Pro, which was outfit with CuKα works at radiation (λ = 0.1542 nm), Ni-filter linked with the detector. The diffractograms were operated at a 2θ range of 0.5°–90° and size of 0.02 Å. All measurements and calculation were conducted at Research Central Metallurgical Research and Development Institute.

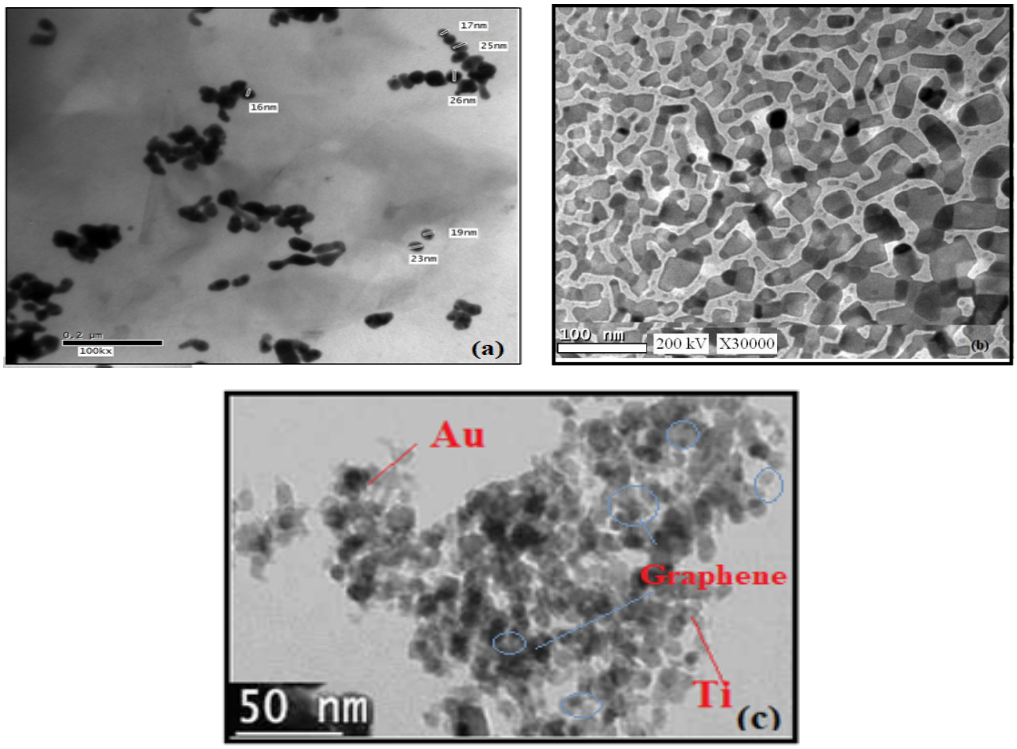

Figure 3. a) TEM Au-NPs, **b)** TiO_2, **c)** Graphene assembled NPs Metal

Referring to figure 4 explained XRD characterize for TiO_2, the intensity numerous of various peaks have sharply appeared area at 2θ angles: 21°, 25.5°, 27 °, 38°, 57°, and 63° with slightly shifted appear in composite on the same figure, furthermore, there are new peaks of XRD patterns appeared and disappeared in new composite. for instance, the high intensity at θ 19 °,27 °, 38 °, and 52 ° indicate the TiO_2 submerged or deposited on a graphene sheet.

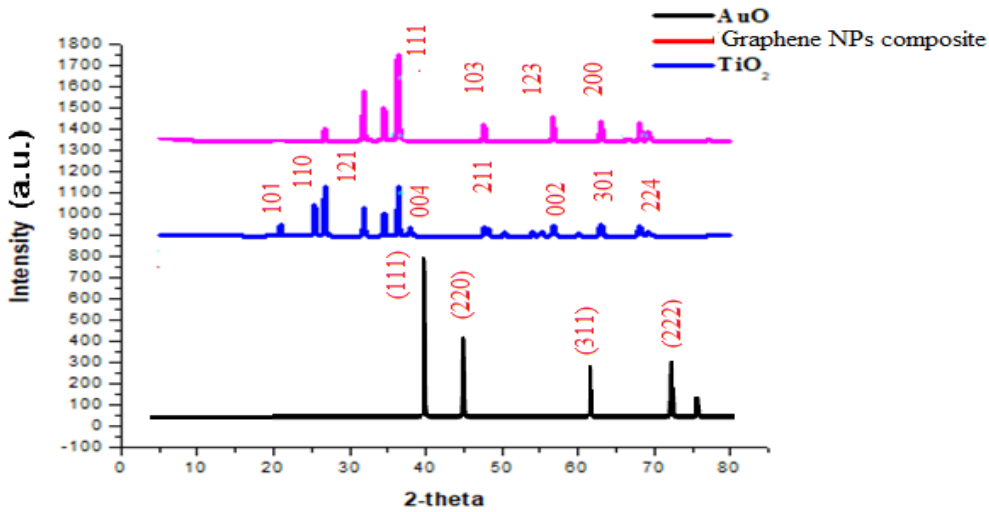

Figure 4. XRD for gold, Titanium, and Graphene NPs composite

Also, figure 4 affirm synthesis **Au NPs**, which appear purely crystalline in their nature, its unique size around 20 to 25 nm, and appearance of new lines at 2θ angles: 18°, 38°,43° and 63° regarded to XRD analysis in figure 4 furthermore, observed there were slightly displacement of some peaks and New Peaks of XRD patterns appeared which are high intensity at θ 19°,27 °,38 °, and 52 ° due to new composite compound has been formed.

Ultraviolet-visible (model UV-1800 Shimadzu UV spectrophotometer) spectral analysis specific wavelength around between 300 and 800 nm. All measurements have been conducted in the research center at Beni Suef University. figure [5] show as three spectrums for Au-NPs, TiO-NPs and, colloidal solution graphene loading nanoparticles figure [5]. We found Au NPs appear at 520 nm, addition to specific signal for titanium also appears between 370 to 420 nm. two peaks appeared on mixture colloidal with small shifted than origin peak, which is indictors for assembled of nanoparticles on the thin surface of Graphene.

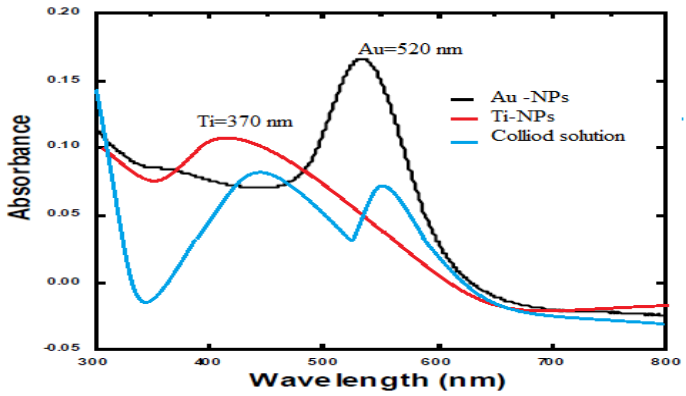

Figure 5. UV measurement for NPs metals colloid solution

Inductively coupled plasma (ICP) has been conducted in national central research, Cairo. It is used to a physical method of chemical analysis. It takes simultaneously a few minutes with using blank HNO_3 its conc. (2-5 %). colloidal solution sample is injected into an argon plasma (temperature around 6000K). Procreated by a pneumatic device (nebulizer). With regarding to Figure 6 shows the sample contains numerous of elements with specific concentrations, different signals appear gold, titanium and carbon-

related to graphene in solutions. To investigated the Au, And Ti NPs suspended and intergraded inside and on the surface of graphene thin layer.

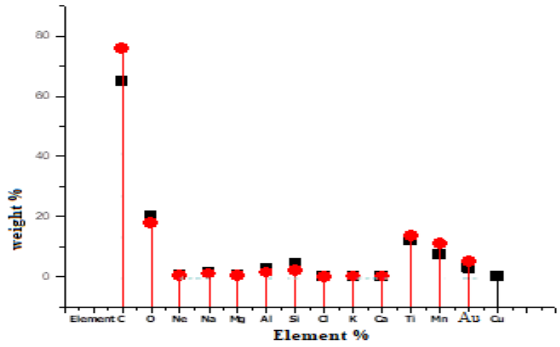

Figure 6. ICP colloid solution

3.3 Pyrolysis system design.

Pyrolysis system was set up research the laboratory environment department, Beni-Suef university using a fixed bed reactor, an electrical furnace temperature control, and quartz sampler collector .in order to apply prepared composite, we need to set up the pyrolytic system, which is consist of main parts (furnace, bed reactor, thermocouple controller and feeding parts (valves, N_2 cylinder, union connection, and Quartz sampler collector) as shown as figure 7 below.

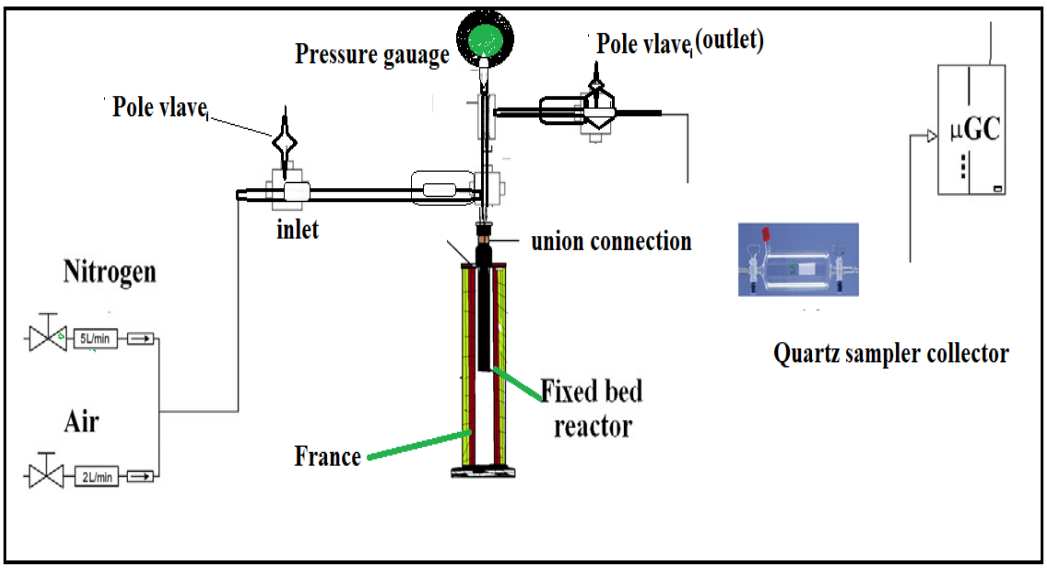

Figure 7. pyrolysis system setting up

In the beginning, various running had been done to justify and optimize the best conditions (reaction time, heating rate, feeding catalyst, and plastic samples). Using 1g of the plastic waste sample plus to loading catalyst, close outlet valve, open N_2 flow, then closer inlet valve, adjust all parameters (the temperature at 600 $^{\circ}$C, for 40 min.). Eventually, switch off the furnace, leave it until being cool at room temperature, after that open outlet valve, collection gases to GC analyzer using quartz tuber sampler with displacement. Char also collected using physical methods to be weighted and characterized.

3.4 Studying thermo- catalytically on plastic waste (PW) degradation.

in order to get the best results with high gas yield and char products, we have to Optimize different parameters to upgrade and improve the performance of the reactor. Temperature one of that factor,

plastic waste TGA measurement is one important guide for us to know initials temperature range, effecting of composite on decrease rate of reaction (ΔH), and reduction time of the process. Throughout our experiments and data summarized in figure [8]. There are certain conditions to finalize of pyrolysis reaction, we noticed increasing of pressure with the increasing temperature gradually until to be constant between 590 °c to 600 °c. that indicates complete cracking and conversion solid to gases, that's reaction happen at a certain time which takes place 45 minutes. Regard to Figure 9 explained the different comparison plastic waste (PW) pyrolysis in presence of prepared composite and non-composite. reaction has been occurred at 600° C for 40 minutes. There were different results during the reaction in case existence composite which conclude follow: gas yield ratio is higher than in presence of composite catalyst, it is increasing rapidly until reach more than 0.08 Kg/M^3, associated with a high ratio of char conversion is equal % 0.47 wt.

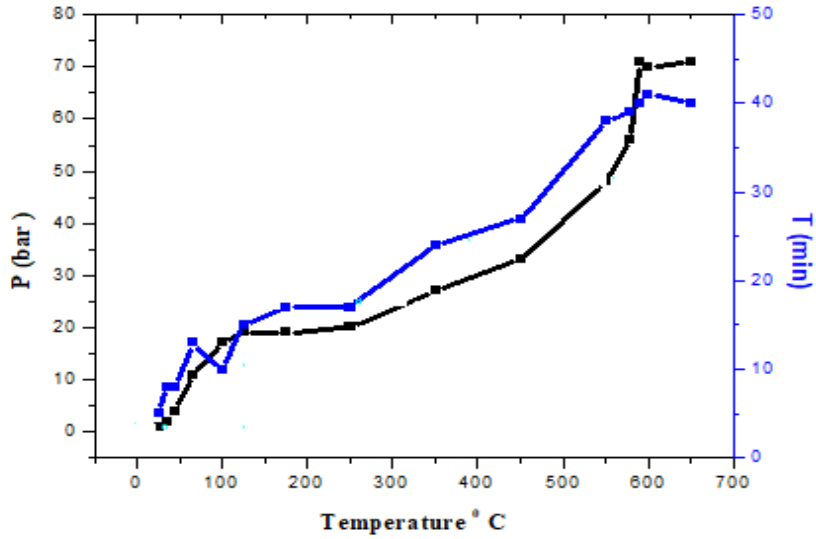

Figure 8. show the optimize conditions pyrolysis reaction

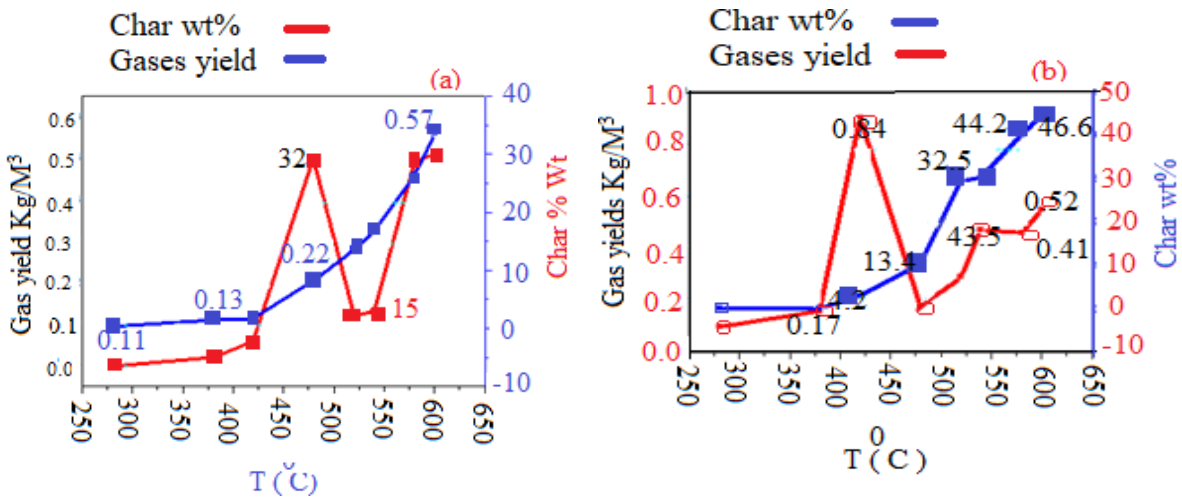

Figure 9. a) pyrolysis non additives **b)** pyrolysis at 0.1 % loading graphene composites

Furthermore, quality of products (dry not tar residual) is a good grade in case composite. On the other hand, to investigated papered composite, we have to choose and quantify the best loading that will work during the pyrolysis process. In that experiment, we used various amounts of loading composite 0.02,0.08,0.1,0.25, and 0.4 at constant parameters such as temperature and reaction time. Results were proofed, the best ratio of used catalyst is wt.0.1 of material. due to, getting highly reading which was summarized in figure 10 the best quantity of gas yields, and char conversion.

3.5 Evaluation of effecting of composite material on gas yields distributions.

Gaseous yield products distributions. pyrolytic Gases collector were measurement using GC, at the Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo using a VARIAN model CP-3800. To judge and measurement the efficiency of prepared composite .it has to show the effecting of its material on final products upon quality, new products, forming and deforming components, and quantities. Referring Figure 11 which show the comparison of GC for PW pyrolysis at different cases, non-additives composite, with the material, and stander GC, we noticed increasing in quantity of specific element components such as Methane, Hydrogen, and also decreasing of the others like CO_2, $N_2$and CO, that is good indicators, to justify reaction has been done with the good conversion.

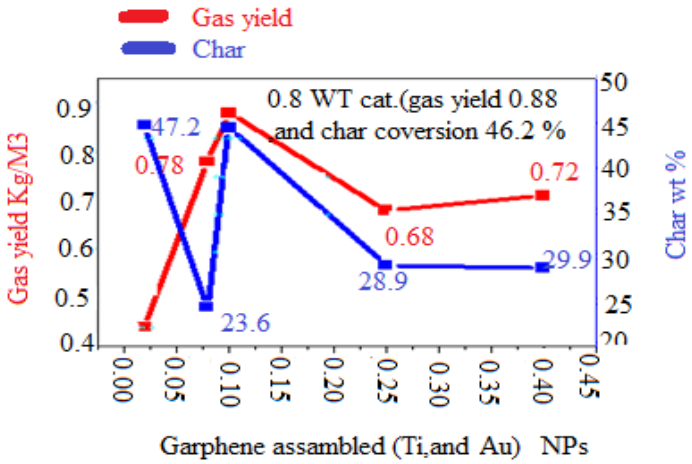

Figure 10. pyrolysis at different loading ratio of prepared graphene NPs -catalyst.

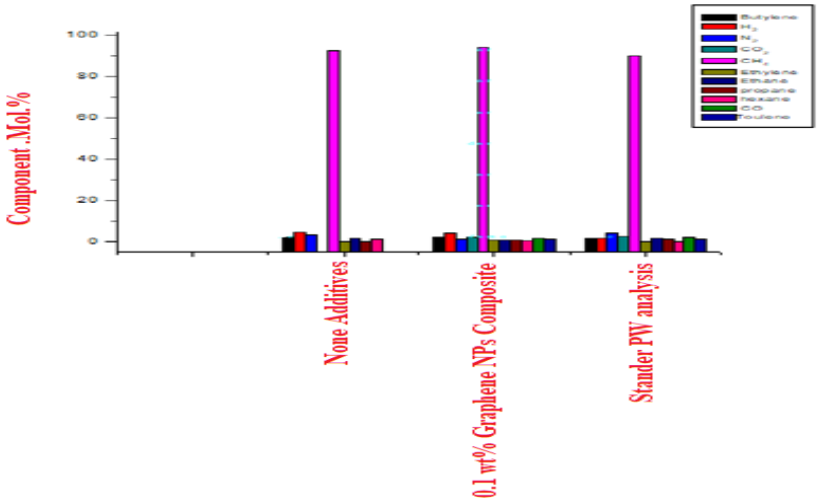

Figure 11. GC gas yields distribution product.

Methane value is reached out % 95 in case adding 0.1 of composite, compared to 90, and 91 % to the others. Also, the ratio of H_2 is also equal to 4.8, that is means there is de- hydrogen reaction, forming unsaturated components, also CO, H_2 and syngas are produced during pyrolysis reaction, and increase of CO_2, it is also explained effecting of the new composite to capture CO to CO_2.

Char sample SEM analysis.

The SEM technique was used to study and describe the surface morphologies of pyrolytic product samples. According to figure 12 below, it describes the surface morphologies of the char samples contains numerous of spread particle on its surface black carbon and residual of graphene nanoparticles moreover

there is some fracture and deformation of the sample. On other figure13 shows a massive layered structure with tiny flakes and some formed interlayer spaces and some brightness of metals oxides appear on the surface ,it is indictors for titanium and gold oxides on a sample . SEM image description agree with EDX analysis in Figure 14. All measurements were carried out in Egyptian petroleum researcher center, using The Energy Dispersive X-ray Analysis (EDXA) to investigate the pyrolytic char samples at certain condition (feeding PW and 0.1 % of composite catalyst at temperature 600 °C, for 40 min.). Results are agreed with the same material composites. We found some ratio of the gold element, titanium oxides, and black carbon Skelton results from the decomposition of polymeric materials under high temperature. There are some other elements that appear in the diagram, it might be due to presence of impurities in the sample in figure [14].

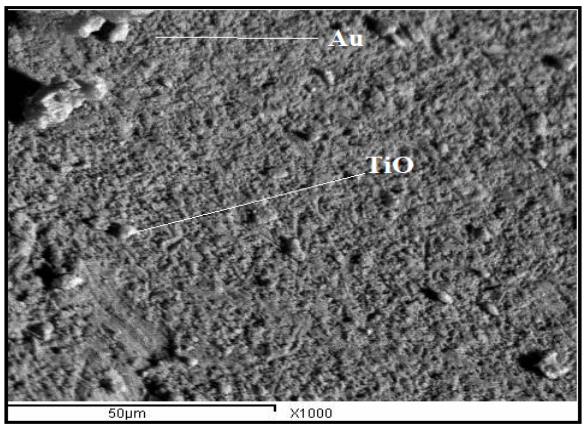

Figure 12. SEM composite materials

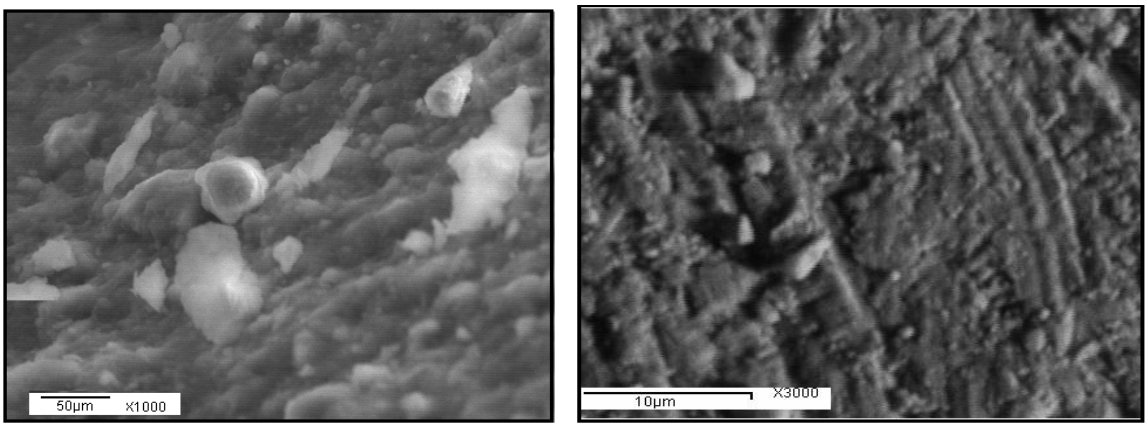

Figure 13. SEM sample coke after pyrolysis

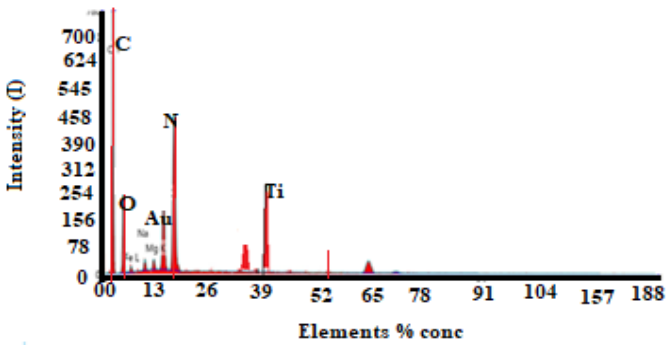

Figure 14. EDAX for gasified char sample

Conclusion

Today worlds forward to promote alternative energy using many resources, one of that resources is plastic waste recyclable. Plastic waste, it takes hundred –hundred years to decay .recyclable plastic waste is too costly, especially pyrolysis and gasification methods but, they are better than other ways such as landfill, underground dumping, and burnt as incineration. In order to reduce cost and environmental problem issues (green gases emission, climate change), we reached to fabricated composite materials composed of nanoparticles metals (Ti and Au) assembled on a thin layer of graphene used as a catalyst to thermo-cracking of plastic waste .we got good results during their application. High Gas yields and black carbon char were obtained at % 0.1 these composite. The catalytic activity of graphene is increased by impregnated and assembled Ti, and Au metals. we conclude composite material is capable to work as a reducer for organic compounds during the pyrolysis process.

THE AUTHORS ORCID ID

Ameen Abdelrahman https://orcid.org/0000-0002-7177-2687
Ahmed Farghali https://orcid.org/0000-0002-9270-9855
Ayman Zaki https://orcid.org/0000-0003-0026-1721
Asmaa S. Hamouda https://orcid.org/0000-0002-1991-2347

Acknowledgement-I would like to thank my former and current lab members Dr Ali Radwan and all his Colleagues in National Research Center (NRC), Cairo Egypt for their help and expertise complete my research work in biomass field

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

References

[1] P.T. Williams, J.Scheirs, W. Kaminsky W (Eds.) Feedstock recycling and pyrolysis of waste plastics: Converting waste plastics into diesel and other fuels. John Wiley & Sons Press, West Sussex, .(2006), pp. 285–309 https://doi.org/10.1016/j.psep.2016.06.022

[2] P.T. Williams Pyrolysis of waste tyres: A review. *Waste Management* 33 (2013) 1714– 1728. https://doi.org/10.1016/j.wasman.2013.05.003

[3] X. Yang, L. Sun, J. Xiang, S. Hu, S. Su, Pyrolysis and dehalogenation of plastics from waste electrical and electronic equipment (WEEE): A review. *Waste Management* 33 (2013) 462–473. https://doi.org/10.1016/j.wasman.2012.07.025

[4] A. Quek, R. Balasubramanian Liquefaction of waste tires by pyrolysis for oil and chemicals – A review. *J Anal Appl Pyrolysis* 101 (2013) 1–16. https://doi.org/10.1016/j.jaap.2013.02.016

[5] SM. Al-Salem, P. Lettieri, J. Baeyens, The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals. *Prog. Energy Combust. Sci* 36 (2010) 103–129. https://doi.org/10.1016/j.pecs.2009.09.001

[6] Q. Cepeliogullar , AE Putun Utilization of two different types of plastic wastes from daily and industrial life. In: Ozdemir C, Sahinkaya S, *Kalipci E OM (Eds.) ICOEST Conference, part 2, appadocia*, pp 694-706 (2013).

[7] BLF. Chin, S. Yusup, A. Al Shoaibi, P Kannan, C. Srinivasakannan, S.A. Sulaiman, Comparative studies on catalytic and non-catalytic co-gasification of rubber seed shell and high density polyethylene mixtures. *J. Clean. Prod* (2014) 303–314. https://doi.org/10.1016/j.jclepro.2014.02.039

[8] M. Hasegawa ,J. Fukuda, D.Kunii Gasification of solid waste in a fluidized bed reactor with circulating sand. *Resour Conserv Recycl.* 3 (1979) 143–153. 10.1016/0361-3658(79)90004-3

[9] A. López ,I. de Marco ,BM. Caballero ,MF . Laresgoiti ,A. Adrados Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. *Fuel Process. Technol* 92 (2011) 253–260. https://doi.org/10.1016/j.fuproc.2010.05.008

[10] A. López, I. D. Marco, B. M. Caballero, M F. Laresgoiti, A. Adrados , A. Aranzabal Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. Appl. Catal. B". 104 (2011) 211–219. https://doi.org/10.1016/j.apcatb.2011.03.030

[11] W.J. Hall ,PT. Williams Removal of organobromine compounds from the pyrolysis oils of flame retarded plastics using zeolite catalysts. *J Anal Appl Pyrolysis* 81 (2008) 139–147. https://doi.org/10.1016/j.jaap.2007.09.008

[12] O. Terakado , R.Ohhashi, M.Hirasawa Thermal degradation study of tetrabromobisphenol A under the presence metal oxide: comparison of bromine fixation ability. *J Anal Appl Pyrolysis* 91 (2011) 303–309. https://doi.org/10.1016/j.jaap.2011.03.006

[13] O. Terakado, R.Ohhashi M., Hirasawa Bromine fixation by metal oxide in pyrolysis of printed circuit board containing brominated flame retardant. *J Anal Appl Pyrolysis* 103 (2013) 216–221. https://doi.org/10.1016/j.jaap.2012.10.022

[14] S. Jung ,S.Kim, J.Kim Fast pyrolysis of a waste fraction of high impact polystyrene (HIPS) containing brominated flame retardants in a fluidized bed reactor: The effects of various Ca-based additives (CaO, Ca(OH)2 and oyster shells) on the removal of bromine. *Fuel* ,95 (2012) 514–520. https://doi.org/10.1016/j.fuel.2011.11.048

[15] R.A. Garcia, D.P. Serrano, D. Otero Catalytic cracking of HDPE over hybrid zeolitic-mesoporous materials, *J Anal Appl Pyrolysis,* 74 (2005) 379–386. https://doi.org/10.1016/j.jaap.2004.11.002

[16] N. Miskolczi, L. Bartha, G. Deàk Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks. *Polym. Degrad. Stab* 91(2006) 517–526. https://doi.org/10.1016/j.polymdegradstab.2005.01.056

[17]. J. Aguado, DP. Serrano, GS. Miguel, MC Castro ,S. Madrid Feedstock recycling of polyethylene in a two-step thermos-catalytic reaction system. *J. Anal. Appl. Pyrolysis* 79 (2007) 415–423. https://doi.org/10.1016/j.jaap.2006.11.008

[18] A. Marcilla, MdR. Hernandez, AN Garica, Study of the polymer-catalyst contact effectively and the heating rate influence on the HDPE pyrolysis. *J Anal Appl Pyrolysis* 79 (2007) 424–432. https://doi.org/10.1016/j.jaap.2006.10.017

[19] M. Olazar , G.Lopez, M.Amutio ,G. Elordi,R. Aguado ,J. Bilbao Influence of FCC catalyst steaming on HDPE pyrolysis product distribution. *J Anal Appl Pyrolysis* 85 (2009) 359–365. https://doi.org/10.1016/j.jaap.2008.10.016

[20] H. Kumar , Manisha, P.Sangwan .Synthesis and Characterization of MnO2 Nanoparticles using Co-precipitation. *Int. J. Chem. Eng.* 3 (2013) 155-160. https://doi.org/10.46602/jcsn.v45i4.489

[21] A.J. Magenau, Y.Kwak, &K. Matyjaszewski, ATRP of methacrylates utilizing CuIIX2/L and copper wire. *Macromolecules,* 43(23) (2010) 9682-9689. https://doi.org/10.1021/ma102051q

[22] L. Xue, ,U.S. Agarwal, & P.J Lemstra, High molecular weight PMMA by ATRP. *Macromolecules,* 35(22) (2002) 8650-8652. https://doi.org/10.1021/ma020905s

[23] O. Harizanov, & A.Harizanova, Development and investigation of sol–gel solutions for the formation of TiO2 coatings. Sol. Energy Mater Sol. *Cells* 63(2) (2000) 185-195. https://doi.org/10.1016/S0927-0248(00)00008-8

[24] B. Li, X.Wang, M. Yan, & L.Li, Preparation and characterization of nano-TiO2 powder. *Mater. Chem. Phys*. 78(1) (2003) 184-188. https://doi.org/10.1016/S0254-0584(02)00226-2

[25] M.A. Behnajady, N. Modirshahla, M.Shokri, H. Elham, & A. Zeininezhad, The effect of particle size and crystal structure of titanium dioxide nanoparticles on the photocatalytic properties. *J. Environ. Sci. Health A,* 43(5) (2008) 460-467. https://doi.org/10.1080/10934520701796267

[26] K.M. Lee, V. Suryanarayanan, &K.C. Ho, A study on the electron transport properties of TiO2 electrodes in dye-sensitized solar cells. Sol. Energy Mater Sol. *Cells* 91(15-16) (2007) 1416-1420. https://doi.org/10.1016/j.solmat.2007.03.007

[27] S. Bagheri, N. Muhd Julkapli, & S.Bee Abd Hamid, Titanium dioxide as a catalyst support in heterogeneous catalysis. *Sci. World J* , (2014). | https://doi.org/10.1155/2014/727496

[28] K.S. Novoselov, A.K Geim, S.V Morozov, D. Jiang,Y. Zhang, S.V. Dubonos, &A.A Firsov, Electric field effect in atomically thin carbon films. *Science,* 306(5696) (2004) 666-669. DOI: 10.1126/science.1102896

[29] D.A. Dikin, S.Stankovich, E.J. Zimney, R.D. Piner, G.H. Dommett, G. Evmenenko, & R.S.Ruoff, Preparation and characterization of graphene oxide paper. *Nature,* 448(7152) (2007) 457-460.

[30] S. Stankovich, D.A. Dikin, R.D. Piner, K.A., Kohlhaas, A. Kleinhammes, Y. Jia, & R.S Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon,* 45(7) (2007) 1558-1565. https://doi.org/10.1016/j.carbon.2007.02.034

[31] H. Peng, W. Dang, J. Cao, Y. Chen, D. Wu, W, Zheng, & Z. Liu, Topological insulator nanostructures for near-infrared transparent flexible electrodes. Nature chemistry, 4(4) (2012). 281-286. H.Peng, W. Dang, J.Cao, Y. Chen, D. Wu, W, Zheng, & Z. Liu, Topological insulator nanostructures for near-infrared transparent flexible electrodes. *Nature chemistry,* 4(4) (2012) 281-286.

[32] R. Karthick ,M.Brindha ,M. Selvaraj andS. Ramu Stable Colloidal Dispersion of Functionalized Reduced Graphene Oxide in Aqueous Medium for Transparent Conductive Film, *J. Colloid Interface Sci*. 406 (2013) 69 https://doi.org/10.1016/j.jcis.2013.06.006

[33] J. Liu, N.R. Davis, D.S. Liu & P.T Hammond, Highly transparent mixed electron and proton conducting polymer membranes. *J. Mater. Chem*. 22(31) (2012) 15534-15539. DOI: 10.1039/C2JM32296J

[34] SH. Kim, Y. Yu, Y.Z. Li ,T. Xu and J.F Zhi A hybrid reduction procedure for preparing flexible transparent graphene films with improved electrical properties, *J. Mater.Chem.* 22 (2012) 18306 DOI: 10.1039/C2JM31048A

[35] I. Khrapach ,F. Withers ,T.H. Bointon, Polyushkin D K,Barnes W L, Russo S and Craciun M F Adv. Mater. (2012) 24 2844. https://doi.org/10.1002/adma.201200489

[36] Y. Zhu, S. Murali, W. Cai, X.Li, ,J.W Suk, J.R. Potts& R.S. Ruoff Graphene and graphene oxide: synthesis, properties, and applications. Advanced materials, 22(35), (2010). 3906-3924. https://doi.org/10.1002/adma.201001068

[37] D.S. Hecht, L. Hu and G. Irvin, Emerging Transparent Electrodes Based on Thin Films of Carbon Nanotubes, Graphene, and Metallic Nanostructures, *Adv. Mater.* 23 (2011) 1482 https://doi.org/10.1002/adma.201003188

[38] Q. Zheng, B. Zhang, X. Lin, X. Shen, N. Yousefi, Z.D Huang, & J.K Kim Highly transparent and conducting ultralarge graphene oxide/single-walled carbon nanotube hybrid films produced by Langmuir–Blodgett assembly. *J. Mater. Chem,* 22(48), (2012) 25072-25082. https://doi.org/10.1039/C2JM34870E

[39] X. Li, G. Zhang, X. Bai, X. Sun, X, Wang, E. Wang, & H. Dai. Highly conducting graphene sheets and Langmuir–Blodgett films. *Nat. Nanotechnol.* 3(9) (2008) 538-542. https://doi.org/10.1038/nnano.2008.210

[40] J. Kim, L.I. Cote, F. Kim, W. Yuan, K.R. Shull, & J. Huang .Graphene oxide sheets at interfaces. *J. Am. Chem. Soc.* 132(23) (2010) 8180-8186. https://doi.org/10.1021/ja102777p

[41] M. Kole, & T.K Dey. Investigation of thermal conductivity, viscosity, and electrical conductivity of graphene based nanofluids. *J. Appl. Phys.* 113(8) (2013) 084307. https://doi.org/10.1063/1.4793581

[42] M. Hadadian, E.K. Goharshadi, & A.Youssefi, Electrical conductivity, thermal conductivity, and rheological properties of graphene oxide-based nanofluids. *J. Nanopart Res.* 16(12) (2014) 2788. https://doi.org/10.1007/s11051-014-2788-1

[43] E.K. Goharshadi, H. Azizi-Toupkanloo, & M.Karimi ,Electrical conductivity of water-based palladium nanofluids. *Microfluid Nanofluidics.*18(4) (2015) 667-672. DOI 10.1007/s10404-014-1465-0

[44] H. Azizi-Toupkanloo, E.K Goharshadi, & P. Nancarrow, Structural, electrical, and rheological properties of palladium/silver bimetallic nanoparticles prepared by conventional and ultrasonic-assisted reduction methods. *Adv Powder TechnoL,* 25(2) (2014) 801-810. https://doi.org/10.1016/j.apt.2013.11.015

[45] J. Fal , A. Barylyak, K., Besaha, Y.V. Bobitski, M. Cholewa, I. Zawlik, & G. Zyła, Experimental investigation of electrical conductivity and permittivity of SC–TiO2–EG , *Nanoscale Res. Lett.* 11(1) (2016) 1-9. DOI: 10.1186/s11671-016-1590-7

[46] E.M.S. Azzam, N.G. Kandile, A.M Badawi & R.M. Sami, Influence in the surface activity for some cationic thiol surfactants using their nanostructures. *Journal of dispersion science and technology,* 32(9) (2011) 1325-1331. https://doi.org/10.1080/01932691.2010.505825

(2021) ; http://www.jmaterenvironsci.com