

Morphology Change and Structural Evaluation of Carbon Nanostructures

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Abstract

In this study, the change of porosity and roughness of carbon nanostructures, including fullerenes, carbon nanotubes and graphene was investigated according to oxidation process. The effect of oxidation was more sensible on smoother surface of nanostructures. Oxidation increases surface roughness of graphene up to 5.2% and porosity up to 35.2%. While, roughness of hummers graphene is 13.1% higher than pure graphene. According to AFM results, oxidation can increase porosity and roughness of the surface. The amount of this increase is clearly a function of surface smoothness and multi-dimensional geometry of nanostructure. The functionalization processes have a positive effect on reducing the clustering phenomenon of nanoparticles and reduction of nanostructure particle size in their clusters that causes increases in surface porosity and roughness. So, functionalization processes can strongly change morphology of the nanoparticles in terms of structure, surface properties and geometry and according to these changes, nanostructures shows different behaviors.

Keywords: Fullerene, Carbon Nanotubes, Graphene, Morphology, Roughness, Nanostructures.

1. INTRODUCTION

Using different synthesis methods of nanoparticles and variety techniques of their treatment creates diverse surface properties and therefore changes physical behavior of nanoparticles. Moreover, there are same nanoparticles, which produced with different geometries and based on this express have different effects and functions. Carbon nanotubes (CNTs) and Graphene nano sheets are two main types of carbon nanostructures. Carbon nanotubes have drawn extensive attention owing to their promising applications in various fields [1]. Graphene, a sheet with thickness of one carbon atom, is made from carbon atoms in a hexagonal lattice structure [2]. Since the carbon nanostructures have hydrophobic

properties, two methods are used to stable them in water:

- 1- Application of surfactants
- 2- Physical and chemical treatment

Obviously, in first method morphology of nanostructures remain unchanged when surfactants are used for stability of them in water. Meanwhile physical and chemical treatment change morphology of nanostructure and these changes have direct effect on nanostructure behavior. This article investigates how to change morphology of carbon nanostructures and also how identifying and analyzing them.

2. SURFACE MODIFICATION OF CARBON NANOSTRUCTURES

Nowadays, carbon allotropes in different geometries synthesize with various methods and use in a lot of processes.

Carbon nanostructures divided into three main groups: zero-dimensional (fullerenes), one-dimensional (carbon nanotubes) and two-dimensional (graphene). Morphology and Surface properties of these nano structures can be improved by variety of chemical and physical methods for application in various fields. Acid oxidation is one of the usual processes for functionalization of these structures, so it is used for grafting hydrophilic functional groups on graphene and carbon nanotubes. In acid functionalization process, carboxyl groups tied up with the carbon structure [3]. In this method, at first 2gr of carbon nanostructure was added into 500 ml of mixture of concentrated sulfuric and nitric acid (3:1% wt.). The mixture was sonicated for 3 hr at 60 °C. Then washed to take the pH to neutral and dried at 50°C for 8 hr. Obtained soft powder used as an acidic oxide nanostructure [4]. Figure1 shows schematic cross of functional groups to the surface of graphene. For surface modification of fullerene, 1 g of its powder was poured in 500 cc of isopropyl alcohol and sonicated for 4 hr at room temperature.

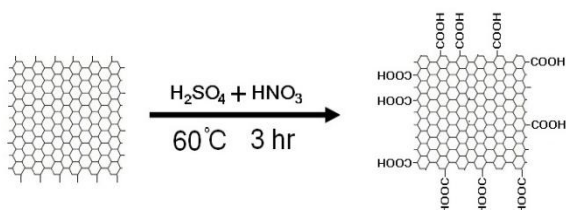


Figure 1. Schematic cross of carboxyl groups to the surface of graphene.

The mixture was ball milled with bullet weight ratio of 10:1 (50 rpm and 72 hr). The mixture sonicated for 30 min. Then the powder in solution was separated from isopropyl alcohol by a high-speed centrifuge, washed and dried in oven at 35°C for 5 hr. Dried fullerene had good stability in water [5].

3. SURFACE CHARACTERIZATION

Each atom can absorb emitted light or emit a new photon, which both has distance and specified delay in frequency

from first emitted light. The necessary information about type of atom, its bonds and determination of molecular structure can be obtained from these delay and peaks. These two phenomena are base of identifying and measuring materials by the spectroscopy method. The X-ray wavelengths are equal to the distance between atoms in crystalline materials, so the crystalline material can play a role of diffraction for X-ray. Therefore, information about crystallinity of structure and type of material can be obtained by using X-ray. Moreover, crystal size of material can be calculated by width of XRD peak.

Compounds that have different covalent bonds absorb different frequencies of electromagnetic radiation in the infrared region on the basis of their bonds. Therefore, energy absorption by specific functional groups was performed spontaneously at specific wavelengths. This adsorption leading to a reduction in light intensity and are plotted as a function of the wave number. Thus, FTIR spectrum provides information about the chemical structure of a molecule and its functional groups. Specific area is the total surface area of porous material per unit of mass. BET method is most common technique to measurement porosity and specific area of nanoparticles based on adsorption. This method is base on measurement of volume of nitrogen that is adsorbed and is desorbed by surface of material at constant temperature of liquid nitrogen [6].

Sample preparation are included drying and degassing, for this purpose samples must be heated in a vacuum at 120°C for 10 to 15 min until water vapor, carbon dioxide or other molecules that may have occupied the volume of pores of material are eliminated. Then the samples were cooled to 77K and were subjected to a certain amount of nitrogen gas, and the opportunity was created to balance. With respect to gas pressure at equilibrium and gas law, the amount of gas adsorbed was calculated.

Atomic force microscopy (AFM) is widely used to study a variety of levels and interactions between particles [7]. In this microscope, a beam with 100 microns diameter acts as a very sharp pencil and by placing close to the sample surface draws its image. Because of using atomic force such as vanderwaals force in AFM to analyze the surface, this microscope can examine topography of phase image, magnetic properties, grading and thickness of each layer. AFM microscope under air atmosphere and Tapping mode was used to evaluate the surface roughness of the carbon nanostructures.

4. RESULTS AND DISCUSSION

4.1. XRD analysis

XRD analysis of multi walled carbon nanotubes (MWNT) after oxidation process in acidic media was shown in figure (2-a). The XRD of MWNT has a long and narrow peak at $2\theta=26^\circ$ and one short peak at 43.6° . The first peak appears because of hexagonal structure of MWNT relates to the class of (002) sheets with distance of 0.34 nm and the second peak relates to (100) sheets [8]. These peaks are evident in figure 2-a. Graphene has one short peak at 26° and graphene oxide has a long and broad peak at 12° [9]. The peak at 26° is for (002) sheets with distance of 0.34 nm and peak at 12° is for (111) sheets with distance of 0.75 nm. XRD analysis of graphene and graphene oxide is compared in figure (2-b) and figure (2-c).

It can be observed that in the oxidation process of graphene the indicator peak of graphene at 26° shifted to 12° and it is strained very high.

This means that the crystal structure of graphene is slightly irregular. Thus, this result can be obtained during the process of oxidation, crystal structure of graphene has changed and a new morphology is created. In spherical structure of fullerene, peaks at 11° , 18° and 21° are as the characteristic peaks. These peaks are representative of class of (111), (200) and (220) sheets [10]. A comparison between XRD analysis of

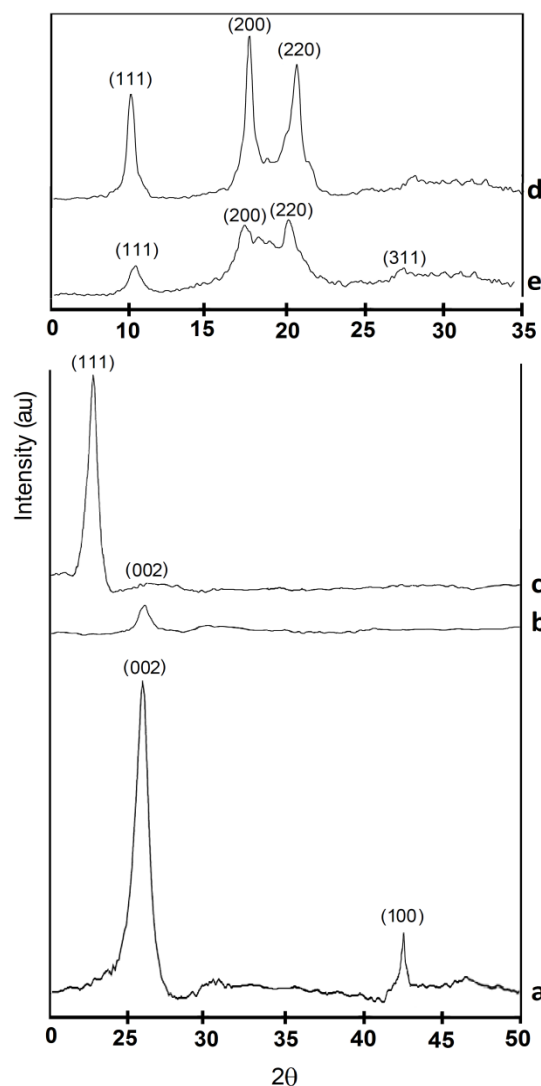


Figure 2. Comparison of the XRD analysis (a) Oxides of carbon nanotube, (b) graphene oxide, (c) graphene, (d) fullerene, (e) modified fullerene

fullerene and its modified structure was shown in figure (2-d) and (2-e). It can be observed that the prepared fullerene nanostructure has characteristic peaks of fullerene structure with a spherical structure. After modification of surface, crystal structure of fullerenes slightly degraded. Structural defects on surface of fullerene have emerged due to the ball milling process.

4.2. FTIR analysis

FTIR of carbon nanotubes has an index peak at 1560 cm^{-1} relates to carbon double bonds (C=C) and indicate of aromatic structure [11]. functional carbon nanotube,

has some peaks at 3400 cm^{-1} and 1620 cm^{-1} and 1070 cm^{-1} relates respectively hydroxide groups (O-H) and oxygen-carbon double bond (C=O) and oxygen-carbon bond (C-O).

The peak at 800 cm^{-1} relates to tensile groups (C-O-C) [12-15]. Figure (3-b) and (3-c) compares the FTIR of f-SWNT with f-MWNT nanotube. It was observed that emergence of the peaks at 3423 cm^{-1} and 1618 cm^{-1} and 1068 cm^{-1} relates to carboxyl groups, which have created during oxidation process. These peaks confirm oxide structure of carbon nanotubes.

In the process of producing graphene oxide with acid treatment, only the carboxylate functional groups bonds to the edges of graphene. Fullerene has four characteristic peaks at 525 cm^{-1} , 575 cm^{-1} , 1180 cm^{-1} and 1430 cm^{-1} [16]. Characteristic peaks of spherical structure of fullerene is at 531 cm^{-1} , 576 cm^{-1} , 1178 cm^{-1} and 1432 cm^{-1} and showed in figure (3-g). Therefore, the FTIR analysis proved the spherical fullerene structure. By comparing FTIR of figure (3-g) and (3-h), it's observed that the peak at 531 cm^{-1} moved to 527 cm^{-1} and its intensity slightly decreased. In addition, the peak at 576 cm^{-1} moved to 566 cm^{-1} and its intensity strongly decreased.

Moreover, after modification of fullerene surface the peak at 1178 cm^{-1} was missed and peak at 1432 cm^{-1} was moved to 1378 cm^{-1} . Location changing of this peak to the backward represented that fullerene structure was destroyed, because this peak location is related to the pattern of FTIR spectra of fullerene with C70 structure. Therefore, ball mill process leads to destruction on the surface of fullerene. Increment of fluctuation in figure (3-h) confirms fullerene surface destruction. This phenomena is because of increment of fluctuation at shorter wavelengths in C70 fullerene structure. Widening peak at 1378 cm^{-1} revealed fullerene structures have been destroyed and structural defects have been arisen on the surface.

This widening makes the fullerene surface susceptible to bonding with other compounds; this is because of increased number of active sites on the surface of the fullerene due to the breaking of surface bonds and creating active radicals on surface. It means that the number of free electrons on the surface of fullerene has increased dramatically and consequently there are active sites for bonding with the right compounds.

4.3. BET analysis

Porosity of carbon nanostructures were measured by BET method and the results were presented in table1. According to table1, it can be understood that the functioning of carbon nanotubes that occurs in acidic media increase the specific area of the nanoparticles. The main reason is due to opening of initial and end of nanotubes by acid. Therefore, more porous surface including inner and outer surface of nanotubes were available and desired nanostructure became more porous. Porosity of single-walled carbon nanotube increased 41% by oxidation and its specific surface enhanced from $635.2\text{ m}^2/\text{g}$ to $895.6\text{ m}^2/\text{g}$. However, oxidation of multi-walled carbon nanotube increased the porosity of 56.5%.

Generally, oxidation process increased porosity of carbon nanotubes. Oxidation had more destructive effect on multi-walled carbon nanotubes and it changed surface morphology and the porosity in multi-walled carbon nanotubes was a little more than single-walled carbon nanotubes [17].

It was observed that in graphene nano sheets, oxidation process effects on the total porosity was positive and increased to 35.2%. Although the porosity of pure graphene nanosheets was much less than nanotubes but these nanostructures showed more resistant to acid media and consequently were less destroyed. One of the main reasons was facilitating of percolation phenomena in carbon nanotubes than graphene nanosheets.

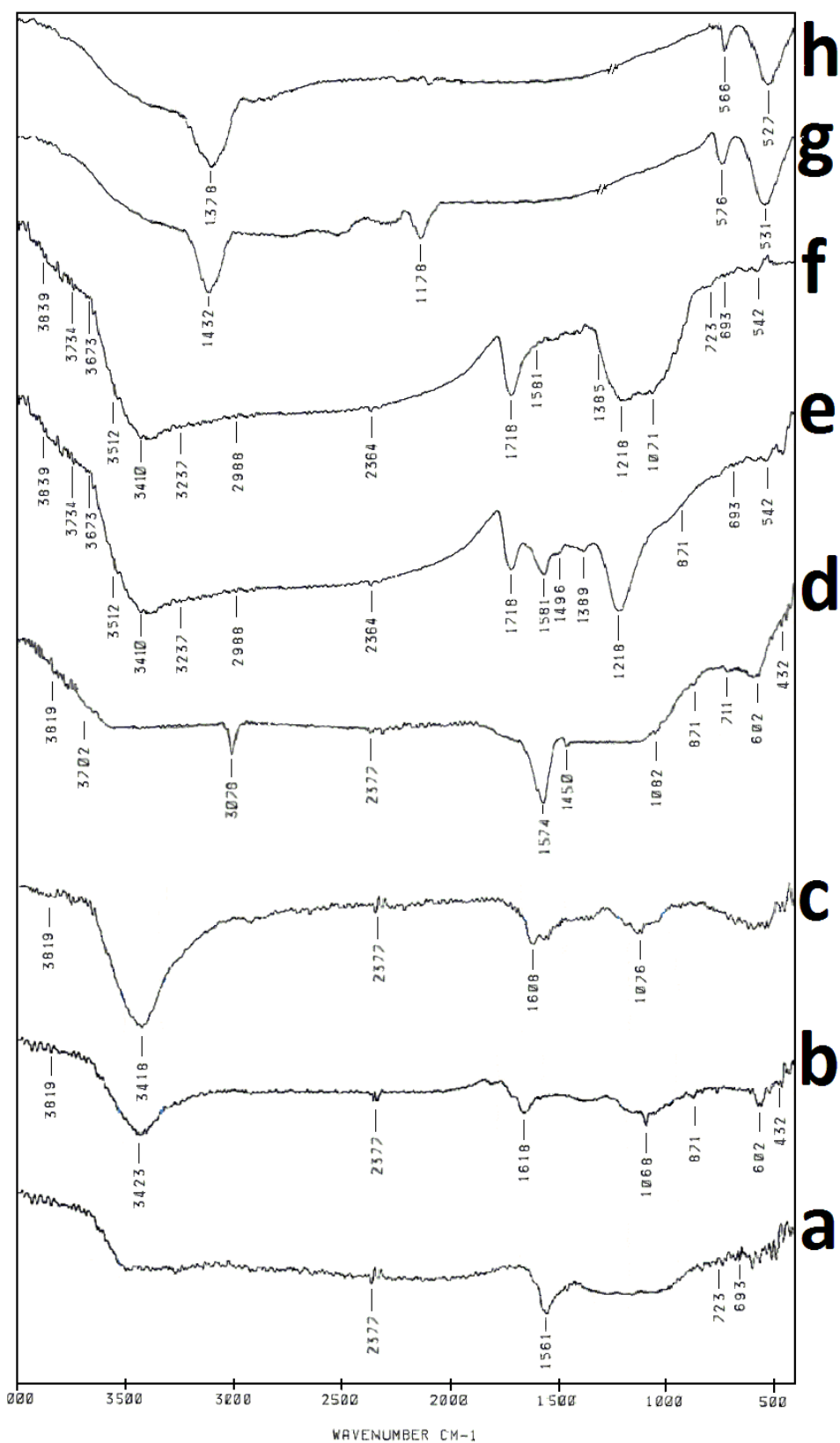


Figure 3. Comparison of FTIR spectrum. (a) Pure carbon nanotubes, (b) Single-walled carbon nanotube oxide, (c) Multi-walled carbon nanotubes oxide, (d) Pure graphene, (e) Graphene oxide, (f) Hummers graphene, (g) Pure fullerene, (h) Modified fullerene

Table 1. BET of Carbon Nanostructures.

| | Nanoparticles | Name | BET (m ² /g) |
|---|---|------------|-------------------------|
| 1 | Functionalized single-walled nanotube | f-SWNT | 895.6 |
| 2 | Pure single-walled carbon nanotube | SWNT | 635.2 |
| 3 | Functionalized multi-walled carbon nanotube | f-MWNT | 688.4 |
| 4 | Pure multi-walled carbon nanotube | MWNT | 439.7 |
| 5 | Functionalized graphene | f-G-CVD | 305.2 |
| 6 | Pure graphene | G-CVD | 225.7 |
| 7 | Hummers graphene | GO-hummers | 340.9 |
| 8 | Functionalized fullerene | f-C60 | 193.4 |
| 9 | Pure fullerene | C60 | 238.5 |

Thus, percolation of carbon nanotubes became smaller spaces between nanotubes and creates a new porosity and increase the porosity that reported. Such porosity can be beneficial overall. It is noteworthy that the obtained result of the treatment process in fullerene was reverse, so by functioning of fullerene the porosity decreased to 18.9%.

Since treatment of fullerene in most cases caused lack access to internal cavities, that was followed by relative decreasing in pore structure. According to table (1), treatment process of carbon nanostructures had changed porosity, consequently affected the surface properties of the nanostructures, and thus altered the morphology. Type and level of these impacts was not only function of process but also was strongly function of the initial geometric of nanostructures.

Therefore, the treatment process had positive effect and maximum impact was for carbon nanotubes and has negative effect for fullerene. The results showed that treatment processes caused changes in the morphology of the nanostructures [18].

It has been observed that roughness in single-walled and functionalized carbon nanotubes, on a surface 10×10 square micrometer was about 7.8 and 9.3 nm, respectively. Roughness of functionalized carbon nanotubes strongly depends on the type and amount of functional groups on the surface. In acidic oxidation process, roughness depends on the thickness that created by oxide groups on the surface of nanotubes. Therefore, treatment process was increased the surface roughness of single-walled carbon nanotubes. Results were in good agreement with the obtained results of BET, because of BET had been increased about 41% by treatment process on single-walled carbon nanotube which showed an increasing of porosity and thereby increasing roughness, because the roughness had been increased by 6.9%.

The roughness had been calculated for carbon nanotubes (about 6.6 nm) and also for functionalized carbon nanotubes in acidic media (about 7.6 nm). These numbers are in good agreement with the results that obtained from BET analysis, such that treatment of multi-walled carbon nanotubes had increased porosity by 56.5% and this followed by surface roughness by 15.1%.

Therefore, there are a direct relationship between surface roughness and porosity of the nanotubes. This relationship is not linear and it is exponentially, so with increasing porosity, roughness increases with less intensity. Because of linearity of porosity in carbon nanotubes, it is expected roughness has an increase about 56.5% while this value is only 15.1%.

Roughness of graphene was 3.4 nm. The roughness of graphene changed its optical properties. The average roughness of graphene and functionalized graphene had been obtained 3.8 nm and 4 nm respectively. So, treatment had increased roughness of graphene by 5.2%, while at the same condition this process had increased relative roughness of single-walled and multi-walled carbon nanotubes to 6.9% and 15.1% respectively. Although

the structure of graphene essentially has dissimilar wrinkles but the oxidation process has increase the severity and extent of these dissimilarity. The dissimilar wrinkles are product of the cooling process of graphene after growth stage of nano sheets in CVD process.

The relative roughness of Hummers graphene was measured 4.3 nm. Since Hummers graphene is kind of graphene oxide, its relative roughness is not same as graphene oxide obtained from oxidation process and this difference is about 0.3 unit. So, Hummers graphene structure is rougher. There are various impurities in the Hummers graphene structure such as H, N, CO₂, CH₄, SiO₂ and Al₂O₃, increase roughness of Hummers graphene. It can be clearly concluding that the functionalized nano-porous graphene has structural tendency to be rougher and grosser surface. Surface roughness of graphene was calculated about 4.2 nm and this value for functionalized graphene was 4.4 nm.

Functionalizing process of nano-porous graphene increased its relative roughness to 4.7%. This rate was the lowest compared to other recent nanostructures. The surface roughness of fullerene has calculated about 3.1 nm and this value for modified fullerene has been about 3.6 nm. This is consistent with the results of BET analysis of fullerene. Before and after surface modification process, steady increased in structure of modified fullerene was observable due to mean reduction of free path between fullerene particles [19].

Therefore, the distance between particles decreased and this reduction of gap between fullerene spheres increased false porosity in fullerene network, which was not calculated by the BET results. However, it had a positive effect on the fullerene surface roughness and characterized by AFM microscope probe. Thus, it was observed that the surface modification of fullerene decreased the porosity but increased the surface roughness. It seems that the false increase

in surface roughness of fullerene due to the reduced size of the fullerene clusters, lead available morphology of this nanostructure to a more disordered structure.

5. CONCLUSION

The effect of oxidation process on surface properties of nanoparticles is function of type of nanoparticle and its geometry. Although fullerene, CNT and graphene have same carbon structure but the geometry of zero, one and two-dimensional as well as the number of layers are effective on the effect of oxidation on surface properties. So, reduction in the number of layers of one-dimensional structures leads their behavior to two-dimensional structures. Increasing structural cracks and wrinkles in two-dimensional structures has increased the graphene surface roughness and dissimilarity in the structure. Beside it, they have disrupted electron transport properties on graphene surface.

Oxidation process in structure with high porosity and at same condition has less effect on increasing of surface roughness. Oxidation processes are not necessarily lead to a substantial increase in surface roughness and their effectiveness depends on the initial porosity and surface properties of nanoparticles. If one surface of the nanoparticles has high uniformity and low porosity, its potential in increase of porosity and surface roughness is higher than one surface which has enough porous. The morphology of nanoporous graphene is flatter than nanoporous functionalized graphene mainly due to the absence of structural defects that appeared because of treatment. Surface modification has increased uniformity of fullerene particle due to size shrinkage of fullerene clusters. Although treatment of fullerene decreases the porosity but increases surface roughness.

REFERENCES

1. Safi, M.A., Ghozatloo, A., Hamidi, A.A., Shariaty-Niassar, M., (2014). "Calculation of Heat Transfer Coefficient of MWCNT-TiO₂ Nanofluid in Plate Heat Exchanger", *International Journal of Nanoscience and Nanotechnology*, 10(3): 153-162.
2. Ghozatloo, A., Shariaty-Niassar, M., Rashidi, A.M., (2014). "Investigation of Heat Transfer Coefficient of Ethylene Glycol/ Graphenenanofluid in Turbulent Flow Regime", *International Journal of Nanoscience and Nanotechnology*, 10(4): 237-244.
3. Chiang, Y., Lin, W.H., Chang, Y.C., (2011). "The influence of treatment duration on multi-walled carbon nanotubes functionalized by H₂SO₄/HNO₃ oxidation", *Applied Surface Science*, 257(6): 2401-2410.
4. Avilés, F., Cauich-Rodríguez, J.V., Moo-Tah L., May-Pat, A., Vargas-Coronado, R., (2009). "Evaluation of mild acid oxidation treatments for MWCNT functionalization", *Carbon*, 47(13): 2970-2975.
5. Margetić, D., Štrukil, V., (2016). "Chapter 7 – Applications of Ball Milling in Nanocarbon Material Synthesis", *Mechanochemical Organic Synthesis*, 3: 323-342.
6. Jabari Seresht, R., Jahanshahi, M., Rashidi, A.M., Ghoreyshi, A.A., (2013). "Synthesize and characterization of graphene nanosheets with high surface area and nano-porous structure", *Applied Surface Science*, 276: 672-681.
7. Kuhlmeier, D., Rodda, E., Kolarik, L.O., Furlong, D.N., Bilitewski, U., (2003). "Application of atomic force microscopy and grating coupler for the characterization of biosensor surfaces", *Biosensors and Bioelectronics*, 18: 925-936.
8. VanderLee, M.K., VanDillen, A.J., Bitter, J.H., DeJong, K.P., (2005). "Deposition Precipitation for the Preparation of Carbon Nanofiber Supported Nickel Catalysts", *the American Chemical Society*, 127: 13573-13582.
9. Park, O., Jeevananda, T., Kim, N.H., Kim, S., Hee, L.J., (2009). "Effects of surface modification on the dispersion and electrical conductivity of carbon nanotube/polyaniline composites", *Scripta Materialia*, 60(7): 551-554.
10. Sathish, M., Miyazawa, K., (2012). "Synthesis and Characterization of Fullerene Nanowhiskers by Liquid-Liquid Interfacial Precipitation: Influence of C60 Solubility", *Molecules*, 17: 3858-3865.
11. Lefrant, S., Baibarac, M., Baltog, I., Mevellec, J.Y., Godon, C., Chauvet, O., (2005). "Functionalization of single-walled carbon nanotubes with conducting polymers evidenced by Raman and FTIR spectroscopy", *Diamond and Related Materials*, 14(3): 867-872.
12. Hontorialucas, C., López-Peinado, A.J., López-González, J., de, D., Rojas-Cervantes, M.L., Martín-Aranda, R.M., (1995). "Study of oxygen-containing groups in a series of graphite oxides: Physical and chemical characterization", *Carbon*, 33(11): 1585-1592.
13. Li, C.C., Lin, J.L., Huang, S.J., Lee, J.T., Chen, C.H., (2007). "A new and acid exclusive method for dispersing carbon multi walled nanotubes in aqueous suspensions", *Colloids Surf. A: Physicochem. Eng. Aspects*, 297: 275-281.
14. Tessy, T.B., Ramaprabhu, S., (2010). "Investigation of thermal and electrical conductivity of graphene based nanofluids", *Applied Physics*, 108: 124308, 1-8.
15. Akhflash, M., Boxall, J.A., Aman, Z.M., Johns, M.L., May, E.F., (2013). "Hydrate formation and particle distributions in gas-water systems", *Chemical Engineering Science*, 104: 177-188.
16. Iglesias-Groth, S., Cataldo, F., Manchado, A., (2011). "Infrared spectroscopy and integrated molar absorptivity of C60 and C70 fullerenes at extreme temperatures", *Monthly Notices of the Royal Astronomical Society*, 413(1): 213-222.
17. Lin, C.C., Kuo, C.L., (2013). "Effects of Carbon Nanotubes Acid Treated or Annealed and Manganese Nitrate Thermally Decomposed on Capacitive Characteristics of Electrochemical Capacitors", *Nanomaterials*, 35: 1-8.
18. Kim, J.Y., Jang, J.W., Youn, D.H., Kim, H., Kim, E.S., Lee, J.S., (2012). "Graphene-carbon nanotube composite as an effective conducting scaffold to enhance the photoelectrochemical water oxidation activity of a hematite film", *RSC Advances*, 2: 9415-9422.
19. Zhang, L., Wang, Y., Xu, T., Zhu, S., Zhu, Y., (2010). "Surface hybridization effect of C60 molecules on TiO₂ and enhancement of the photocatalytic activity", *Molecular Catalysis A: Chemical*, 331(1): 7-14.