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Synthesis of Carbon Nano Rods from Plastic Waste (PP) Using MgO AS A Catalyst

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Abstract

In this research, CNRs have been synthesized using pyrolysis of plastic waste(pp) at 1000 ° C for one hour in a closed reactor made from stainless steel, using magnesium oxide (MgO) as a catalyst. The resultant carbon nano rods were purified and characterized using energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD). The surface characteristics of carbon rods were observed with the Field emission scanning electron microscopy (FESEM). The carbon was evenly spread and had the highest concentration from SEM-EDX characterization. The results of XRD and FESEM have shown that carbon Nano rods (CNRs) were present in Nano figures, synthesized at 1000 ° C and with pyrolysis temperature 400° C. One of the advantages of this method is that using one reactor for a short time and without any use of inert gas as opposed to previous researches which used two reactors.

Key words: Carbon Nano rods, Nano Carbon, Plastic waste, Polypropylene, Pyrolysis.

Introduction:

Trashing of waste plastics is well acknowledged as a huge problem for the environment, with over 8 million tons of plastics being thrown in oceans (1). Even though huge efforts are being made to reduce the damage of waste plastics, rates of recycling are still somewhat low, for example just about (12%) from total plastic waste was recycled in the United States (2). In the European Union, over (40%) from plastic waste was dumped in landfills in 2010 (3). Researchers have been searching for different solutions to solve the troubles of huge amounts of waste plastics for years. At present time, the usage of landfills and incineration are some of the most widely used solutions, but the rising prices, environmental troubles and the reduction of area for landfills make other processing choices demanded. Different alternative ways have been submitted so that the plastic wastes can be processed. However, not every one of these alternatives is widely-used, because of the economic applicability (4). Currently, there are three methods of energy recovery to collect and recycle waste plastics from households which are thermal recycling, chemical recycling, and material recycling. Energy retrieval is quite efficient and simple.

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It recovers thermal energy through pyrolysis. Even though energy recovery is simple and efficient, it should be considered as a last option from an ecological point of view. Chemical recycling is not widely utilized because of requires a lot of energy and extremely complex processes. The best way would be to recycle materials several times and use energy recovery only when recycling is difficult or is not possible (5). Plastic waste is blends of several polymers, like PE (Polyethylene), PP (Polypropylene), PS (Polystyrene), PVC (Polyvinyl chloride), PA (Polyamide), etc. Also, to develop plastics properties, worthy quantities of additives, "such as Chlorine, Bromine, Nitrogen, Antimony, Zinc, Titanium, Calcium, etc." are usually added into the pure polymer through the manufacture operation. Then these elements appear in pyrolysis products which causes troubles for their usage in additional implementation. Although pyrolysis of plastic waste has been explored for quite a long time in order to obtain worthy products like "gasoline, syngas, pyrolysis oil, etc."; this choice of recycling of raw material was notified to be just (0.3%) from plastic waste in 2007(6).

Even though plastic waste from domestic wastes to the industrial remains, rise harmful effects on environmental and health of human which is regarded a source of air, soil, water and marine pollution; wastes can be used as tools to produce useful goods. A significant technique to obtain this goal is pyrolysis. Pyrolysis relates to thermal decomposition that is operated in an air-free condition (7). Pyrolysis is a probable alternative to landfill for processing plastic waste, and the resulting decomposition products which can be used as” fuels instead of gas, diesel or fuel oils” (8). Additionally, pyrolysis of plastics has also been utilized to manufacture various types of Nano Carbon such as nanotubes, nanofiber, nanorods, nanowires, etc., Carbon nanorods which have high value and exceptional physical and chemical properties because of their impressive characteristic like high surface area, porous-rich structure, high conductivity and excellent chemical stability, by blending plastics and catalyst in one reactor. The application of CNRs such as use as supports for metal nanoparticles, gas storage, electrochemical energy storage (9), biosensors (10), efficient electrodes for rechargeable batteries, supercapacitors and electrocatalysis (11). The research objective is to produce new nanomaterials that inter into the technological industry.

Materials and Methods:

Waste of polypropylene was collected from local grocery stores. The samples were washed, air-dried and shredded into small pieces of an area that’s around (1mm²). 25 g of shredded PP was placed inside a stainless-steel reactor which has a height of 11cm and a diameter of 5.5cm. 0.5 g of (MgO) was placed in tube nozzle connected with reactor. The reactor was tightly closed and put in an electric furnace to be heated. This reactor is connected to Condenser and then to three neck round-bottom flask for product collection, Fig.1and 2. The temperature of the furnace was gradually raised. When the temperature of 400°C was reached and the polypropylene began to decompose, the catalyst was added from the tube nozzle. At this level the distillation process began and at the end of distillation the temperature was raised to 1000 °C at a heating ramp rate of 15 °C/min, and maintained for 1 h, then allowed to cool to room temperature naturally. It was found that the final product in the reactor included carbon powder.

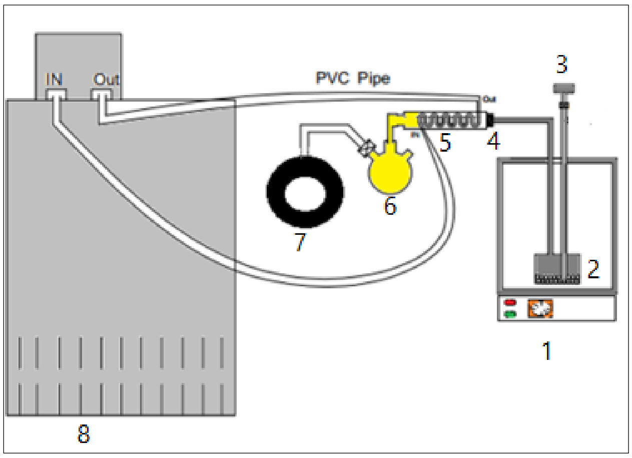

Figure 1. Schematic diagram of unit used for synthesizing carbon nanostructures by pyrolysis method. In this diagram, 1) Electric furnace, 2) Stainless steel reactor, 3) tube nozzle containing catalyst, 4) Rubber, 5) Condenser, 6) three neck round-bottom flask, 7) Rubber bag to collect the resultant gas, 8) Water bath.

Figure 2. Designing of carbon nanorods synthesized system

Carbon Nano Rods Identification.

To identify CNRs properties, the following equipment were used:

X-Ray Diffraction (XRD).

The X-ray diffraction (XRD, X’PERT PRO from Philips, Netherlands) was evaluated to determine the crystal structure and phase the samples, with Cu-Kα radiation (λ=1.54178 Å), operated at 40 kV and 40 mA, was measured in 2θ range from 10^o to 80^o, performed on a University of Kashan (Iran).

Field Emission Scanning Electron Microscopy (FESEM):

The morphology and size of samples were studied by scanning electron microscopy (SEM; FEG-SEM MIRA3 TESCAN, Czech Republic), which is configured to operate at (15.0 kV) various magnification level.

Energy Dispersive X-Ray Analysis (EDS):

The elemental composition of samples was studied by (EDS, MIRA3 TESCAN, Czech Republic).

Results and Discussion:

Figure 3 shows the XRD patterns of the CNRs, the diffraction peaks at the three values of 23.2°, 28.5° and 43° were ascribed to the (002), (100) and (101) reflections, respectively of the CNRs (JCPDS PDF no. 41-1487)(12-14), and the Nano-MgO showed peaks corresponding to (111), (200) and (220), (222) planes, indicating the presence of cubic face centered MgO and the intense peaks were observed at 18°, 36.8° , 62.1° and 75.5° can be assigned to a pure phase of MgO (JCPDS PDF no. 77-2364)(15,16). The XRD patterns of the MgO/CNRs hybrid are shown in Fig.3. Excluding the characteristic CNRs (002), (100) and (101) peaks, all the other peaks could be indexed to the cubic phase of MgO, revealing that MgO had been incorporated into the MgO/CNRs hybrid sample.

Many other peaks for other elements which were added to polymer can also be noticed. (pp).

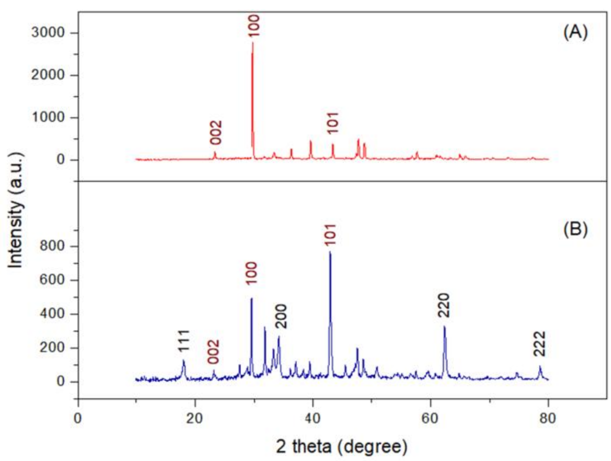

Figure 3. XRD Pattern of the CNRS. (A) PP without catalyst at 1000 ºC for one hour of pyrolysis. (B) PP with catalyst MgO at 1000 ºC for one hour of pyrolysis.

Average crystal size in the product can be found by using X-ray diffraction profile. Calculating the particle size (D) can be done by using the Debye Scherrer equation, equation 1:

$$D = \frac{K\lambda}{\beta cos\theta} \quad \text{........1}$$

Where K is the Scherrer constant, λ is the wavelength of light used for the diffraction, β is the full width at half maximum of the sharp peaks and θ is the angle measured. The Scherrer constant (k) in the above formula accounts for the shape of the particle and is generally taken to have the value 0.9 (17).

Table 1. Structural parameter of Carbon Nano Rods (CNs)

2θ (deg)	FWHM (deg)	Cos θ	FWHM (rad)	I/I1	D (nm)
23.27	0.09	0.979446452	0.001570681	29	90.26925
28.5	0.1604	0.967438401	0.002799302	82	51.27851
43.0	0.248	0.930396035	0.004338569	99	34.40282

From Table 1, The average crystal size of CNRs could be calculated as shown below:

Average crystal size = 58.6 nm

The morphology of the sample was revealed by FESEM. Fig. 4A shows a typical FESEM image of the sample. It is found that large quantities of nanostructures (CNRs) were obtained. These nanorods are carbon (25-46) nm in diameter, and a few micrometers in length, as shown in Fig 4B and 5 show the EDS for the CNRs. The result shows the ratio of the elements, which is confirmed by the result of the XRD. The other peaks notices in EDS refer to the additives of polymer and the substrate used in the measurement.

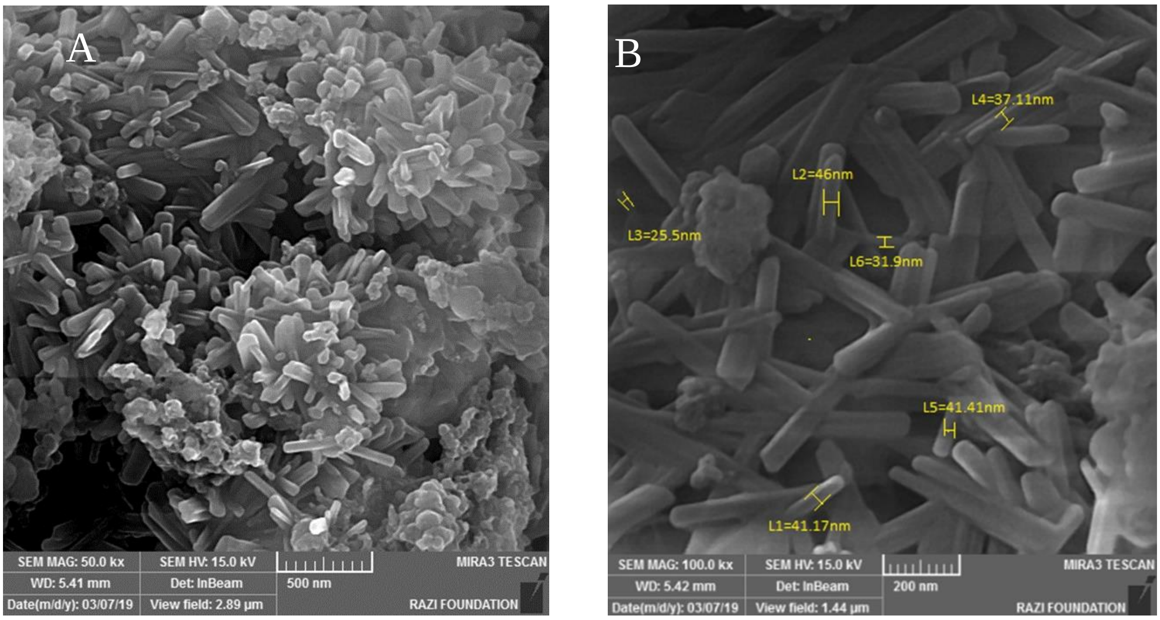

Figure 4. FESEM image of CNRs grown on MgO (A) 500nm (B) 200nm

Figure 5 the energy dispersive x-ray analysis shows the high concentration of the carbon content which indicates high purity, and shows the amount of catalyst used in pyrolysis. The other components (Ti, Ca, Mo, Fe and Na) are additives to improve properties of polymer, and the other elements noticed (Si, Al and Cl) refer to the elements in standard in analysis device.

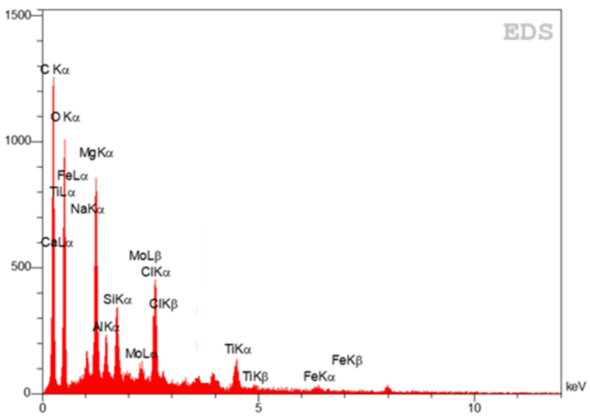

Figure 5. EDS spectra

Conclusions:

The conclusion of this research is that the temperature of the pyrolysis of polypropylene is at 400 ° C for about 30 minutes and the result of XRD and FESEM shows there is carbon nanorod at all temperatures and marked by a peak intensity at $2\theta = 43$. Moreover, the range of crystallite size of CNRs (90-34) nm.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of AL-Anbar.

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تحضير قضبان الكاربون النانوية من المخلفات البلاستيكية (البولي بروبيلين) بأستخدام اوكسيد المغنيسيوم كعامل مساعد

امال شاكر عبود **ابراهيم جليل ابراهيم**

قسم الكيمياء، كلية العلوم، جامعة الأنبار، الأنبار، العراق.

الخلاصة:
في هذا البحث، تم تحضير قضبان الكاربون النانوية بأستخدام الانحلال الحراري للنفايات البلاستيكية (بولي بروبيلين) عند درجة حرارة 1000 درجة مئوية لمدة ساعة في مفاعل مغلق مصنوع من الفولاذ المقاوم للصدأ باستخدام اوكسيد المغنيسيوم كعامل مساعد. تمت تنقية الكربون الناتج و تشخيصه باستخدام التحليل الطيفي للأشعة السينية (EDX) ، حيود الأشعة السينية (XRD). وقد لوحظت الخصائص السطحية لقضبان الكربون بأستخدام المجهر الألكتروني الماسح (FE-SEM). من خلال قياس (SEM-EDX) تبين أن الكربون منتشر بالتساوي وكان هو الأعلى تركيز. أظهرت نتائج XRD, FE-SEM أن قضبان الكربون النانوية (CNRs) كانت موجودة في الأشكال النانوية، التي تم تصنيعها عند درجة حرارة 1000 درجة مئوية ومع درجة الانحلال الحراري 400 درجة مئوية. من مميزات هذه الطريقة أننا أستخدمنا مفاعل واحد لفترة زمنية قصيرة و دون أي أستخدام للغاز الخامل على عكس البحوث السابقة التي كانت تستخدم مفاعلين.

الكلمات المفتاحية: قضبان الكاربون النانوية، الكاربون النانوي، المخلفات البلاستيكية، بولي بروبيلين، الانحلال الحراري.