

Synthesis And Entrapment of Polyynes Inside Nano-Pores of Anodized Alumina Membrane:A Linear Allotrope of Carbon

Sibananda Sana¹, Chandan Adhikary²

¹Government Training College, Hooghly; West Bengal 712103, India

²Institute of Education (P.G.) for Women, Chandernagore, Hooghly, West Bengal 712138, India

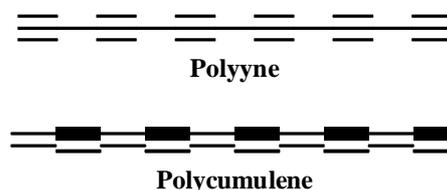
Abstract- The polyynes have been synthesized by modified Glaser-Hey coupling in solution by employing elementary laboratory conditions. The polyyne molecules are unstable in both pure state and in solution. The polyyne molecules are susceptible to crosslink producing carbonaceous materials. So it is necessary to put them apart in order to prevent crosslinking and to attain stability. In this study this problem was solved by pouring the linear rod like polyyne molecules inside the nano pores of anodized aluminum oxide (AAO) membrane, which was also synthesized by simple electrochemical process. The insertion of linear rod like polyyne molecules inside nano pores of anodized aluminum oxide (AAO) membrane was facilitated by the application of osmotic pressure. The presence of linear rod like polyyne molecules inside the nano pores of anodized aluminum oxide (AAO) membrane was verified by measuring its electrical transport property. The replicate measurement under same substantial condition after two months revealed its consistent electrical property and stability. This Stable polyyne-alumina composite membrane revealed moderate conducting and biological properties.

Keywords- Polyyne; Anodized aluminum Oxide (AAO) membrane; Nanopores; Osmotic Pressure.

I. INTRODUCTION

The polyyne [1-2], the precursor oligomer of α -carbyne[3-4] and the most controversial allotrope[5] of carbon is an unstable polymer in its pure state but fairly stable in very dilute solution. Different theoretical studies namely DFT (Density Function Theory) and MBPT (Many Body Perturbation Theory) [6] suggest that the polyyne has some unique properties and if it becomes stable for using in ambient environment then it will rule the coming decades. The polyyne is the strongest material and even harder than diamond [7]. Further the polyyne shows stress dependent semiconducting nature and spin dependent electrical transport property [8]. The other isomer polycumulene, the precursor oligomer of β -carbyne is less stable than polyyne and constantly undergo a Peierls transition into polyyne in solution [9-10]. This isomer of polyyne shows metallic conduction [11]. The polyyne along with its isomer not only show properties for engineering

materials and application in nano-devices but also its solution has some bio-medical properties like anti-TB[12], anti-cancer[13], antifungal, anti HIV and anti-bacterial properties[14].



The polyyne can easily synthesized by different techniques-

- Oxidative coupling namely historical Glaser Coupling (1869), Straus coupling, Hay coupling, Cadiot-Chodkiewioz hetero-coupling, Eglinton condition for oxidative coupling[15] etc,
- Electrical arc through carbonaceous materials like graphite (99.99%) electrode in organic solvent [16],
- Irradiating pure graphite (99.99%) [17-19], diamond [20] or solid hydrocarbon [21] with laser in any organic solvent like acetone, methanol, ethanol etc,
- Laser ablation of C₆₀ particles suspended in solution [22-23],
- Nanosecond pulsed laser deposition of carbon films in a background gas [24],
- Fritch-Buttenberg-Wiechell (FBW) Rearrangement [Forbidden 1,2 carbanion sift]: Tykwinski and his coworkers recently synthesized polyyne chains of as many as 22 $\text{C}\equiv\text{C}$ moieties by combining traditional oxidative coupling with the FBW rearrangement of dibromoolefinic precursors [25].

Of these above processes for synthesizing polyyne, modified Glaser-Hay coupling is one of the simple processes to synthesize polyyne in elementary laboratory condition. Though polyyne molecules are unstable in pure state but are moderately stable in dilute solution. The preservation of solution of polyyne mixture of different length of molecule is difficult. It not only reacts with oxygen but also photosensitive as well as forms crosslinks when they come close to each

another [2, 27]. The cross-linking of polyynes is depicted in Figure 1.

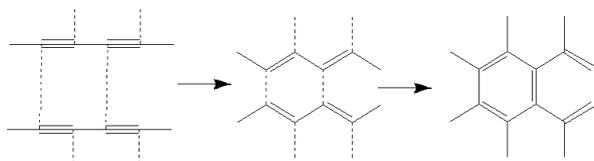


Figure 1 Cross-linking of polyynes.

The purpose of this study is to synthesize polyynes through simple process and make some arrangements to preserve and use polyynes in future for different functionalities at ambient conditions. If linear rod like polyynemolecules put apart from each other the conversion to carbonaceous material through crosslinking will be prevented and then it will attain stability. This can be accomplished by inserting these linear rods like polyynes into the nano pores of some unreactive insulating materials. The linear rods like polyynemolecules inside nano pores of insulating materials or better say polyynes-insulating materials composite can be preserved and used in any device for certain targeted functionality. One material, suitable for this purpose is Nano porous anodized aluminum oxide (AAO) membrane. If any how linear rods like polyynes molecules are inserted into the nano pores of insulating anodized aluminum oxide (AAO) membrane, the requirement may be reached.

II. EXPERIMENTAL

2.1 Synthesis and characterization of Polyynes

The copper complex of polyynes or copper polyynides were synthesized by modified Glaser-Hay coupling method [28] in a interlinked three round bottomed flasks (Figure 2) where the polymerization flask was fitted with a syringe and balloon for oxygen supply during oxidative coupling. Here 50 ml of methanol, 2 g of cupric chloride, 1 g of cuprous chloride and 2 ml of tetra methyl ethylene di amine (TMEDA) were added to the polymerization flask on a magnetic stirrer for constant stirring. 12 g of calcium carbide was added to the third flask fitted dropping funnel filled with de-mineralized water and linked to the first flask through the second flask and glass tube for acetylene supply. Copper polyynides were precipitated out as brown coloured materials and hydrolyzed to polyynes by 20 ml of concentrate hydrochloric acid after adding 50 ml pure heptane. The synthesis of polyynes was confirmed by the transformation of organic layer into bright yellow colour [4, 15]. As polyynes were precipitated as Copper polyynides and re-hydrolyzed to generate polyynes, so freshly prepared polyynes were almost pure but on standing even in high dilution the polyynes molecules come close to

each other and produce carbonaceous materials. So, all the characterization and further experiments were carried out with freshly prepared polyynes in heptane solution. All the chemicals used of reagent grade and were obtained from Sigma Aldrich Chemical Ltd.

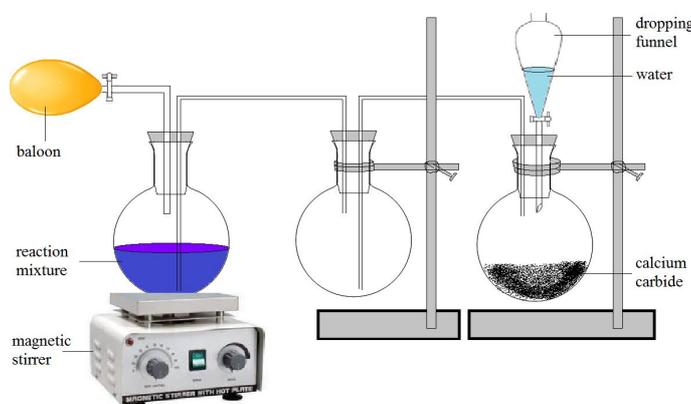


Figure 2 Schematic diagram of arrangement for polymerization through Modified Glaser-Hay Coupling

In the UV-VIS spectra of polyynes in heptane solution, the absorption peaks appear in the spectra (λ_{max}) 270, 315, 349, 377 and 402 nm (Figure 3). In addition there is a plateau in shorter wave length due to solvent and other effects. The λ_{max} values 270, 315, 349, 377 and 402 nm clearly corresponds to C_8 , C_{12} , C_{16} , C_{20} and C_{24} carbon chain [25,26] but the λ_{max} values are shifted to the longer wave length i.e. red shift occur as in the present study polyynes are Hydrogen ended, so no case of delocalization from end capped group. From the heights of the peaks it is clear C_{16} i.e. polyynes with eight units of $C\equiv C$ is the major product in the mixture.

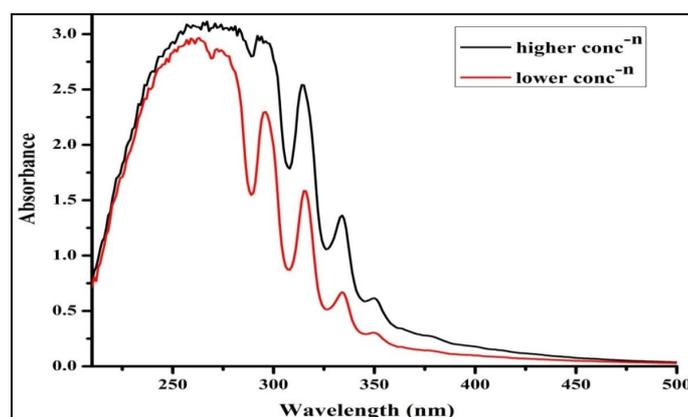


Figure 3 UV-VIS spectra of polyynes in heptane solution

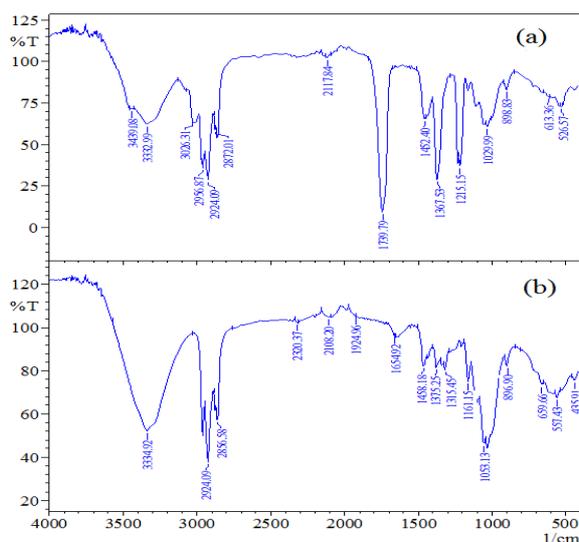


Figure 4 FTIR Spectra of polyne in heptane, (a) Freshly synthesized polyne and (b) after aging polyne in heptane for 3 days.

The FTIR spectra of the polyne mixture in heptane was carried out in an FTIR spectrometer (Bruker FTIR, TENSOR 27) at the department of chemistry, the University of Burdwan, shows absorption peaks at 3332, 3026, 2956, 2924, 2872, 2117, 1739, 1452, 1367, 1215 cm^{-1} . Of these peaks 2117 and 1739 cm^{-1} are characteristics peaks of $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ stretching. The peak at 3332 cm^{-1} is a characteristics peak of $\text{C}\equiv\text{C}-\text{H}$ stretching and peaks from 2872 to 3026 cm^{-1} are characteristics peaks alkenyl $\text{C}-\text{H}$ and alkyl $\text{C}-\text{H}$ stretching. The other peaks are mainly alkyl $\text{C}-\text{H}$ and $\text{C}-\text{C}$ bending which was come from solvent (Figure 4). The spectra clearly show freshly prepared polyne mixture in heptane contains both polyne and polycumulene, but on aging polycumulene constantly undergoes a Peierls transition into polyne [9].

2.2 Electrochemical synthesis and characterization of porous anodized aluminum oxide (AAO) membrane

In this experimental study a two steps anodization process [29] was followed to synthesize porous anodized aluminum oxide (AAO) membrane using a one end closed pure aluminum tube (99%) as anode after electro-polishing, pure graphite cathode and 0.3 M oxalic acid as electrolyte (Figure 5). A 20 volt potential difference for 40 hour in the second anodization step was applied to synthesize the AAO membrane and then it was treated with 5% H_3PO_4 solution for 20 minutes to remove the barrier layer which was standardized (Table 1) in this experiment to get less than 1nm opening in

the inner surface of the tubular AAO membrane after etching excess inner aluminum layer of the AAO membrane in CuCl_2 (80g/L) solution for 30 minutes [30, 31].

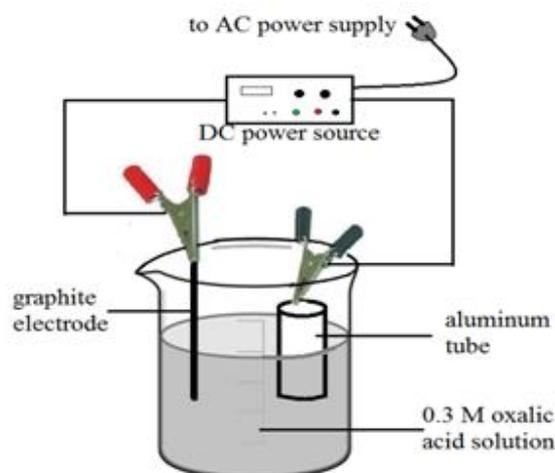


Figure 5 Schematic diagram of synthesis of Porous Anodized aluminum Oxide tubular membrane

SEM image of porous AAO membrane carried out in ZISS SEM at IIT, Kharagpur, India. In Figure 6a SEM image of the outer surface of AAO tubular membrane shows 10 to 20 nm pores in the surface of the membrane, while Figure 6b SEM image of the inner surface of AAO tubular membrane shows that it is almost pore less but in the forth coming conductivity measurement after polyne entrapment inside nano pores clearly indicates at least few 1-2nm pores in the inner surface.

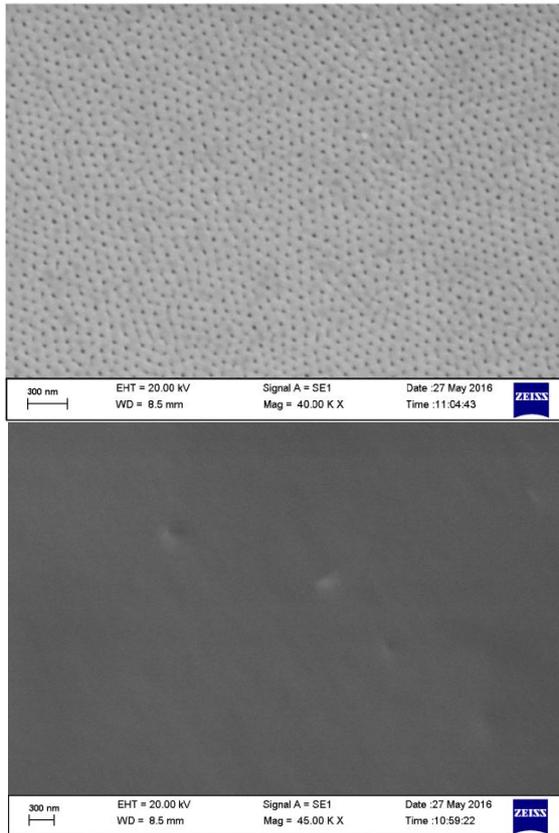
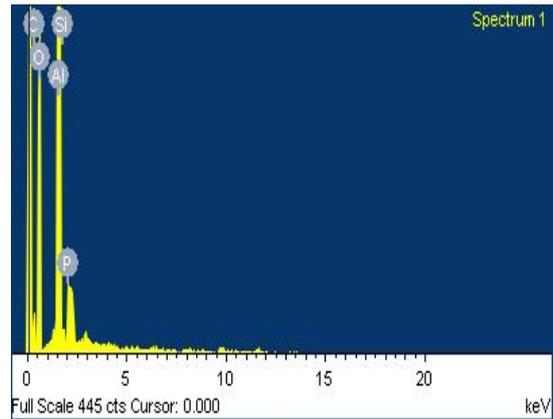
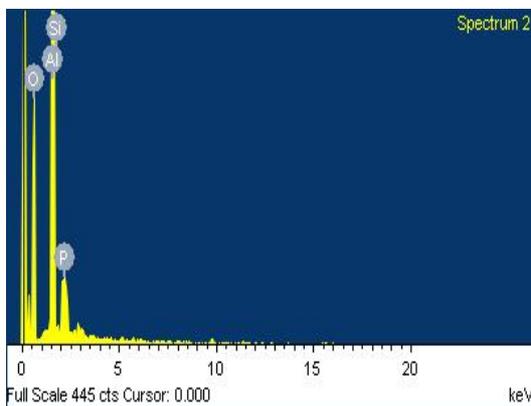


Figure 6a SEM image of the outer surface of AAO tubular membrane, **b** SEM image of the inner surface of AAO tubular membrane.



Element	Weight%	Atomic%
C	16.02	24.18
O	42.39	48.03
Al	39.40	26.47
Si	0.71	0.46
P	1.48	0.87
Totals	100.00	

Figure 7b EDX analysis of polyne AAO tubular composite membrane



Element	Weight%	Atomic%
O	44.22	57.36
Al	52.57	40.44
Si	0.69	0.51
P	2.52	1.69
Totals	100.00	

Figure 7a EDX analysis of AAO tubular membrane

The EDX analysis (Figure 7a & b) clearly reveals that pure alumina membrane and composite alumina membrane contain silicon and phosphorus as impurities which come from glass apparatus and barrier layer removal step respectively.

2.3 Insertion of polyne inside nano pores of AAO Membrane

Freshly synthesized polyne solution in heptane was poured outside the AAO tubular membrane placing in a small sample tube and pure heptane solvent was poured inside the porous AAO tubular membrane. The height of the solution outside the tube was higher than the height of pure solvent inside the tube and that will generate osmotic pressure which will facilitate the linear rod like polyne molecules to creep across the nano pores of the porous AAO tubular membrane and thus polyne - AAO composite membrane was synthesized (Figure 8).

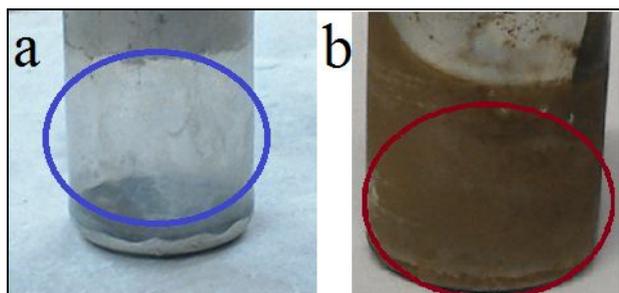


Figure 8(a) Nano porous AAO membrane, (b) Polyne AAO composite membrane.

2.4 Measurement of electrical transport

The electrical transport across the membrane was measured using a constant DC digital power source of 100 milli volt to 10 volt and a multi-meter. The Ohmic contacts were made using mercury i.e. mercury poured inside and outside the one end closed tubular polyne alumina composite membrane and the observed current across the polyne-alumina composite membrane (Figure 9) was measured and it was in the micro ampere range viz. 1.2 μ A under the application of 500mvolt potential difference which is quite in agreement with the reference [32] where polyne was synthesized in a different synthetic route by unraveling carbon atoms from graphene ribbons and passing electrical current through the ribbon. The replicate measurement of electrical transport of polyne alumina composite membrane under same substantial condition after two months revealed its consistent electrical property and stability (Table 1).

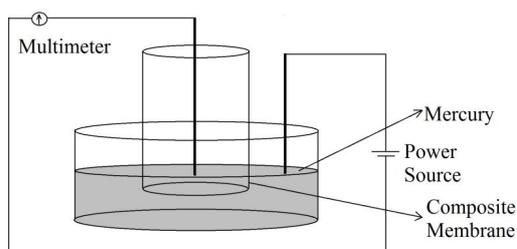


Figure 9 Schematic diagram for the measurement of electrical transport of polyne.

Table 1 Summary of the electrical Measurement:

Expt. No	Treatment Time with 5% H ₃ PO ₄ (Min.)	Preparation Time of composite (hrs)	Conductivity of	Comments
1	40	24	Metallic	>1nm pore in the inner surface, crosslinking of polyne and pure graphitic conduction.
2	30	24	Metallic	do
3	20	24	Semiconducting	<1nm pore in the inner surface and some polyynic contacts.
4	10	24	Insulating	Barrier layer was not completely removed.
5	No treatment	No treatment	Insulating	Pure alumina membrane with barrier layer.

The nature of I vs. V curve (Figure 10) shows that intensity of electrical transport slowly increases as the applied voltage increases, finally goes steeply upward and follows almost parallel to I axis indicates the semiconducting nature of polyne which is quite consistent with nature of the curve reported by Cretu O. et al where they synthesized polyne in a different synthetic route by unraveling carbon atoms from graphene ribbons and passing electrical current through the ribbon [32].

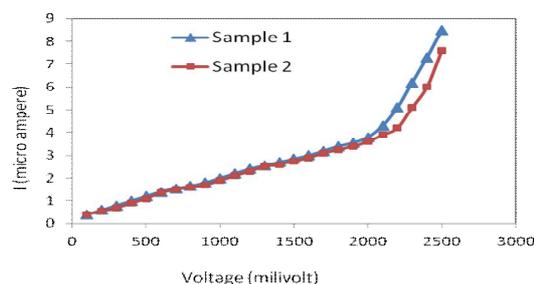


Figure 10 I vs. V curve of polyne chains inside nano pores of alumina membrane of two different samples show the almost similar nature of I vs. V curve (viz. exp.3).

III. RESULTS AND DISCUSSION

The mixture of Polyne molecules in heptane, synthesized by modified Glaser-Hay coupling contains eight units of $\text{C}\equiv\text{C}$ moiety as the major part which is evident from the UV-VIS spectroscopy (Figure 3). The length of polyne molecule containing C₁₆ moiety is almost half of the breadth of porous AAO membrane and which is quite sufficient (Figure 9) to make a bridge between inner and outer surface of the AAO membrane. Though in the carved perforated outer surface of AAO membrane polyynes get crosslinked producing amorphous carbon and graphite but few of them reach to the inner surface without losing the polyynic character and thus make Polyynic Bridge between outer and inner surface through the nano pores of AAO membrane. For

this purpose the diameter of nano pores in the inner surface have to be controlled and it was done in the barrier layer removal step by standardizing the time of treatment of 5% H_3PO_4 .

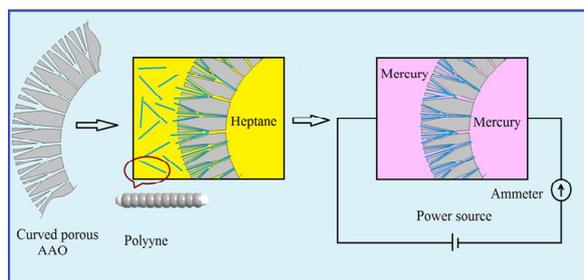


Figure 11 Schematic diagram of procedure for synthesis of stable polyynes inside nano pores of AAO and the measurement of electrical transport

The value of current passed against different potential differences suggests the polyynic contacts across the polyynes-alumina composite membrane is lower than theoretically expected and can be explained by the following three reasons:

- 1) The lesser time of treatment with 5% H_3PO_4 solution with membrane for removal of barrier layer of AAO membrane (which was standardized to 20 minutes to get ~ 1 nm pore in the inner surface) decreases the number of through holes across the composite membrane,
- 2) Carved nature of the membrane due to which the few pores in the outer surface join together to make one single pore in the inner surface of the tubular membrane which again lessen the number of pores in the inner surface in comparison to the outer surface and
- 3) Finally the clogging of the polyynemolecules inside nano pores decreases the chance of reaching of the polyynemolecule in the inner surface of membrane.

These three facts combine together to lessen the polyynic contacts enormously across the membrane. The nature of I vs. V curve shows the semiconducting nature of polyynes molecules which was predicted by different theoretical studies and was verified in this experiment (Figure 11).

IV. CONCLUSION

Chemically synthesized polyynes molecules in solution is unstable but, in this experimental study, it is clearly depicted that the simple route for the synthesis of stable polyynes inside nano pores of anodized aluminum oxide membrane in elementary laboratory condition. The polyynes anodized aluminum oxide composite membrane can be used

for fabricating some modern devices in future with different functionalities. Semiconducting behaviour of the linear rod like polyynes molecules inside the nano pores of anodized aluminum oxide membrane was clearly experimentally evaluated and verified with the calculated and theoretically established values. The other properties of polyynes can be evaluated and verified using this composite membrane in the follow up developmental experiments. The polyynes has vast field of application depending on its excellent conducting and biological properties. So this stable polyynes-alumina composite synthesized in this experiment will open up new advanced field of research and application.

V. ACKNOWLEDGEMENTS

This work was sponsored by University Grants Commission, Bahadur Shah Zafar Marg, New Delhi – 110 002, India (Sanctioned Letter No. PSW-017/13-14, ID No. WB1-028, Dated 18 March 2014) and the research work was carried out in the laboratory of chemistry department at Government Training College, Hooghly, West Bengal 712103, India.

Funding

University Grants Commission, New Delhi, India [grant number PSW-017/13-14 ID No. WB1-028, Dated 18 March 2014].

REFERENCES

- [1] R.B. Heimann, Carbyne and Carbynoid Structures. New York: Kluwer Academic; (1999).
- [2] F. Cataldo, Polyynes Synthesis, Properties, and Applications. New York: Taylor & Francis Group, LLC; (2006).
- [3] P. Delhaes, Carbon-based Solids and Materials. Hoboken: John Wiley & Sons, Inc. (2011) 39-45.
- [4] F. Cataldo, Polymer Int. 44 (1997) 191-200.
- [5] E.H.L. Falcao, F. Wudl, 82 (2007) 524-531.
- [6] B. Florian, Beilstein J. Nanotechnol. 6 (2015) 559-569.
- [7] L. Itzhaki, E. Altus, H. Basch, S. Hoz, Angew. Chem. 117 (2005) 7598-7601.
- [8] Z. Zanolli, G. Onida, J-C. Charlier, ACS Nano. 4 (9) (2010) 5174-5180.
- [9] M.J. Rice, A.R. Bishop, D.K. Campbell, Phys. Rev. Lett. 51(23) (1983) 2136-2139.
- [10] M. Liu, V. I. Artyukhov, H. Lee, et al. ACS Nano. 7 (11) (2013) 10075-10082
- [11] Y. Zhang, Y. Su, L. Wang, et al. Nanoscale Research Lett. 6 (2011) 577-581.
- [12] S. Deng, Y. Wang, T. Inui, et al. Phytother Res. 22(7) (2008) 878-882.

- [13] W-H.Huang, L.Shao, C-Z.Wang, et al. *Molecules*19 (2014) 6142-6162.
- [14] V. T.Tripp, J. S.Lampkowski, R.Tyler, et al.*ACS Comb. Sci.* 16 (2014) 164–167.
- [15] P.Siensen, R. C.Livingston, D. Francois,*Chem. Int. Ed.* 39 (2000) 2632-2657.
- [16] F. Cataldo,*Carbon.* 41 (2003) 2653 –2689.
- [17] A.Hu, J.Sanderson, A.A.Zaidi, et al. *Carbon*46 (2008) 1792-1828.
- [18] R.Matsutani, T.Kakimoto, K.Wada, et al. *Carbon*46 (2008) 1091–1109.
- [19] C.H.Wu, S.Y.Chen, P. Shen,*Carbon*67 (2014) 27 –37.
- [20] H.Tabata, M.Fujii, S. Hayashi,*Carbon*44 (2006) 522–529.
- [21] G.Compagnini, L.D’Urso, O.Puglisi, et al. *Carbon*47 (2009) 1605–1612.
- [22] M.Tsujia, S.Kuboyamab, T.Matsuzakib, et al.*Carbon*41 (2003) 2141–2148.
- [23] R.Matsutani, T.Kakimoto, H.Tanaka, K. Kojima,*Carbon*49(2011) 77–81.
- [24] C.S.Casari, C.S.Giannuzzi, V. Russo,*Carbon*104 (2016) 190-195.
- [25] W. A.Chalifoux, R.R. Tykwinski,*Nature Chem.* 2 (2010) 967-971.
- [26] K.Inoue, R.Matsutani, T.Sanada, K.Kojima,*Carbon*48 (2010) 4197–4214.
- [27] S.Okada, M.Fujii, S. Hayashi,*Carbon*49 (2011) 4704–4709.
- [28] K. Sanghee,*Angew. Chem. Int. Ed.* 48 (2009) 7740–7743.
- [29] H.Masuda, K. Fukuda,*Science.* 268 (1995) 1466-1468.
- [30] A.Nazemi, A.Seyed, S.Seyed,*Mat. Sc.-Pol.*32(4)(2014) 565-570.
- [31] A.Belwalkar, E.Grasing, V.W.Geertruyden, et al. *J. Membrane Sc.* 319 (2008) 192–198.
- [32] O.Cretu, A.R.Botello-Mendez, I.Janowska, et al. *Nano Lett.*13(2013)3487-3493.