

# Renewable Sources of Energy Generated by Changing Nanostructure of Carbon

Hind A. AL-Salihi

Energy and Renewable Energies Technology Center, University of Technology-Iraq, Baghdad, Iraq  
Email address: 100343@uotechnology.edu.iq

**Abstract**— Various type of renewable energy sources were subject of researcher in recent decades to connect with conventional energy and to find a new form of energy. In this study, it has been tried using the transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) to analyze the nanostructure of graphene in order to find the energy stored. In this investigation, the influence of microstructures and capacitive productivity was primarily investigated by changing the ratio of reduced graphene oxide and multilayered carbon nanotubes (MWNTs). Furthermore, a combination of graphene with other carbon nanomaterials was also investigated. According to the results, it can be indicated that an excellent charging capability up to 81.72% was also obtained at high current densities ( $> 1A \cdot g^{-1}$ ). In application of fuel cells, the benefits of heteroatomic doping in the carbon structure and the expansion of functional groups in connection with the growth of active sites, which can provides an inexpensive alternative to the precious metal electrocatalysts in fuel cells.

**Keywords**— Renewable energy, Nanostructures, Carbon structure, Graphene sheets, TEM, Energy storage.

## I. INTRODUCTION

Renewable energy sources (wind, hydro-electric, geothermal, biological, nuclear, solar) attract more attention of researchers in connection with the limited reserves of fossil fuels [1-5]. However, the nature of renewable energy resources is unstable, which means that storage systems are required to store energy. Energy saving systems includes pumped storage, storage of thermal energy, storage of compressed air energy, storage of energy on the flywheel. Recently, electrochemical energy saving systems (ECSE) has been actively developing-including electrochemical capacitors, batteries and fuel cells. Carbon structures and their multifunctional composites with a large specific surface area and electrical conductivity are used as the elemental base for ECCE.

Electrochemical capacitors are used in batteries with a bridge circuit (high power density at low energy density) and traditional capacitors due to their durability and reliability. Such carbon nanostructures as carbon nanotubes, carbon nanofibers, carbon onions and graphene are used to create electric double-layer capacitors due to a unique specific surface and electrical conductivity. The energy is stored by physical adsorption / desorption of ions at the electrode-electrolyte interface. This is a non-ferrous process in which there is no oxidation-reduction reaction. The mechanism of energy storage provides a fast charge / discharge rate, i.e. high power density ( $> 10 kW \cdot kg^{-1}$ ) and excellent cycle stability ( $> 106$  cycles). However, the energy density in such ECs is lower than in pseudocapacitors, in which charge is stored or released

through oxidation-reduction reactions occurring near the surface of the electrode [6, 8].

To increase the energy density of carbon nanostructures, various strategies have been used, for example: increasing the effective use of a specific surface or introducing a pseudocapacitor into an electrode material [8]. Thus, several studies have been devoted to an attempt to fully involve the surface of graphene. This material was supposed to be the next generation of electrode materials for ESCE due to the large specific surface (theoretical value is  $2630 m^2 \cdot g^{-1}$ ), sufficient porosity, excellent electrical conductivity, a wide potential window and unique chemical properties [5]. Oxidation and subsequent reduction of graphene oxide is the most effective method of mass production of graphene [4, 5]. Unfortunately, the reduced graphene oxide is prone to coarsening, which is caused by a strong van der Waals interaction between graphene sheets. As a result, this leads to unsatisfactory performance of supercapacitors [6]. A combination of graphene with other carbon nanomaterials was also investigated. As shown in Figure 1, carbon nanotubes were grown between graphene sheets and distributed non-uniformly, 3D CNT / graphene sandwich structures were formed for the remainder of the surface [7, 8]. Here, CNTs play the role of an interlayer - their goal is to prevent contact between graphene so that they can attach electrolytic ions.

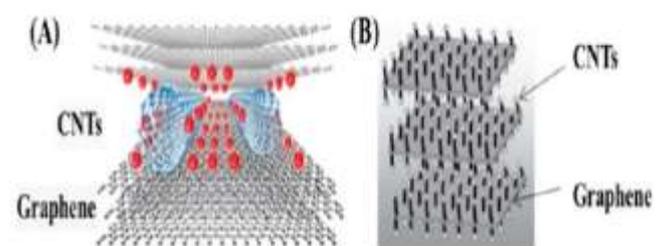


Fig. 1. Two models of CNT-graphene sandwich structures [7].

Young's scientific group [9] developed a simple way to increase the productivity of graphene sheets and improve the capacitive properties by combining CNT and graphene. The influence of microstructures and capacitive productivity was studied by changing the ratio of reduced graphene oxide and multilayered carbon nanotubes (MWNTs). Figure 2 shows a snapshot of the CNT graphene sandwich (ratio of reduced graphene oxide to MWNT-9: 1), which shows a more crumpled and rough surface compared to other samples. Laying graphene sheets on top of each other is prohibited due

to the presence of MWNTs. The scanning speed was 20 mV • s<sup>-1</sup>, which indicates the highest energy storage capacity. The corresponding calculated specific capacitance was 326.5 F/g, which is significantly higher than that for samples with a different ratio of graphene-MWNT and indicates the most efficient use of reduced graphene oxide in composites. From Figure 2, it can be seen that this sample reports an energy density of 45.3 W • h • kg<sup>-1</sup> at a power density of 3.3 kW • kg<sup>-1</sup> for a long time of current drainage (50 s) in a three-electrode installation, much higher than the recovered graphene (11.5 W • h • kg<sup>-1</sup> at 0.8 kW • kg<sup>-1</sup>). This indicates the promise of three-dimensional hierarchical CNT-graphene nanocomposites as materials for electrochemical capacitors.

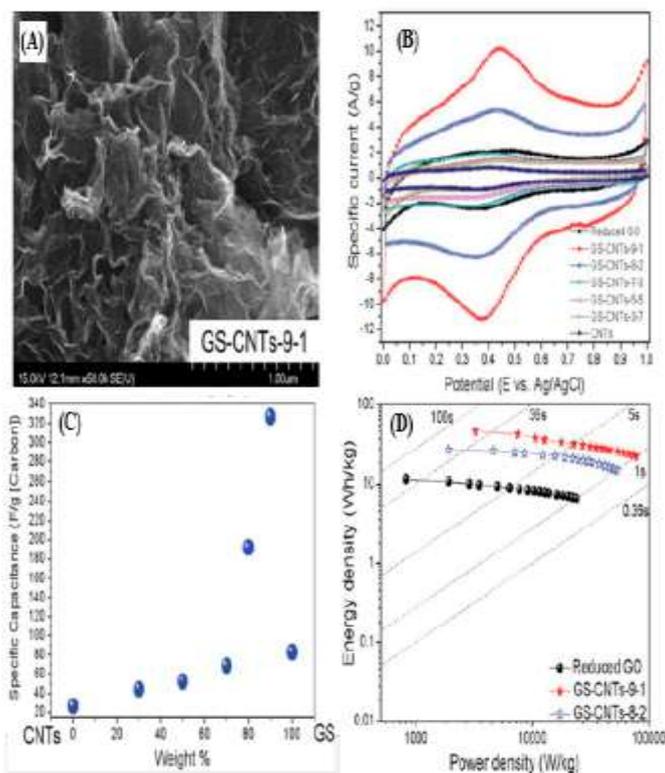


Fig. 2. a) a snapshot of a CNT graphene sandwich made using a scanning electron microscope (graphene: CNT 9: 1); b) current-voltage characteristics for sandwiches with different ratios of graphene: CNT; c) the resistance dependence on the graphene-CNT ratio; d) the dependence of the energy density on the power density for reduced graphene and CNT graphene composites [9].

The aim of this research was to investigate the effect of microstructures and capacitive productivity by changing the ratio of reduced graphene oxide and multilayered carbon nanotubes (MWNTs). Furthermore, the carbon nanofibers were polymerized with polypyrrole at different temperatures (500,700,900, and 1100 °C) and N<sub>2</sub> atmosphere. In addition, this work was carried out on how the changing nanostructure of carbon on energy storage of electrochemical capacitors.

## II. METHODS AND MATERIALS

Another effective strategy for increasing the energy density of EC on carbon structures is the introduction of

pseudocapacity in ECSE. There are two similar approaches. The first is the introduction of heteroatoms into the carbon skeleton [10, 11]. The most multifaceted method is doping with nitrogen atoms, which allows maintaining excellent cyclic stability [12]. A simple method for obtaining porous carbon nanofibers with a high nitrogen content has been described [13]. Carbon nanofibers were polymerized with polypyrrole followed by carbonization at different temperatures (500,700,900,1100 °C) and N<sub>2</sub> atmosphere.

Transmission electron microscope (TEM) was used in this test to measure the Nanosheets of graphene structure by image with high scale. The measurements process starts with the interaction of the electrons with sample to form the TEM image when the beam of electrons is transmitted through the specimen. An imaging device is used to magnify the image with high scale and high resolution onto a fluorescent screen. The second equipment was used during the research is X-ray photoelectron spectroscopy (XPS) and N<sub>2</sub> adsorption measurements. The XPS is used to analyze the elemental composition at the parts per thousand ranges and also the surface chemistry of a material. Also it can be measure the kinetic energy and number of electrons (from 0-10 nm) of the material.

## III. RESULTS AND DISCUSSION

According to the results, X-ray photoelectron spectroscopy and N<sub>2</sub> adsorption measurements have shown that nitrogen-enriched carbon nanofibres obtained by annealing at 900 °C (N-UNV-900) have localized graphite structures or profitable morphologies with a large number of specific surfaces and pores. A snapshot of N-UNV-900 obtained with the help of a transmission microscope with high resolution is shown in Figure 3a. As shown, N-UNV-900 demonstrates a higher specific electric capacity with a change in charge / discharge current density compared to its analogs in the three-electrode configuration (Figure 3b). An excellent charging capability up to 81.72% was also obtained at high current densities (> 1A • g<sup>-1</sup>). The Nyquist impedance spectrum (Figure 3c) shows a small semicircle, characteristic for low resistance to charge transfer, in the high-frequency region of the N-UNV-900 electrode. Equivalent series resistance for N-UNV-900 is very small, about 0.14 Ohm, for comparison: UNB at polypyrrol 1.25 Ohm, UNV-900 0.92 Ohm. Such low resistance plays a decisive role in achieving high charge rates and power densities for electrochemical capacitors. A good cycle stability was found: 97% of the initial capacity is retained after 3000 cycles.

In case of fuel cells, the carbon nanostructures are used for the oxygen reduction reaction (RVC) in fuel cells to replace platinum-based catalysts that are expensive and have limited access and low durability [11]. Both experimental and theoretical studies show the possibility of creating p- and n-type semiconductors by replacing C atoms with B and N atoms in the carbon frameworks of graphene and CNT. Doped atoms are capable of modifying the electronic band structure of carbon nanostructures and, consequently, regulating mechanical properties and electrocatalytic activity. For example, a simple catalyst-free approach to the synthesis of

boron-doped graphene (BG) by thermal annealing of graphene oxide in the presence of B<sub>2</sub>O<sub>3</sub> was presented in the study [11, 12].

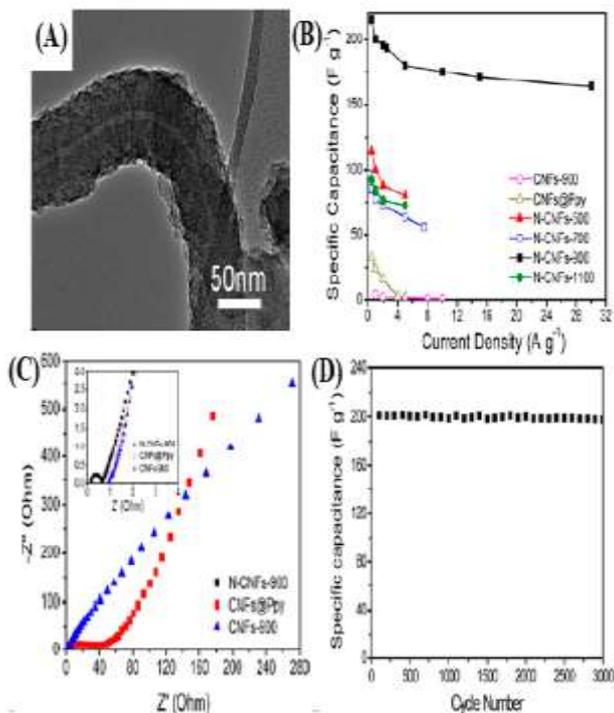


Fig. 3. a) a snapshot of a transmission electron microscope of carbon nanofibers doped with nitrogen obtained after annealing at 900 °C; b) resistivity of N-UNV-900, UNB at polypyrrol, N-UNV-700, N-UNV-900, N-UNV-1100 at different current densities; c) the spectrum of the electrochemical impedance at a voltage of 5 mV; d) the cyclic productivity of N-UNV-900 as the gravimetric capacitance calculated from the discharge after 3000 cycles [10]

Electrocatalytic productivity was evaluated in a three-electrode installation using BG or a pure graphene-modified glass-carbon electrode (designated as BG / LPG and graphene / LPG, respectively) in an oxygen-saturated aqueous medium. Fig. 4a shows a photograph of a transmission electron microscope (TEM) in which the flattened BH nanosheets are randomly grouped with a scaly structure similar to the structure of pure graphene. Figure 4b shows linear sweeps of the voltammetric curves for the oxygen reduction reaction in BH / LPG, graphene / LPG and platinum electrode with a scanning frequency of 10 mV • s<sup>-1</sup>. Initial potentials for RVC in deformed graphene are ~ -0.15 and ~ 0.59 V, respectively. This indicates that the RVC process catalyzed by pure graphene is a two-stage two-electron pathway with the formation of intermediate HO<sub>2</sub> ions.

In contrast, BG / LPG, in the case of the Pt electrode, demonstrates a one-step process for RVC with an initial potential of about -0.05 V, which is about 100 mV greater than in pure graphene/LPG. A one-step process offers a four-electron path for RVC in boron graphene. Both a positive shift in the initial potential and an increased recovery current for RVC on BG / LPG demonstrate that BG has a much higher electrocatalytic activity with respect to RVC than graphene,

which can be explained by the faster reaction of kinetics with a higher number of transported electrons per molecule oxygen (Figure 4c). The average electron transfer number *n* for SRS on BG / LPG was 3.5 for the potential range from -0.4 to -0.9 V, which is significantly higher than for pure graphene (2.1-2.7). All this indicates that nitrogen-doped carbon materials exhibit much better electrocatalytic activity with respect to SRS than pure carbon. The BG catalyst exhibits considerable stability during the SRS after 5000 cycles (Figure 4d), which indicates excellent electrocatalytic properties of BG. Recently, researchers have also found that graphene doped with elements that have the same electronegativity to carbon, for example sulfur and selenium, can also exhibit better catalytic activity than the commercial Pt / C catalyst in alkaline media [13, 14]. This study not only provides additional insight into the mechanism of stimulated Raman scattering of these nonmetallic carbon-impregnated carbon materials, but also opens the way for the manufacture of other new cheap catalysts with a low content of precious metals. However, these doped carbon materials usually exhibit SRS activity in alkaline electrolytes, but have low activity in acids.

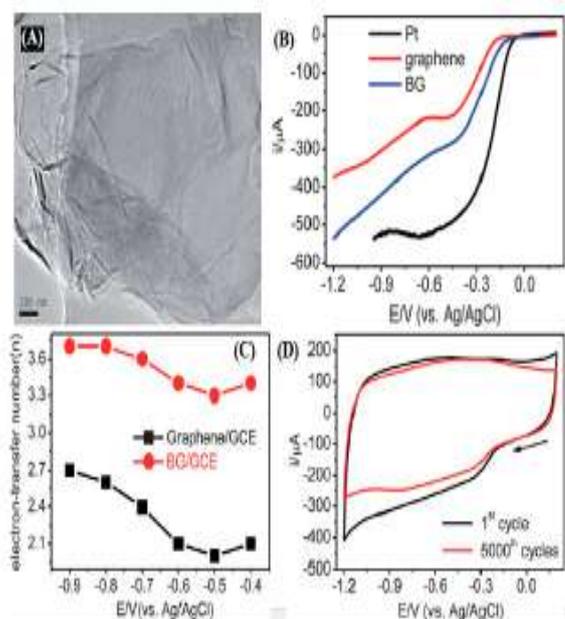


Fig. 4. a) TEM image of graphene doped with boron (BH); b) voltammetric SRS for graphene/LPG (red), BG / LPG (blue) and platinum electrode in an oxygen-saturated aqueous medium (scanning speed 10 mV • s<sup>-1</sup>); c) the dependence of *n* on the potential barrier for BH / LPG and pure graphene / LPG; d) VAC of BG / LPG for RVC in an oxygen-saturated aqueous medium 0.1 KOH. [13-17].

To solve this problem, the research team of Lee [16-19] made complexes of low-walled carbon nanotubes and graphene (NT-G), which show the activity of stimulated Raman scattering in both acidic and alkaline solutions. Figure 5a shows NT-G images made with high-resolution TEM. Nanotubes, mostly two- or three-layered, their outer walls are damaged and delaminated to form single-layered nanosized graphene pieces (~ 5 nm) or tape-like structures as a result of the oxidation process. These graphene structures have

saturated bonds at the edges and are often attached to nanotubes. Areas with undamaged inner walls on stratified nanotubes are also often observed. In Figure 5 b, c compares the catalytic activity of SRS for 20% Pt on carbon black of the volcano and HT-G in acidic and basic media, respectively. The catalyst exhibits significantly higher catalytic activity than the previous CNT-based electrocatalysts in an acidic medium of 0.1-M HClO<sub>4</sub>. In the 0.1-M KOH-electrolyte, HT-G catalyst shows SRS activity close to that of Pt / C [20-23]. Figures 5d, d show the polarization curves of a rotating annular disc, measured in the presence of 0.5 M methanol. A sharp decrease in SRS activity in Pt / C is observed. In contrast, HT-G catalyst exhibits a slight loss of activity, exhibiting excellent tolerance for methanol poisoning. In Figure 5e, curves of the I-V characteristic curves for HT before and after iron purification are shown. The steps of purification and removal of iron cause a large loss of SRS activity in purified HT-G with a SRS start potential of ~ 100 mV more negative than NT-G, which indicates a positive effect of iron impurities. Similarly, the benefits of heteroatomic doping in the carbon structure and the expansion of functional groups have been demonstrated in connection with the growth of active sites, which provide an inexpensive alternative to the precious metal electrocatalysts in fuel cells.

depends on their structure and interphase interactions with the surrounding bulk materials or other nanomaterials. Improved development and testing of these carbon nanostructures for energy storage devices are illustrated by many examples. There are still some disadvantages and disadvantages associated with different carbon nanostructures, such as irreversible power loss, large voltage pickup, low density, and so on. These devices have a number of disadvantages associated with carbon structures: irreversible power loss, large voltage pickup, low density and so on. New composites containing multifunctional nanostructured carbon and other impurities can synergistically take advantage of the combination of ordered blocks with other desirable properties. From all of these, it can be indicates the possibility of a breakthrough in the performance of electrical data storage devices, in the event that the fundamental theoretical calculations are systematically accompanied by experiments.

LIST OF ABBREVIATIONS

- ECSE - electrochemical energy saving systems
- EC - electrochemical capacitors
- CNT - carbon nanotubes
- MWNT - multilayered carbon nanotubes
- CNF - carbon nanofibers
- RVC - oxygen reduction reactions
- BG - graphene doped with boron
- LPG - graphene-modified glassy carbon
- TEM - transmission electron microscope
- VAC - current-voltage characteristic
- NT-G is a complex of low-walled carbon nanotubes and graphene

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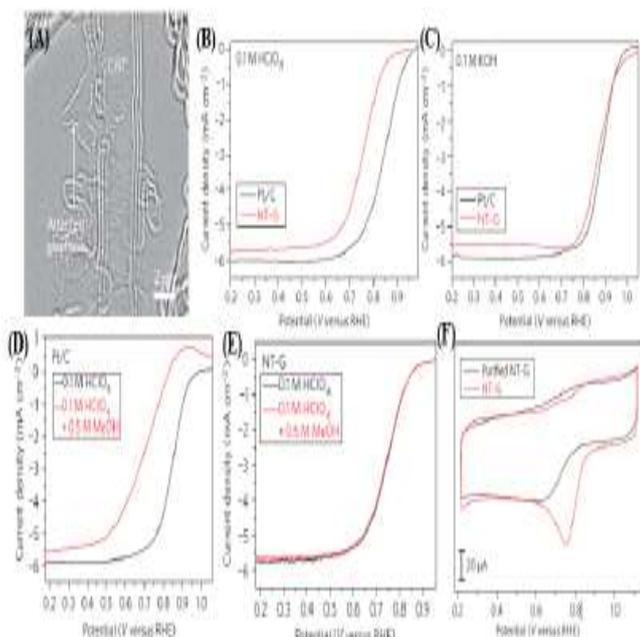


Fig. 5. a) NT-G images made with high-resolution TEM. Polarization curves for 20% Pt / C (black) and NT-G (red); b) oxygen-saturated medium HClO<sub>4</sub>; c) in the KOH medium. g, e) the polarization curves of the rotating annular disc, measured in the presence of 0.5 M methanol; e) curves of the current-voltage characteristics for HT before and after purification of iron [23, 26].

IV. CONCLUSIONS

In this research, the latest developments in the field of energy storage and nanostructure devices were studied. In particular, electrochemical capacitors and fuel cells based on carbon nanostructures. At the nanoscale, the physical and chemical behavior of such carbon nanostructures strongly

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