VOL. 11, NO. 19, OCTOBER 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

# INVESTIGATION OF THE OPTIMUM CONDITIONS FOR GREEN CARBON NANO-SPHERES PREPARATION USING SUGAR ACID HYDROLYSIS

Nabila H. Hussien, H. S. Hussein, H. H. Shaarawy and S. I. Hawash
National Research Centre, Department of Chemical Engineering & Pilot Plant, Dokki, Cairo, Egypt
E-Mail: hala.hussein21@yahoo.com

**ABSTRACT**

Nano size spherical carbon particles of less than 100 nm diameters are attracting for new applications in human life and industry fields. In this work, different nano carbon particles structures including spherical shape were synthesized by phosphoric acid dehydration process. Shape and size of the obtained nano sized carbon sphere particles were characterized by means of JEOL-JEM-1200 Transmission Electron Microscope (TEM). The effect of different phosphoric acid concentrations, 0.06M, 0.1M and 0.5M respectively was studied. Also, influence of sugar concentration, temperature and heating time were investigated. The optimum conditions were concluded as, 0.1M phosphoric acid, 50g/l sugar concentration, 100ºC and 15minutes heating time was selected for carbon nano spheres preparation.

**Keywords:** carbon nano spheres, Acid dehydration, sugar hydrolysis.

## 1. INTRODUCTION

The exclusive properties of nano size particles led to a lot applications in the human life fields such as agriculture, industry, and medicine beside global attention towards science and technologies of nano materials (Serrato-Valenti, G., *et al*2000). Different authors cited that different types of nano particles have the ability to penetrate walls of cell plants (e.g.) (I) Gold,capped meso-porous silica nano particles (MSNs) were able to penetrate cell wall and provide plant cell with DNA by bombardment method.(II) Penetration of the cell wall and cell membrane of tobacco cells using cell- walled carbon nano carbon tubes(SWNTs, and (III) penetration of carbon-coated iron nano tubes in plant cells using pumpkin plants as previously reported (Torney, F.,*et al* 2007; Gonzales-Melendi, P., *et al* 2008). Currently, there are great interest about the penetration of nano carbon materials in the plant and its ability to be used as smart treatment-delivery systems and their impact on the plant physiology. It was found that the interference of carbon nano particles to seeds of crops increase the germination percent and enhances the growth of seedlings. Preparations of nano carbon by chemical vapor deposition are reported within different techniques (Calderon-Moreno, J.M., *et al* 2007). Pyrolysis of hydrocarbon precursors (Lee, E. J., *et al* 2005, Wang, Z.D., *et al* 2008) and sol–gel emulsification (Pekala, R.W. 1989, Hasegawa, T., et al., 2004, Chandra S., *et al* 2009) are also reported. Investigations of carbon nano spheres preparation are very few (Lee, E. J., *et al* 2005,Calderon-Moreno, J.M., *et al* 2007, Wang, Z.D.,*et al* 2008), while there is a significant literature on the preparation of circular carbon granules. Synthesis of different nano carbon particles structures including spherical shape has received a considerable attention in recent years due to their enormous prospective.

### 1.1 Electro spraying technique

Electro spraying is one of the promising methods for synthesis carbon nano particles (Cloupeau.M., *et al* 1989;Cloupeau M.,1990;Cloupeau M., *et al* 1994;Bagheri-Tar., F., *et al* 2007;Jaworek, A., 2007;Yiquan, Wu., *et al* 2007;Jaworek, A., *et al.* 2008;Valvo,M. *et al.* 2009). Electro spraying has several advantages over other techniques, which offer preparation of homogeneous spherical granules with a narrow distribution and high yield (Jaworek, A., 2007; Jaworek, A., *et al* 2008) and may be used as drug delivery carrier (Arya, N., *et al.,* 2009). Spray techniques can give simple scalable and continuous method, for absorbent carbon production (Suslick, K.S., *et al* 1999; Bang, JH., *et al* 2010; Skrabalak SE., 2009; Hampsey, JE., 2005; Yan.Y., *et al* 2007; Hu, Q., *et al* 2008; KodasTT., *et al* 1999). Carbon spheres (0.5-3mm) diameter , where directly obtained using ultrasonic sprays pyrolysis (USP) from organic salt precursors (Skrabalak SE., *et al* 2007;Skrabalak SE., *et al* 2006;Fortunato ME., *et al* 2010). Meso- and macro-porosity are developed using in situ templates and micro-porosity results from in situ carbon gasification the activity of the methanol fuel cell anode was upgraded by using basic wet Pt-Ru in USP process (Bang JH., *et al* 2007). Other investigators used activated carbon as a catalyst by impregnation of commercial carbon (Liu H., *et al* 2007). Someone used USP as impregnation for preparation of fuel cell catalysts (Hampden-Smith M., *et al* 2003).

### 1.2 Traditional dehydration mechanism

White crystals were obtained by freezing $H_2SO_4$ (98%) at 10.5ºC.These crystals are solid three dimensional hydrogen bonded network persists in liquid and aqueous state. Heating pure acid to evolve $SO_3$ and $H_2O$, this $H_2SO_4$ reaches its boiling point $330^0$C and 98.33%concentration.Concentrated $H_2SO_4$ of 18M is used for gas drying and doesn't react with $SO_2$, $Cl_2$, $N_2$, and $O_2$. So it used for drying out carbohydrates, acids, organic

alcohols, and hydrate crystals. The following equation, shows the reaction of sucrose drying out carbohydrate to carbon then carbon is oxidizes to $CO_2$.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Dehydrate}} 12C(s) + 11H_2O \xrightarrow{\text{Oxidation}} CO_2 + SO_2$$

Time lag one minute before reaction progress was observed. Because the reaction is exothermic, the rate of water removing increases and the acid begins to be yellow. Removing water from the sugar molecules generates heat and converts water to steam which expands the remaining carbon into porous, black smoky columns which leads to sharp acid vapors with burned sugar odour.

## 2. MATERIAL AND METHODS

### 2.1 Material

Commercial sugar produced by El Masreya for Sugar production Co., Phosphoric acid MERK, Distilled water.

### 2.2 Production procedure

Sugar solution 5% solution was prepared by dissolving 50gm of sugar in 1liter distilled water. About 100ml of this solution was used for the preparation of carbon nano sphere. The sugar solution was boiled then 5ml of concentrated phosphoric acid was added with continuous stirring till the color of solution changes from transparent colorless to dark brown. After stopping the stirring and cooling the solution, the sample is analysed by TEM analysis.

### 2.3 Testing

Shape and size of the obtained nano sized carbon sphere particles were characterized by means of a JEOL-JEM-1200 Transmission Electron Microscope (TEM).For TEM test the sample was prepared by adding a drop of the nano carbon solution on a 400 mesh copper grid coated by an amorphous carbon film and keep the sample for drying in open air at room temperature. The diameter of the carbon nano particles was determined by taking the average of 100 nano particles from several chosen areas in enlarged microphotographs. Also, the same apparatus was used for X-ray diffraction test (Hussien, Nabila H., *et al* 2014)

## 3. RESULTS AND DISCUSSIONS

### 3.1 Influence of $H_3PO_4$ concentration

The influence of phosphoric acid concentration on the nano carbon spheres size at operating conditions of sugar concentration 50g/l, temperature 100ºC and heating time 15min. with stirring of 150rpm are shown in Figs (1, 2, 3).

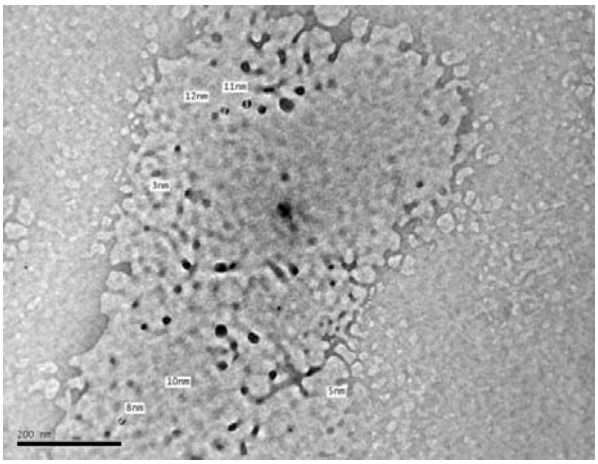


**Figure-1.**TEM measurement of 0.06M phosphoric acid sugar concentration 50g/l, temperature 100ºC and heating time 15min with stirring of 150rpm.

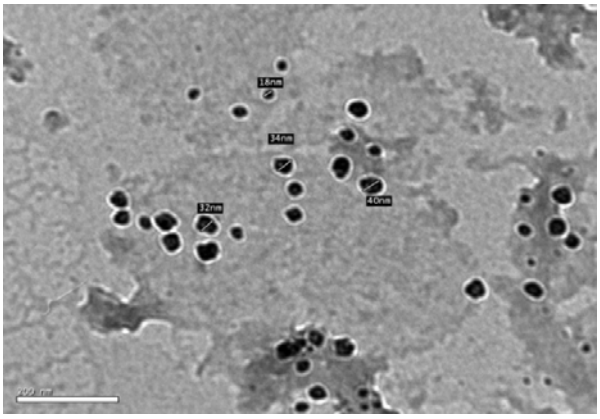


**Figure-2.**TEM measurement of 0.1M phosphoric acid sugar concentration 50g/l, temperature 100ºC and heating time 15min with stirring of 150rpm.

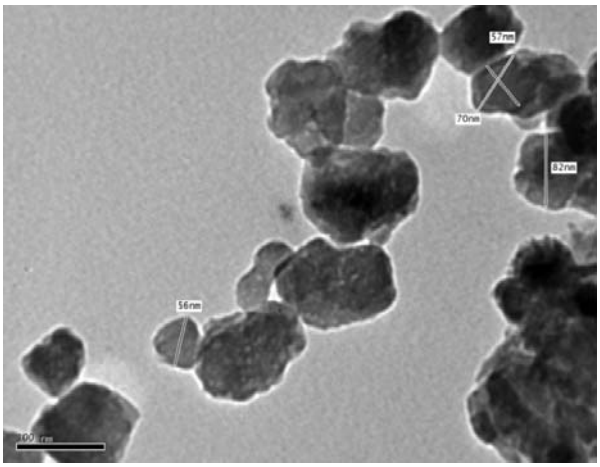


**Figure-3.** TEM measurement of 0.5M phosphoric acid at sugar concentration 50g/l, temperature 100ºC and heating time 15min with stirring of 150rpm.

The results show that as the phosphoric acid concentration increases from 0.06M to 0.5M the particles size increases too and the obtained particles sizes were 11nm, 40nm and over 70nm at phosphoric acid concentration of 0.06M, 0.1M and 0.5M respectively. Also the results show that as the phosphoric acid concentration increases to 0.5M the shape of the obtained carbon particles changed from spherical shape to flakes shape as shown in Figure-3. Figures 4-6 show the histogram of the obtained nano carbon particles at different phosphoric acid concentration ranged from 0.06M to 0.5M. From these figures and the above mentioned results and according to the optimum particle size of nano carbon used in the agriculture applications (up to50nm) phosphoric acid concentration of 0.1M was selected as the optimum concentration for the preparation of nano carbon sphere.

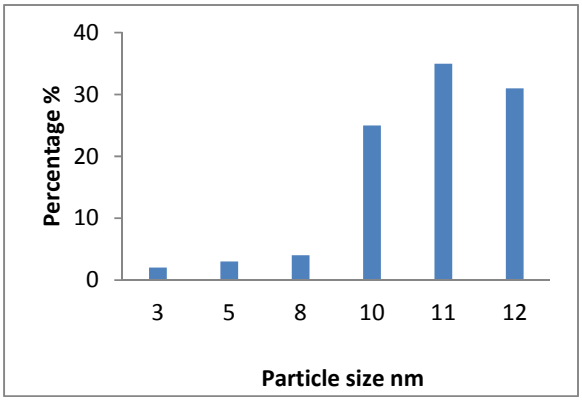


**Figure-4.** Histogram of carbon nano particles, prepared using 0.06M phosphoric acid at sugar concentration 50g/l, temperature 100°C, heating time 15min with stirring of 150rpm.

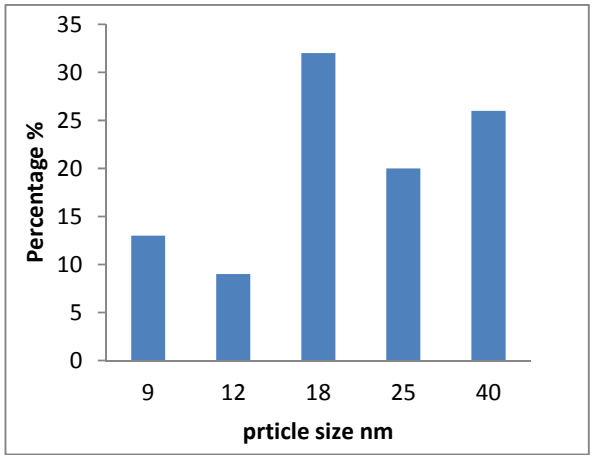


**Figure-5.** Histogram of nano carbon particles prepared using 0.1M phosphoric acid sugar concentration 50g/l, temperature 100°C, heating time 15min with stirring of 150rpm.

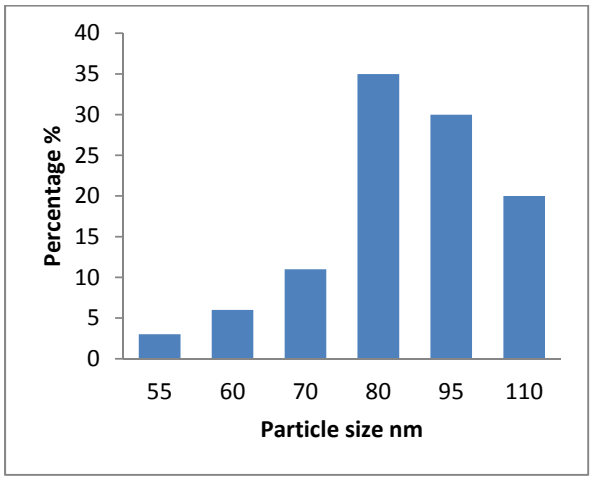


**Figure-6.** Histogram of nano carbon particles prepared using 0.5M phosphoric acid sugar concentration 50g/l, temperature 100°C, heating time 15min with stirring of 150rpm.

### 3.2 Influence of sugar addition

Influence of sugar concentration on the obtained carbon nano particles prepared at phosphoric acid concentration 0.1M, 100°C and 15min heating time at 150rpm were shown in Figures (7, 8 and 2). The results show that as the sugar concentration increases, the obtained particle size of the nano carbon decreases. Also the shape of the obtained nano carbon converted from flake shape at 10g/l sugar to spherical shape at 50g/l. From the above results, it was concluded that the optimum sugar concentration is 50g/l.

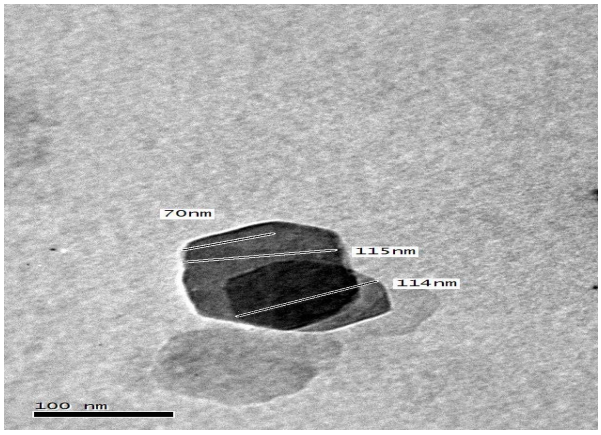


**Figure-7.** Nano carbon particles prepared using 0.1M phosphoric acid at sugar concentration 10g/l, temperature 100°C, heating time 15min with stirring of 150rpm.

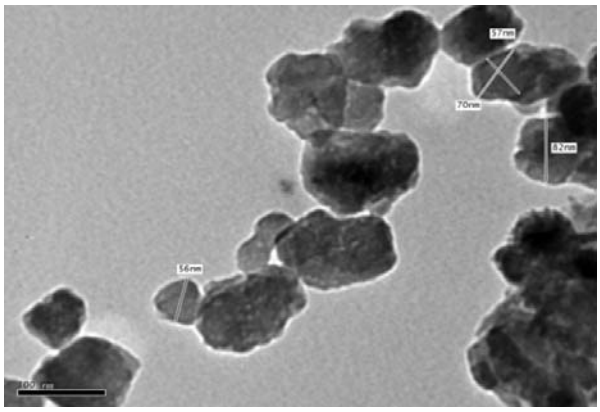

**Figure-8.** Nano carbon particles prepared using 0.1M phosphoric acid at sugar concentration 35g/l, temperature 100ºC, heating time 15min with stirring of 150rpm.

### 3.3 Effect of heating

The effect of heating on the prepared nano carbon spheres at phosphoric acid concentration of 0.1M, sugar concentration 50g/l, heating time 15min, and stirring rate 150rpm was studied from the range of 50ºC to 100ºC as shown in Figs (9,10). The results show that at 50ºC, 80ºC no conversion of sugar to nano carbon were obtained while at 100ºC particles size of nano carbon sphere was 40 nm as illustrated in Figures 2 and 5. So, the temperature 100ºC was selected as the optimum temperature for carbon nano spheres preparation.

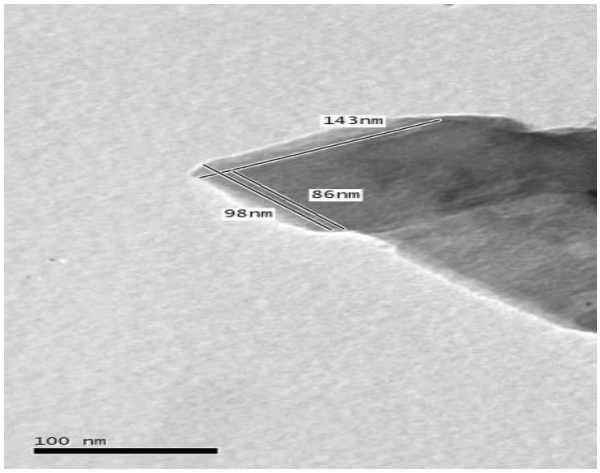


**Figure-9.** Nano carbon particles prepared using 0.1M phosphoric acid at sugar concentration 50g/l, temperature 100ºC, heating time 30min with stirring of 150rpm.

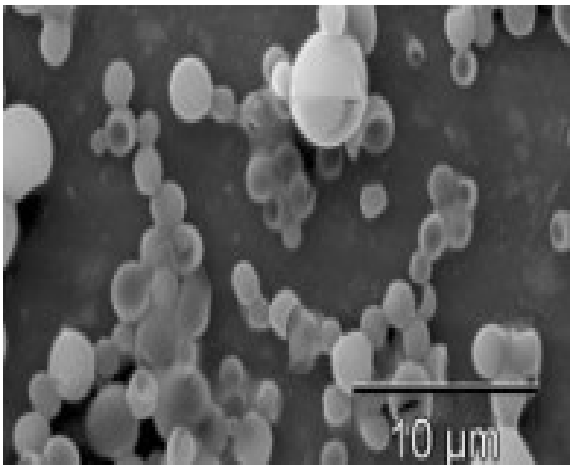


**Figure-10.** Nano carbon particles prepared using 0.1M phosphoric acid at sugar concentration 50g/l, temperature 100ºC, heating time 60min with stirring of 150rpm.

#### 3.3.1 Effect of heating time

The effect of heating time on the prepared nano carbon spheres at phosphoric acid concentration of 0.1M, sugar concentration 50g/l, boiling at 100ºC, and stirring rate 150rpm was studied from the range of 5mins to 60mins. The results show that no conversion to nano size was obtained before 15mins as mentioned in Figures 2 and 5 and after that with increasing of heating time carbon particle size increases where at 30mins it reaches to about 90nm as mentioned in Figure-9 and reaching to micro size at 60mins as shown in Figure-10. Based on that results 15mins was selected as the optimum heating time to converts sugar to the desired carbon nano spheres (50nm). Based on the investigation of the optimum operating conditions for the preparation of nano carbon sphere with the range of 50nm, it is concluded that the optimum conditions were phosphoric acid concentration of 0.1M, sugar concentration 50g/l, boiling at 100ºC for 15mins at stirring rate 150rpm. The obtained carbon nano sphere is suitable to be used as fertilizer and as seed germination enhancement as predicted from the literature review. Figure-11 represents the SAED pattern of the obtained nano carbon sphere at the selected optimum conditions.

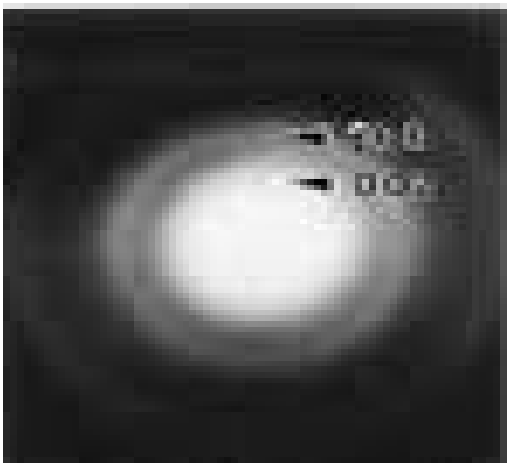

**Figure-11.** SAED pattern of carbon nano sphere optimum conditions.

## 4. CONCLUSIONS

Carbon nano spheres were prepared by acid dehydration process using phosphoric acid. The results show that as the phosphoric acid concentration increases from 0.06M to 0.5M, the particles size increases and varied from 11nm, 40nm to 100nm at phosphoric acid concentration of 0.06M, 0.1M and 0.5M respectively. The optimum acid concentration was 0.1M. Also, as the sugar concentration increases the particle size of nano carbon decreases, the optimum sugar concentration was 50g/l. at heating conditions 100ºC for heating time 15mins, were selected for carbon nano sphere preparation. It is recommended in the next investigation to apply these carbon nano spheres in agriculture testing.

## REFERENCES

Serrato-Valenti G., Cornara L., Modenesi P., Piana M., Mariotti M. G. 2000. Structure and Histochemistry of Embryo Envelope Tissues in the Mature Dry Seed and Early Germination of Phacelia tanacetifolia. Ann. Bot. 85, 625-634.

Torney F., Trewyn B., Lin V.S.-Y., Wang K. 2007. Mesoporous Silica Nanoparticles Deliver DNA and Chemicals into Plants. Nat. Nanotechnol.2, 295-300.

Gonzales-Melendi P., Fernandez-Pacheco R., Coronado M. J., Corredor E., Testillano P. S., Risueno M. C., Marquina C., Ibarra M. P., Rubiales D., Perez-De-Luque A. 2008. Nanoparticles as Smart Treatment-Delivery Systems in Plants: Assessment of Different Techniques of Microscopy for Their Visualization in Plant Tissues. Ann. Bot.101, 187-195.

Calderon-Moreno J.M., Labarta A., Batlle X., Pradell T., Crespo D., Binh V.T. 2007. Magnetic properties of dense carbon nanospheres prepared by chemical vapor deposition. Chem. Phys. Lett. 447, 295-299.

Lee E. J., Oh K. C. and Shin H. D. 2005. Soot Formation in Inverse Diffusion Flames of Diluted Ethene, Fuel. 84:543-550.

Wang, Z.D., Tao, M.X., Meng, Q.X., 2008. Research progress of source rocks and formation of low evolution oil and gas in Turpan-Hami Bain.Nat. Gas Geosci. 19, 754-760.

Pekala R.W. 1989. Organic aerogels from the poly condensation of resorcinol with formaldehyde. Journal of Materials Science. 24, 32221–32227.

Hasegawa, T., et al. 2004. Preparation of carbon gel microspheres containing silicon powder for lithium ion battery anodes. Carbon 42, 2573-2579.

Chandra S. Sharmaa, Manish M. Kulkarni, Ashutosh Sharmaa, Marc Madoub. 2009. Synthesis of carbon xerogel particles and fractal-like structures. Chemical Engineering Science. 64: 1536-1543.

Cloupeau M and Prunet-Foch B, 1989. Electrostatic spraying of liquids in cone-jet mode.J Electrostat.22:135.

Cloupeau M and Prunet-Foch B. 1990.Electrostatic spraying of liquids in main functioning mode. J. Electrostat. 25:165.

Cloupeau M and Prunet-Foch, B. 1994.Electrohydrodynamic spraying functioning mode a critical review, J. Aerosol Sci. 25:1021.

Bagheri-Tar.F., M. Sahimiand T. T. Tsotsis. 2007. Preparation of polyetherimide nanoparticles by an electrospraying technique. Industrial and Engineering Chemistry Research. 46(10): 3348-3357.

Jaworek A. 2007. Micro- and Nanoparticle Production by Electrospraying. Powder Technology. 176(1): 18-35, ISSN 0032-5910.

Yiquan Wu, Robert L. Clark. 2007. Controllable porous polymer particles generated by electrospraying. Journal of Colloid and Interface Science. 310: 529-535.

Jaworek A. and Sobczyk A. T. 2008.Electrospraying Route to Nanotechnology: an Overview. Journal of Electrostatics. 66(3-4): 197-219, ISSN 0304-3886.

ValvoM., Lafont UMunao D, *et al.* 2009. Electrospraying-assisted synthesis of tin nanoparticles for Li-ion battery electrodes. J Power Sources. 189: 297-302.

Arya N., et al. 2009. Electrospraying: a facile technique for synthesis of chitosan-based micro/nanospheres for drug delivery applications. J. Biomed. Mater. Res.Part B: Appl. Biomater. 88B(1): 17.

SuslickK. S, Price G.J. 1999. Applications of ultrasound to materials chemistry. Annu Rev Mater Sci. 29:295-326.

Bang JH, Suslick KS. 2010. Applications of ultrasound to the synthesis of nanostructured materials. Adv Mater. 22:1039-1059.

Skrabalak SE. 2009. Ultrasound-assisted synthesis of carbon materials Chem. Phys;11(25):4930–4942.

Hampsey JE, Hu Q, Rice L, Pang J, Wu Z, Lu Y. 2005. A general approach towards hierarchical porous carbon particles. Chem. Commun. 3606-3608.

Yan Y, Zhang F, Meng Y, Tu B, Zhao D. 2007. One-step synthesis of ordered mesoporous carbonaceous spheres by an aerosol-assisted self-assembly. Chem. Commun.2867-2869.

Hu Q, Lu .Y, Meisner.GP. 2008. Preparation of nanoporous carbon particles and their cryogenic hydrogen storage capacities. J Phys Chem. C. 112:1516-1523.

KodasTT, Hampden-Smith MJ. 1999. Aerosol processing of materials. New York: Wiley-VCH.

Skrabalak SE, Suslick KS. 2007. Carbon powders prepared by ultrasonic spray pyrolysis of substituted alkali benzoates. J PhysChem C;111:17807-17811.

Skrabalak SE, Suslick KS. 2006.Porous carbon powders prepared by ultrasonic spray pyrolysis. J. Am. Chem. Soc.128(39):12642-12643.

Fortunato ME, Rostam-Abadi M, Suslick KS. 2010. Nanostructured carbons prepared by ultrasonic spray pyrolysis. Chem. Mater. 22:1610-1612.

Bang JH, Han K, Skrabalak SE, Kim H, Suslick KS. 2007. Porous carbon supports prepared by ultrasonic spray pyrolysis for direct methanol fuel cell electrodes. J. Phys. Chem. C. 111:10959-10964.

Liu H, Song C, Tang Y, Zhang J, Zhang J. 2007. High-surface-area CoTMPP/C synthesized by ultrasonic spray pyrolysis for PEM fuel cell electrocatalysts. Electrochim.Acta. 52: 4532-4538.

Hampden-Smith M, Antanassova P, KodasTT. Fuel cell technology and application. In: Wielstich W, Gasteiger HA, Lamm A, editors. Handbook of fuel cells-fundamentals technology, and applications, vol. 3.JohnWiley and Sons; 2003 [chapter 40].

Nabila H Hussien, Shakinaz Sheltawy, Hammam El Abd, Guzine El Diwani and Hassan H Shaarawy. 2014. Novel and Cost Effective Method for Nanosilver Preparation as Marine Antifouling Additive via Wet Chemical Reduction Method, RJPBCS. 5(4): 166.

Nabila H Hussien, Shakinaz Sheltawy, Hammam El Abd, Salwa Hawash and Hassan H Shaarawy.2014. Green Cost Effective Method for Nano zinc oxide Preparation as Marine Antifouling Additive via Wet Chemical Reduction Method, RJPBCS. 5(4): 149.