

# Investigation of conductivity properties of Hollow Carbon Nanospheres by STM and Scanning Tunneling Spectroscopy technique

M. Teymourzadeh<sup>1,2\*</sup>, M. Seifi<sup>2</sup> and I. Hasanzadeh<sup>3</sup>

<sup>1</sup>Department of Physics, Faculty of Sciences, University of Guilan, Rasht, Iran

<sup>2</sup>Reactor and Nuclear Safety Research School, Nuclear Science and Technology Research Institute, P.O. Box 81465/1589, Isfahan, Iran

<sup>3</sup>Iran Polymer and Petrochemical Institute, Tehran, Iran

Manuscript received March 15, 2019; revised July 1, 2019; accepted July 18, 2019. Date of publication September 14, 2019

**Abstract**—The electronic and conductivity properties of hollow carbon nanospheres (HCNSs) were investigated in this work via scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) technique. Study and estimation of the Quantum behaviour and differential conductance ( $dI/dV$ ) measurements of HCNSs was the most important task. The hollow carbon nanospheres used herein are synthesized by chemical vapour deposition (CVD) method from HgO/C nanocomposite with core-shell structures. The local currents images on the surface of HCNSs was recorded by STM and to measure the differential conductance by STS technique, Perform a current-voltage sweep (I-V curve) and take the mathematical derivative was used. The Differential conductance measurements of the synthesized hollow carbon nanospheres from CVD method was carried out using an improved method. The HCNSs I-V curve follows from the quantum behaviour and it was observed that the HCNSs has a good conductivity for many applications such as electronic devices and electrode materials.

**Index Terms**—hollow carbon nanospheres, STM, STS, Differential conductance.

## I. INTRODUCTION

Hollow carbon nanoparticles are strong, conduct electricity well and have a remarkably large surface area [1]. The applications of some carbon materials such as carbon black are limited because its disordered or amorphous structure leads to low electrical conductivity and insufficient oxidation resistance [2], hence the new carbon-based nanomaterials with highly curved graphitic structures, having well-developed crystalline structures, high electrical conductivity, good thermal stability, and satisfactory oxidation resistance, are highly desirable for a large number of applications [3].

Hollow carbon nanospheres (HCNSs) with a structure of hollow cores and carbon shells have high specific surface area, low density, large pore volume, high surface permeability, good mechanical strength, and high chemical inertness [4]. Hollow carbon spheres possessing the unique properties of durability and stability have promising applications in catalysts, sensors, microelectronics, biomaterials, semiconductors, and many other areas of nanotechnology. It is also worth noting that the carbon-shell has the advantage of high electron transfer rates due to its abundant surface free electrons. Many applications in sensors, fuel cells electrodes, solar cell electrolytes, and batteries have, therefore, been found [5].

Differential conductance measurements are performed in many areas of research, though sometimes under different names. When used to measure the electron energy structure of small devices such as quantum dots, nanoparticles, or artificial atoms, it is sometimes referred to as electron energy spectroscopy. When used to perform non-contact measurements on surfaces within a scanning Tunnelling microscope, it may be called tunneling spectroscopy. When studying ultra-small semiconductor structures or nanotubes

with semiconducting properties, it might be called a density of states measurement. Still other researchers refer to it more mathematically, as the derivative of the I-V curve, or simply  $dI/dV$  or  $\Delta G$ . It can be used to understand conduction phenomenon in cryogenic environments or to observe and predict the conditions when tunneling is more likely to occur [6,7].

## II. MATERIALS AND METHOD

For this work, synthesis of core-shell HgO/C composite with CVD process with acetylene gas ( $C_2H_2$ ) as a carbon source for carbonization was carried out. The HgO nanoparticles, for the first time, were used to production of core-shell structure with Hg liquid cores and carbon shell. In special thermal condition, nanoparticles of these colloids are removed of core-shell composite and hollow carbon capsules are remained. Carbon nanospheres obtained by this method, have a size distribution in the range of 150 to 250 nm and have a hollow structures. The TEM micrographs of HgO/C composite with core-shell structures and the hollow carbon nanospheres are shown in fig. 1.

Fig. 2 demonstrates a corresponding XRD pattern of carbon capsules. This pattern exhibits two peaks at  $25^\circ$  and  $42^\circ$  attributed to carbon with hexagonal crystal structures.

The ability to study topography and electronic properties at the same time makes the STM to an essential tool for surface structure investigation. In this study STM measurements in air, and at room temperature as well as at low temperature were performed. The instrumental configuration of a scanning tunnelling microscope is very simple. A sharp tip scans over a sample surface at a small distance  $d$  on a sub-nm scale. The gap between the sample and the tip represents a potential barrier between both electrodes (sample and tip). An applied voltage between them initiates an electron current due

Corresponding author: M. Teymourzadeh (mehrdad.teymourzadeh@yahoo.com). (For the real e-mail address, see <http://www.journals.procedia.org/Journal-Of-Nanoelectronic-Devices/>).

Associate Editor: Ashkan Horri.

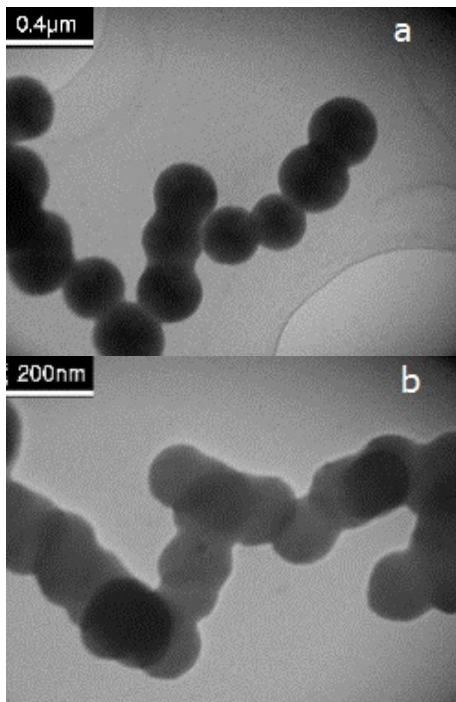


Fig. 1. a) TEM image of HgO/carbon collides, b) TEM image of the HCNSs

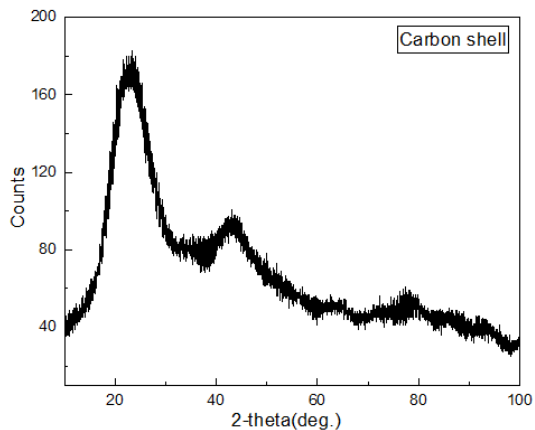


Fig. 2. XRD pattern of carbon shell

to the quantum mechanical tunnelling effect. The resulting tunnelling current is given as:

$$I_t \sim \exp(-2kd) \quad (1)$$

The tunnelling current typically decreases by an order of magnitude when  $d$  is increased by  $1\text{Å}$ . This enables an effective imaging with a reasonable vertical resolution [8]. To obtain a three-dimensional image of the surface two different operating modes (constant current and constant height) are generally used in the field of STM, each holding its own advantages. The constant current mode is based on the feedback loop control. The tip scans laterally over the surface and the tip-sample distance is continuously adjusted by the feedback loop in order to keep the tunnelling current constant when the tip is moving [9]. The STM and STS technique were carried out by Scanning probe microscopy, model DME Doalscop<sup>TM</sup> DS95. In

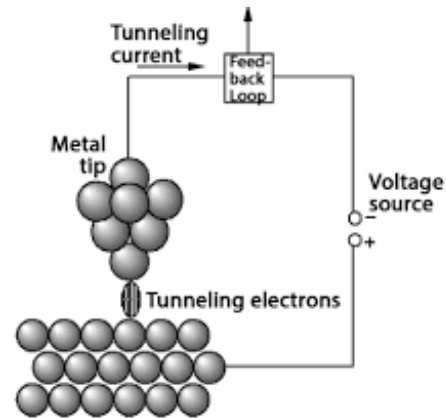


Fig. 3. Schematic of STM on HCNSs

fig. 3, a schematic representation of the STM process is shown on the HCNSs.

While there is no standardized technique to obtain differential conductance, almost all approaches have followed one of two methods: (a) Perform a current-voltage sweep (I-V curve) and take the mathematical derivative, or (b) Use an AC technique of applying a sinusoidal signal superimposed on a DC bias to the sample. Then use a lock-in amplifier to obtain the AC voltage across and the AC current through the DUT (device under test) [6].

### III. RESULTS AND DISCUSSION

The constant current STM image of the hollow carbon nanospheres are shown in fig. 4. According to it, the bright points indicate the establishment of localized currents on the surface of carbon spheres, which occurs due to the phenomenon of electron tunneling. In this way the path of the tip reproduces the shape of the carbon spheres surface. The result is a three-dimensional STM image of the inspected hollow carbon spheres surface. However, the interpretation of STM images is a mixture of topological and electronic information and depends on the type of system [10].

For the investigation of the electronic structure extensive sets of  $dI/dV$  spectroscopy measurements have been taken. The result of the point spectroscopy (Fig.5a) depends drastically on the position on the surface where they were recorded.

Figure 3b shows an I-V curve, a series of sourced and measured values  $(V_1, I_1), (V_2, I_2)$ , etc. The quantum behavior of the current-voltage graph of HCNSs at the nanoscale is evident. Several techniques can be used to differentiate this data, but the simplest and most common uses the slope between every pair of consecutive data points. For example, the first point in the differential conductance curve would be  $(I_2 - I_1)/(V_2 - V_1)$  [10]. Fig. 5c shows the differential conductance curve, and it can be seen that the synthesized hollow carbon nanospheres from CVD method is conductive and it also has a good conductivity property because of the existence of the more points with the maximum voltages, where the electrons are more active [7].

Because of the small differences, a small amount of noise in either the voltage or current causes a large uncertainty in the conductance. To reduce this noise, the I-V curve and its derivative can be measured repeatedly. Noise will be reduced by  $\sqrt{N}$  where  $N$  is the number of times the curve is measured [6].

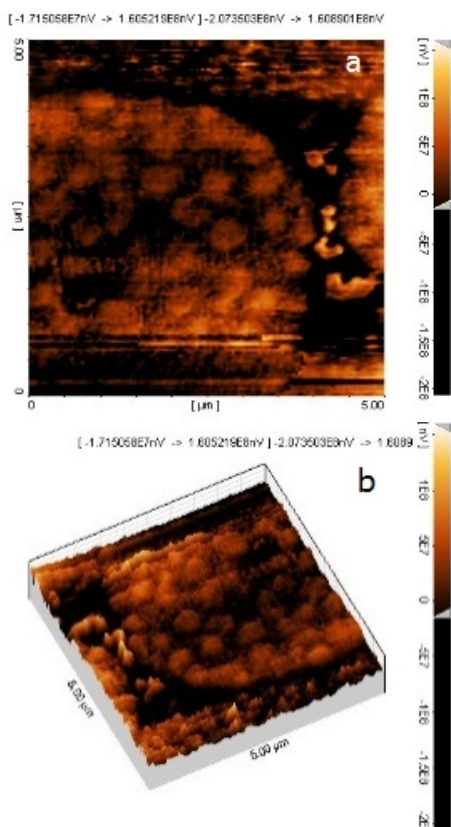


Fig. 4. a) Constant current STM image of the HCNSs, b) 3D STM image of the HCNSs

#### IV. CONCLUSIONS

Given that the HCNSs were expected to have good electron transfer and electronic properties [1-5], therefore we could use from the STS technique on the nanoscale to investigate of the differential conductance of HCNSs. Quantum behaviour such as tunnelling begins to play an important role in the electrical characteristics. In the macroscopic world, conductors may have obeyed Ohm's law, but in the nanoscale, Ohm's definition of resistance is no longer relevant. Because the slope of the I-V curve is no longer a fundamental constant of the material, a detailed measurement of the slope of that I-V curve at every point is needed to study nanodevices and the plot of differential conductance ( $dI/dV$ ) is the most important measurement made on small scale devices, but presents a unique set of challenges. The fundamental reason differential conductance is interesting is the conductance reaches a maximum at voltages (or more precisely, at electron energies in eV) at which the electrons are most active, that this was clearly evident about the electrical conductivity of HCNSs. Due to the good performance of the electrical conductivity of the synthesized HCNSs by the CVD method, it can be used in electronic devices and also as well as electrode materials in fuel cells, solar cells and lithium batteries.

#### REFERENCES

[1] Z-C. Yang, Y. Zhang, J.H. Kong, S. Wong, X. Li\* and J. Wang\*: 'Hollow carbon nanoparticles of tunable size and wall thickness by hydrothermal treatment of  $\alpha$ -cyclodextrin templated by F127 block copolymers', *Chemistry of Materials*, 2013, **25**, pp.704-710.

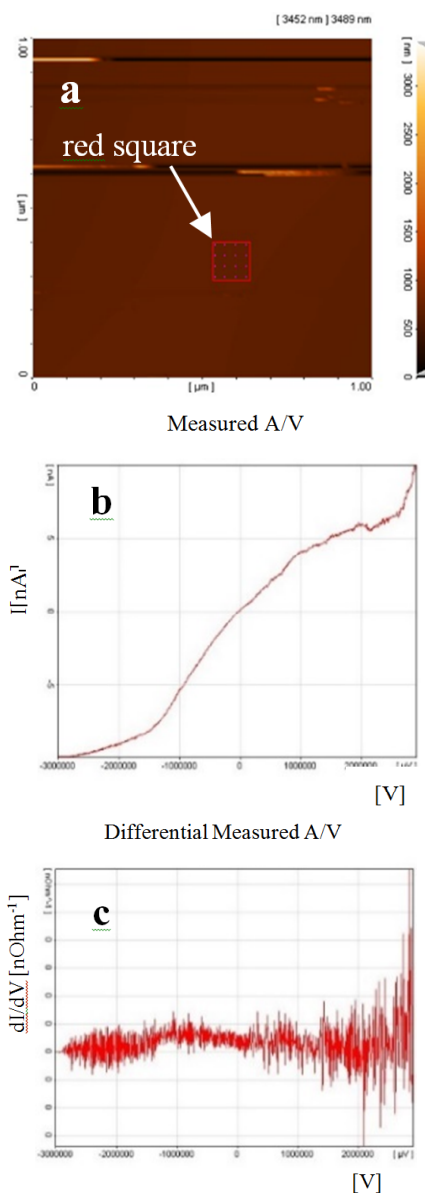


Fig. 5. a) Red square shows selected area for measurement, b) nonlinear I-V curve of selected areas, c) Derived I-V ( $dI/dV$ ); that shows the HCNSs obtained from CVD method, is conductive

- [2] C. Zhang, G. Bhargava, M. Elwell, S. Parash, B. Zhou, D. Yates, I. Knoke, I. Neitzel, Y. Gogotsi: 'Hollow graphitic carbon nanospheres: synthesis and properties', *Journal of materials science*, 2014, **49**, pp.1947-1956.
- [3] Yushin, Gleb, et al.: 'Carbide-Derived Carbons: Effect of Pore Size on Hydrogen Uptake and Heat of Adsorption.', *Advanced Functional Materials*, 2006, **16**, pp.2288-2293.
- [4] Yang, G.Z., Xu, R.S., Min, C.H.E.N., Xia, W.A.N.G., et al.: 'Hollow carbon nanospheres prepared by carbonizing polymethylmethacrylate/polyacrylonitrile core/shell polymer particles', *New Carbon Materials*, 2008, **23**, pp.205-208.
- [5] Tsai, C.K., Kang, H.Y., Hong, C.I., Huang, C.H., Chang, F.C. and Wang, H.P: 'Preparation of hollow spherical carbon nanocages', *Journal of Nanoparticle Research*, 2012, **14**, pp.1315.
- [6] D. Adam: 'An improved method for differential conductance measurements', *Keithley white paper*, 2005, **440**, pp.248-0400.
- [7] Vij, D.R. ed: 'Handbook of applied solid state spectroscopy', *Springer Science and Business Media*, 2007, pp.99164-4630.
- [8] Behm, R.J., García, N. and Rohrer, H. eds: 'Scanning tunneling microscopy and related methods', *Springer Science and Business Media*, 2013, **184**.
- [9] W. Baumeister, P. Grütter, R. Guckenberger, H.J. Güntherodt, T. Hartmann, H.

- Heinzelmann, et al: 'Scanning Tunneling Microscopy II: Further Applications and Related Scanning Techniques', *Springer Science and Business Media*, 2013, **28**.
- [10] Q. Ferreira, A.M. Bragança, L. Alcácer and J. Morgado: 'Conductance of well-defined porphyrin self-assembled molecular wires up to 14 nm in length', *The Journal of Physical Chemistry C*, 2014, **13**, pp.7229-7234.