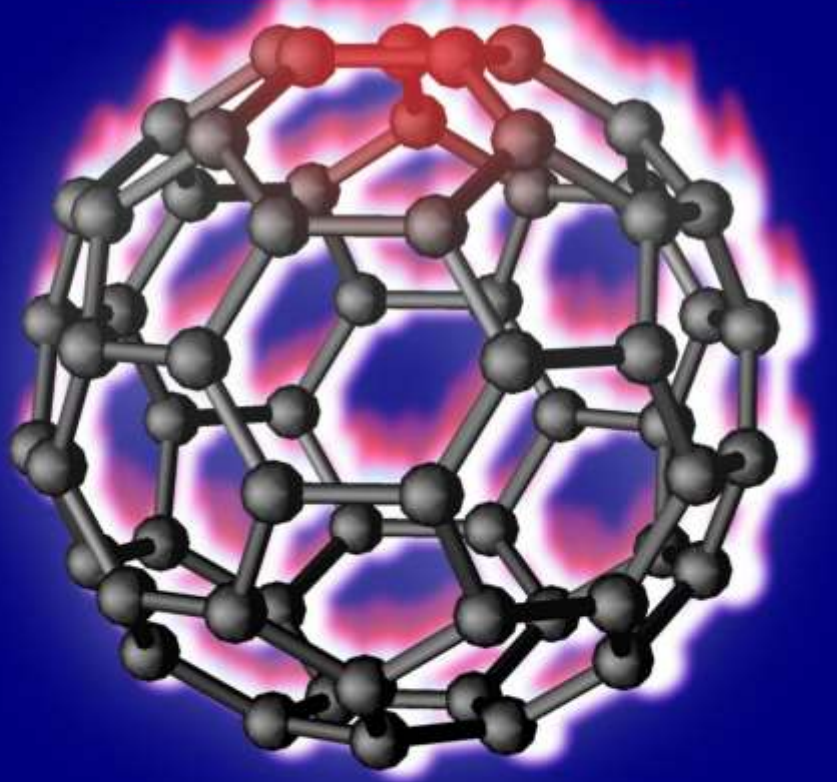
The Ministry of Education & Science of the Republic of Kazakhstan Scientific Committee

Al-Farabi Kazakh National University
International Science and Technology Center
The Institute of Combustion Problems
National Nanotechnology Laboratory of Open Type

X International Symposium

The Physics and Chemistry of Carbon and Nanoenergetic Materials



September 12-14, 2018
ALMATY, KAZAKHSTAN

Chapter 5

ORAL PRESENTATIONS
Day 2, September 13, 2018
Session 3 - Nanomaterials and SHS synthesis; Oil and hydrocarbons processing

TABLE of CONTENTS

OBTAINING GRAPHENE-BASED MEMBRANES

[1,2]Makpal Seitzhanova, [3]Michela Alfe, [3]Valentina Gargiulo, [3]Luciano Cortese,
[1,2]Zulhair Mansurov, [4]Roberto Di Capua
[1]Al-Farabi Kazakh National University, Almaty, Kazakhstan
[2]Institute of Combustion Problems, Almaty, Kazakhstan
[3]Institute for Research on Combustion (IRC-CNR), Naples, Italy
[4]University of Naples Federico II, Naples, Italy

Abstract
Graphenic-based PEI/PVP membranes were obtained by Non-solvent Induced Phase Separation Process (NIPS) method using graphene-related carbons (GRC) obtained from rice husk through a top-down approach. A further tailoring of GRC through a treatment with sulfuric acid was also explored. The GRC-based membranes displayed the presence of fully developed macro-pores and a substructure of smallest micropores.

Introduction

Membranes and membrane processes are not a recent invention. They are part of our daily life and exist as long as life exists. Today, membranes are used to produce potable water from the sea, to clean industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular mixtures in the food and drug industries, and to separate gases and vapors. They are also key components in energy conversion systems, and in artificial organs and drug delivery devices. The membranes used in the various applications differ widely in their structure and function and the way they are operated, thus, it is difficult to obtain a reasonably comprehensive and complete overview of the entire field of membranes and membrane based processes [1].

In recent years, the concept of nanotechnology entered also the membrane production field, indeed by adding nano-functional materials to conventional membrane materials, it was possible to modify and optimize the membrane performances. In particular, in the last years, different attempts to exploit the properties of graphene also in the membrane technology were proposed [2].

The purpose of this work is the production of microporous membranes based on graphene related carbons (GRC), obtained from rice husk (RH) through a top-down approach adapting the synthetic strategy reported in [3,4]. The effect of functionalization with sulfuric acid was also evaluated for the improvement of GRC hydrophilic properties.

Materials and methods

Materials. H_2SO_4 (98 wt.%), Polyvinylpyrrolidone (PVP) average Mw ~1.300.000 Da and N-methyl pyrrolidone (NMP) were purchased from Sigma Aldrich and used as received. Polyetherimide (PEI) 1000 was procured from Ultem. Carbon black (N110 type) by Sid Richardson Carbon & Energy was used as reference material. RH belongs from a deposit in Kazakhstan.

GRC synthesis and purification. The GRC were synthesized at the Institute of Combustion Problems in Kazakhstan by adapting the top-down approach from carbonized rice husk (CRH) reported in [3,4]. Briefly, the CRH was desilicated and then mixed with KOH (ratio carbon to KOH 1:4) and activated in air environment at 850°C for 2 h. After that, the material was washed with water until neutrality and dried at 105°C. The yield was around 1 wt.%.

Material functionalization. 0.3 g of GRC and 10 mL of 15 M H_2SO_4 were mixed in a round-bottom flask and the temperature was controlled at 80ºC. After 24 hours of stirring, the mixture was centrifuged for 10 min (4000 rpm), then the recovered solid was washed with bidistilled water up to neutrality. The solid, recovered by filtration on a PVDF membrane, was dried at 105°C for 16 h. The yield was around 2.5 wt.%.

Membrane preparation. PEI/PVP GRC modified membranes were prepared at IRC-CNR, Naples, by Non-solvent Induced Phase Separation Process (NIPS technique) [5]. Carbon black was also used as carbon model for comparison. Firstly, 0.4 g of PEI and 1,95 mL of NMP were added in a glass vial and heated around 50°C by stirring for 18 h to get a homogeneous polymer solution. Then that solution was divided into four equal aliquots. After that 0.1 g of each GRC sample was dispersed in a little amount of NMP (1 mL) and it was sonicated for 30 min to obtain a uniform dispersion and added to a NMP-dissolved PEI aliquot. After that, 0.1 g of PVP was added to each PEI/GRC suspension and gently stirred for 1 h to get a homogeneous suspension. Each resulting suspension was degasified by sonication to eradicate trapped air bubbles. Each homogeneous casting solution was then cast over a glass plate (adjusting the thickness at 400 microns) and immersed in the coagulation bath containing water as non-solvent at room temperature. The resulting membranes were kept in coagulation bath for 24 h to ensure the complete phase inversion [5] and dried overnight at room temperature. The membrane thickness was measured with a millimetric caliber. The composition of each casting solutions was reported in Table 1 along with the average membrane thickness.

Table 1 – Composition of casting solutions and average membrane thickness

Sample	NMP (ml)	PEI (g)	PVP (g)	GRC washed (g)	GRC washed and functionalized (g)	Carbon black (g)	Average size (μm)
M PVP/PEI	1.95	0.41	0.1	-	-	-	150
M PVP/PEI/GRC_w	1.95	0.41	0.1	0.1	-	-	340
M PVP/PEI/GRC_f	1.95	0.41	0.1	-	0.1	-	228
M PVP/PEI/CB	1.95	0.41	0.1	-	-	0.1	312

Methods. Scanning electron microscopy (SEM) was carried out on a FEI Inspect™ S50 Scanning Electron Microscope. The carbon, hydrogen and nitrogen contents of the samples were measured 628 LECO elemental analyzer according to the ASTM E870 procedure. Infrared spectroscopy (FTIR) analysis of the materials was performed on a Nicolet 5700 spectrophotometer.

Results and discussion

The elemental composition of GRC before and after the washing and functionalization is reported in Fig. 1a. The carbon content slightly increased after both processes.

GRC FTIR spectra are characterized by different signals ascribable to various functional groups (Fig.1b). The sample after washing is characterized by a peak due to C=C stretching modes (ca 1600 cm^{-1}) and overlapped peaks between 900 and 1500 cm^{-1} due to skeleton vibrations (C-C, C-H- C-O stretching and bending modes). The sample after functionalization is characterized as well by a peak ascribable to C=C stretching modes but also by an intense peak at 1090 cm^{-1} likely due to sulfoxide groups. This spectral feature indicated that the functionalization with H_2SO_4 for 24 hours successfully allowed the introduction of sulfonic groups.

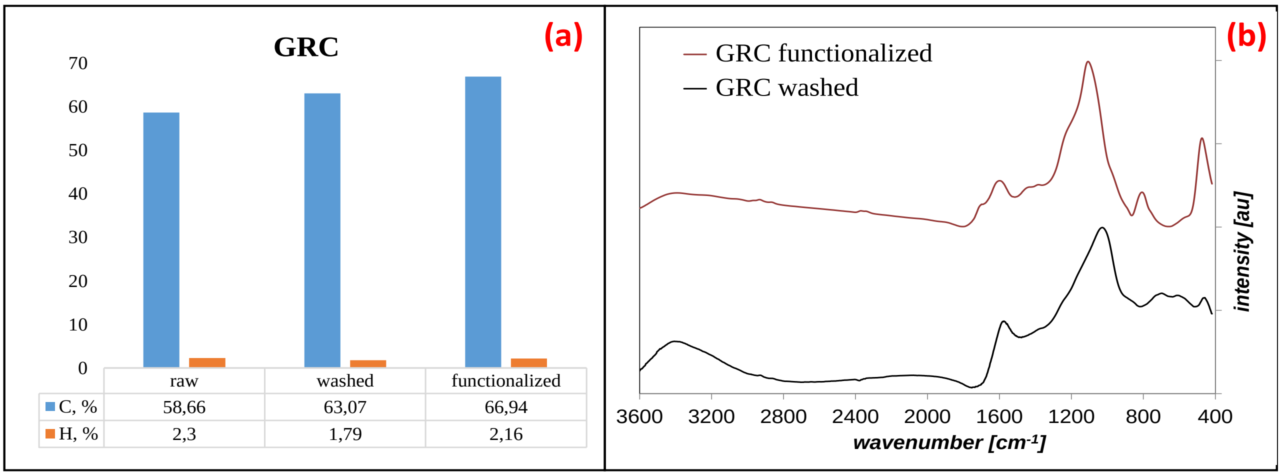
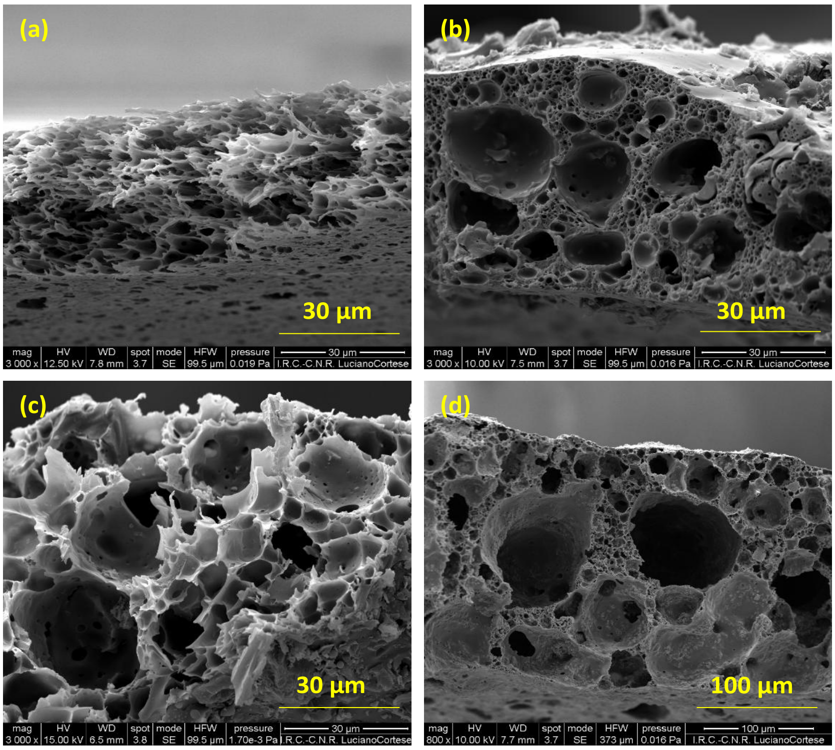


Figure 1 – Elemental analysis (a) and FTIR (b) of GRC samples

The variation in cross sectional morphology of PEI/PVP membranes after the addition of carbonaceous additive (washed and functionalized GRC or carbon black) into membrane matrix was imaged by SEM (Fig. 2).



(a) M PVP/PEI, (b) M PVP/PEI/GRC$_w$,
(c) M PVP/PEI/GRC$_f$,
(d) M PVP/PEI/CB

Figure 2 – SEM images of synthesized membranes

Prior to SEM analysis, each dry membrane was cryogenically fractured in liquid nitrogen and gold sputtered to avoid charging. All the membranes exhibited a porous structure: differently from the reference M PVP/PEI membrane, in which a more homogeneous structure is imaged, in GRC modified membranes macro-pores are fully developed together with a substructure of smallest micropores. Overall the presence of GRC and CB appears to significantly affect the membrane structure. **Conclusions**

GRC obtained from RH through a top-down approach were successfully employed in the preparation of graphene-based PEI/PVP membranes by NIPS method. A functionalization with H_2SO_4 was also performed to improve the hydrophilic properties of GRC. All the membranes were analyzed by SEM imaging revealing the presence of fully developed macro-pores and a substructure of smallest micropores. Overall the presence of GRC and CB appears to significantly affect the PEI/PVP membrane structure. This first attempts of production of graphene-based PEI/PVP membranes demonstrated the potentiality of graphene-related carbons derived from biomass wastes in technological advanced applications.

References

[1] Baker R.W., Membrane Technology and Applications John Wiley & Sons Ltd 2nd edition 2004

[2] Song, N., Gao X., Ma Z., Wang X., Wei Y., Gao C. A review of graphene-based separation membrane: Materials, characteristics, preparation and applications. Desalination 437 (2018) 59–72

[3] Seitzhanova M.A., Chenchik D.I., Mansurov Z.A., Capua R.D. (2017) Development of a method of obtaining graphene layers from rice husk // J. Functional Nanostructures Proceedings 1(3):6-8

[4] Seitzhanova M.A., Chenchik D.I., Yeleuov M.A., Mansurov Z.A., Capua R.D., Elibaeva N.S. Synthesis and characterization of graphene layers from rice husks // (2018) Chem Bull Kazakh Univ. 2(89)

[5] Hebbar R.S., Isloor A.M., Prabhu B., Inamuddin, Asiri A.M., Ismail A.F. Removal of metal ions and humic acids through polyetherimide membrane with grafted bentonite clay // Scientific Reports (2018) 8:4665 DOI:10.1038/s41598-018-22837-1.