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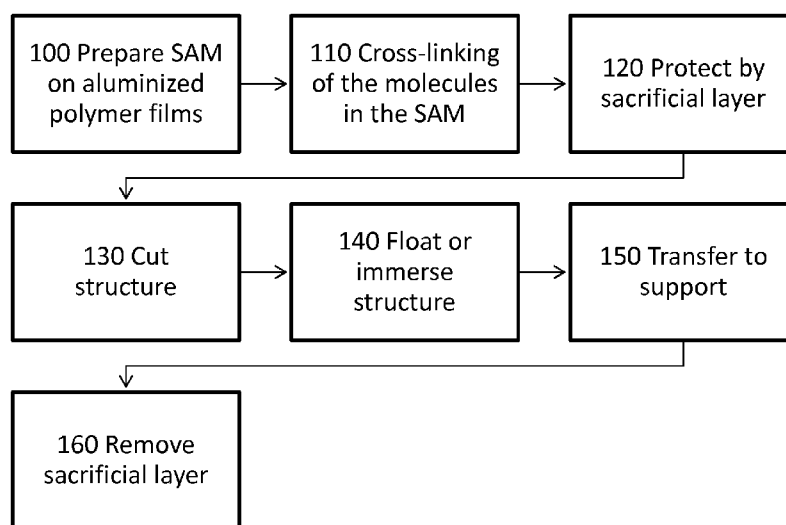
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(54) Title: METHOD FOR MANUFACTURING OF A CARBON NANOMEMBRANE

Fig. 1



(57) Abstract: A method for the manufacture of a carbon nanomembrane is disclosed. The method comprises preparing a metallised polymer substrate and applying on the metallised polymer substrate a monolayer prepared from an aromatic molecule. The aromatic molecule is cross-linked to form a carbon nanomembrane. The carbon nanomembrane is coated by a protective layer and subsequently the carbon nanomembrane and the protective layer are released from the metallised polymer substrate. Finally, the carbon nanomembrane and the protective layer are optionally placed on a support. The protective layer can be optionally removed. The carbon nanomembrane can be used for filtration.



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TITLE:METHOD FOR MANUFACTURING OF A CARBON NANOMEMBRANEDescription

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Field of the Invention

[0001] The invention relates to fabrication of carbon nanomembranes, which are usable for gas separation and ultrafiltration.

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Prior Art

[0002] Currently carbon nanomembranes (CNMs) are produced on the laboratory scale. One method for the production of carbon nanomembranes is disclosed in US Patent No. 6,764,758. The production method involves the following steps: formation of a self-assembled monolayer (SAM) on a solid homogeneous substrate, crosslinking of the individual molecules in the self-assembled monolayer by irradiation to produce a carbon nanomembrane, and separation of the formed carbon nanomembrane from the original substrate. Experiments have demonstrated that the several steps of the production method and expensive substrate materials have to date hindered a large-scale production of carbon nanomembranes.

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[0003] The substrates usually used for the initial formation of the self-assembled monolayer are (mostly atomically flat) special substrates, e.g. gold or silver layers on cleaved mica samples, gold or silver layers on silicon wafers, silicon nitride layers on silicon wafers, or flat copper foils. Common to these substrates are their stiffness (the substrates are not usable for a potential roll-to-roll production), their high price and their limited commercial availability.

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[0004] Zhang et al., Appl. Phys. Lett. 106, 063107 (2015) use, for example, 300 nm polycrystalline gold layer thermally evaporated on mica substrates (supplied by Georg Albert PVD-Coatings, Germany). Such gold layers have large, atomically flat surface domains

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and are favourable for the formation of well-ordered self-assembled monolayers on their surface. These types of substrates have therefore been favoured in the scientific community for studying the self-assembled monolayers. Similarly, silicon-based substrates e.g. silicon nitride membranes, such as those taught in Beyer et al. J. Vac. Sci. Technol. B 28, C6D5 (2010)], are used. One other reason for the use of such gold layers or silicon layers is that the chemistry of forming a self-assembled monolayer on the gold layer or the silicon layer is well-known.

[0005] The substrates of the prior art also need pre-treatment, which could involve, amongst other steps, cleaning from organic adsorbates using, for example, Piranha solution (sulphuric acid and hydrogen peroxide – as for example described by Beyer [A. Beyer et al. J. Vac. Sci. Technol. B 28, C6D5 (2010)], plasma treatment and/or UV/ozone treatment. In the case of the silicon nitride substrate, it is necessary to carry out full oxidation of the uppermost surface layers by using, for example, UV/ozone treatment. In the case of a copper substrate, it is necessary to remove the surface oxide, as well as flattening and recrystallization of the copper substrate by, for example, alternating sputter and annealing cycles. In the case of gold layers, a controlled amount of oxidation of the surface needs to be carried out by, for example, UV/ozone treatment (as described on p S15 in the Supplementary Information to P. Angelova et al., ACS Nano 7, 6489 (2013)). These steps in the pre-treatment add to complexity and are not easily scalable for large-area production.

[0006] The surface chemistry for the formation of a self-assembled monolayer in a solution is usually very sensitive and requires special pre-treatment of the solvents, cleaning of the reaction vessels and reaction under an inert atmosphere or in a vacuum. The pre-treatment of the solvents involves degassing and drying to ensure lowest levels of dissolved gases, such as oxygen. The cleaning of the reaction vessels includes cleaning from the adsorbates by Piranha solution. The reaction under inert atmosphere or vacuum is to ensure lowest levels of oxygen. These steps are necessary to prevent oxidation of the surface-active molecules and competing reactions between precursor molecules in the solution or precursor molecules and surface contaminants.

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[0007] The prior art preparation method also requires separation of the carbon nanomembrane from the original (sacrificial) substrate and includes typically etching of the substrate involving often, at least for mica and silicon-based substrates, concentrated hydrofluoric acid, which is a highly corrosive and an acute contact poison. Such processes involving hydrofluoric acids have to be handled with extreme care, using protective equipment, hoods and safety precautions beyond those used for processes involving other mineral acids.

[0008] There is therefore a requirement to develop a method for improved production of carbon nanomembranes.

[0009] It is known that large area carbon nanomembranes are usually not stable enough to be handled alone because of their thinness. Therefore, the large area carbon nanomembranes in the art are often supported by an additional layer during their separation from the substrate and the transfer to a new support structure (see also Zhang [X. Zhang, Appl. Phys. Lett. 106, 063107 (2015)]). These (sacrificial) layers are typically removed after transfer.

[0010] A universal scheme to convert aromatic molecular monolayers into functional carbon nanomembranes is known from the publication of the same name in ACS Nano, Vol. 7, No 8, 6489-6497 which describes carbon nanomembranes produced from self-assembled monolayers of 1,1'-biphenyl-4-thiol (BPT) and other aromatic sulphur-containing molecules on gold substrates. Similarly, other detailed descriptions can be found in A. Beyer et al. J. Vac. Sci. Technol. B 28, C6D5 (2010) or X. Zhang, Appl. Phys. Lett. 106, 063107 (2015).

Summary of the Invention

[0011] The method described enables the fabrication of carbon nanomembranes on a large scale. The carbon nanomembranes are usable for gas separation or ultrafiltration.

[0012] The method for the manufacture of a carbon nanomembrane disclosed in this document comprises preparing a metallised polymer substrate and applying on the metallised

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polymer substrate a monolayer prepared from an aromatic molecule. The aromatic molecule is subsequently cross-linked to form a carbon nanomembrane and then protected by a protective layer. Finally, the metallised polymer substrate is removed.

5 [0013] The inventors have found that the metallised polymer substrate used enables the formation of the monolayer from the aromatic molecule.

[0014] In one aspect, the metal of the metallised polymer layer is aluminium, which is substantially cheaper than the previously used gold layers and does not need a substantial degree of pre-treatment. Previously the person skilled in the art would not have considered
10 the use of aluminium since the body of opinion would have been to use gold layers as their chemistry is well-known.

[0015] The polymer layer is a PET substrate, as this is a common substrate. However, other
15 types of polymer layers could be used.

[0016] In one aspect of the invention, the carbon nanomembranes are preferably small enough to suppress the permeation of all gases.

20 Description of the Drawings

[0017] Fig. 1 shows the method for fabrication according to this disclosure

[0018] Fig. 2 shows the precursor molecule

[0019] Fig. 3A and Fig. 3B shows the gas separation characteristics of a carbon nanomembrane according to this disclosure (Fig. 3A) and in the prior art (Fig. 3B).
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[0020] Figs. 4A to 4C show a diagram of the carbon nanomembranes during the manufacturing steps

Detailed Description of the Invention

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[0021] The invention will now be described on the basis of the drawings. It will be understood that the embodiments and aspects of the invention described herein are only exam-

ples and do not limit the protective scope of the claims in any way. The invention is defined by the claims and their equivalents. It will be understood that features of one aspect or embodiment of the invention can be combined with a feature of a different aspect or aspects and/or embodiments of the invention.

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[0022] The method for fabrication of the carbon nanomembranes comprises three steps, as shown in Fig. 1.

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[0023] In a first step 100, a self-assembled monolayer from low molecular aromatic precursor molecules with at least one surface active group is prepared on a substrate of an aluminized polymer foil. The aluminized polymer foil is substantially flat and does not require substantial pre-treatment, unlike the gold layers and the silicon layers known in the art.

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[0024] The term “low-molecular molecules” means such compounds that are not in an oligomer or polymer form. The term “aromatics” includes the term “heteroaromatics” in this disclosure, i.e. the term “aromatics” means aromatic compounds that contain no heteroatoms or one or more heteroatoms in at least one aromatic ring. Preferably, the aromatic [precursor molecule] s [are] selected from the group consisting of phenyl, biphenyl, terphenyl, quaterphenyl, naphthalene, anthracene, pyrene, bipyridine, terpyridine, thiophene, bithienyl, terthienyl, pyrrole, and combinations thereof. The aluminized polymer foil could be, but is not limited to, an aluminized polyethylene terephthalate (PET) film.

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[0025] This preparation is done by wet chemistry (from a solution) or by organic vapour phase deposition of the precursor molecules onto the substrate. The surface-active group can be e.g. phosphonic acids, alcoxysilanes, alcohols or carboxylic acids. The aluminized polymer foil can be substituted by an aluminium foil if the aluminium foil has the necessary low roughness for a homogeneous formation of a self-assembled monolayer.

30

[0026] It would also be possible to use other metallised polymer foils. For example, it would be possible to use gold or silver instead of aluminium. It would be also possible to use films made of other polymers, such as polyethylene, polyester, polypropylene, polycarbonate, nylon, polyimide, polyaramide (aromatic amides), silane- and siloxane-based

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polymers like polydimethylsiloxane (PDMS), poly (vinyl trimethyl silane) etc., poly (phenylene oxide), polystyrene, poly (4-methyl pentene-1), polysulfone and others.... Aluminium has the advantage that it is comparatively inexpensive. The PET is used as the polymer substrate because one can create a polymer substrate with a surface having a small degree of roughness.

[0027] The molecules in the self-assembled monolayer are cross-linked in step 110 by irradiation with low energy electrons (10-1000 eV) or by other irradiation to form a carbon nanomembrane.

[0028] The carbon nanomembrane is then released from the aluminized polymer film by means of a protective layer. The CNM/ metallised polymer structure formed in step 110 is first coated with a protective layer, e.g. a layer of polymethylmethacrylate (PMMA) or other polymer in step 120 to form a sandwich structure. The coating can be performed by e.g. spin coating, drop casting, electrospinning. Then the edges of the protective layer/CNM/ metallised polymer sandwich structure are cut in step 130 and the sandwich structure is let to float or is immersed in step 140 into an aqueous sodium hydroxide solution (preferably 5 % concentration) at preferably 50°C or 60°C temperature. This basic solution of sodium hydroxide etches simultaneously the aluminium film and the PET film, which allows the separation of the protective layer/CNM structure from the substrate.

[0029] After the aluminium film is completely etched away, the protective layer/CNM structure floats on the liquid/air interface of the solution and can be optionally transferred to a solid or perforated support in step 150 to create a stack. The support can be of any kind, e.g. a porous polymer, a metallic grid, etc.

[0030] In a last step 160, the protective layer can be optionally removed. For example, a PMMA-based protective layer could be dissolved by immersion of the stack in acetone.

[0031] It is also known that CuCl_2 and KOH can be used as an etchant for the aluminium layer. However, the etching rate is much slower. In the case of CuCl_2 the protective layer/CNM structure does not lift easily off the metallised polymer when the polymer is a

PET foil. In this case, an additional slight dipping in 1-5% NaOH solution is necessary to promote the separation of the polymer PET layer from the protective layer/CNM.

[0032] Should other metals (Au, Ag, Cu) be used, then a different etchant needs to be used. It is thought, for example, that a gold layer could be removed using aqua regia or an iodine solution.

[0033] The substrate used in step 100 is flexible and cheap. The role of the substrate is to reduce the material costs and allow upscaling of the production process.

[0034] The surface-active group of the aromatic precursor molecules described in this method is a phosphonic acid, which is known to be very stable in air and in water. Therefore, it does not require special equipment, work under inert atmosphere and preliminary drying and degassing of the organic solvent. These phosphorus-based organic compounds have strong chemical affinity towards aluminium, which rules out the necessity of harsh cleaning of the vessels, used for preparation of the self-assembled monolayer.

[0035] The solution for the preparation of the self-assembled monolayer can be handled in air. The formation of the self-assembled monolayer happens in shorter time (e.g. less than 6 hours for a biphenyl-based self-assembled monolayer on the aluminized polymer substrate, in comparison to three days for a biphenyl-based self-assembled monolayer on a gold substrate according to the procedure used to date). The formed self-assembled monolayer from step 100 is more stable in ambient environment.

[0036] It has been found that unlike prior art methods the solution does not substantially degrade and can be used multiple times.

[0037] The process of releasing the carbon nanomembrane from the substrate does not involve hydrofluoric acid.

[0038] Figs. 4A to 4C show the various manufacturing methods. In Fig. 4A a metallised polymer has a self-assembled monolayer placed on top of the metallised polymer film (step

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100). The self-assembled monolayer is then irradiated with electrons to form the CNM/metallised polymer structure (step 110).

[0039] Fig. 4B shows the subsequent step in which the CNM/metallised polymer structure is coated with a polymer film as the protective layer (step 120) which is then etched to form a protective layer/CNM structure.

[0040] In Fig. 4C the protective layer/CNM structure can be left alone (top path), have a support layer attached (step 150, middle path) and /or then the protective layer removed (step 160, lower path).

[0041] The carbon nanomembranes can be used as ballistic membranes (separation according to the kinetic diameter of the particles) for gas separation and ultrafiltration. It is possible to control properties like the density and size distribution of intrinsic pores (pores formed during the fabrication without additional efforts like treatment of the substrate or formed membranes by e.g. ion bombardment or etching) by the selection of the precursor molecules and process parameters for the formation of the self-assembled monolayer by analogy with the methods described in ACS Nano, Vol. 7, No 8, 6489-6497.

Example

[0042] Preparation of a self-assembled monolayer of the precursor [3-([4'-Nitro-1,1'-biphenyl]-4-yloxy)-propyl]-phosphonic acid (as shown in Fig. 2) onto an aluminized polyethylene terephthalate film as the substrate with a minimum thickness of the PET film of 75 microns and a thickness of the Al-layer of 14 nm. Preparation was done by immersion of the substrate into a solution of the precursor molecule in technical ethanol.

[0043] Crosslinking of the molecules in the self-assembled monolayer by irradiation with low energy electrons (100 eV) with an electron dose of 50 mC/cm².

[0044] Transfer of thus prepared carbon nanomembrane from the aluminized PET foil to a perforated polymer support. The CNM/Al/PET structure is first protected by a protective layer of polymethylmethacrylate (PMMA) attached to the surface by consecutively spin

coating of 50 K and 950 K PMMA solutions. Then the edges of the PMMA/CNM/Al/PET sandwich structure were cut and the sandwich structure was immersed into or let to float on an aqueous 5%-NaOH solution at 60°C temperature. This basic solution etches simultaneously the aluminium film and the PET film, which allows the separation of the PMMA/CNM structure from the substrate. After the aluminium is completely etched away, the PMMA/CNM structure floats on the liquid/air interface and can be transferred to the porous polymer support. In a last step, the sacrificial PMMA-layer is dissolved by immersion of the stack in acetone.

- 10 [0045] The so prepared composite membrane (Figure 3A) is very dense with a permeance of hydrogen lower compared to a traditionally prepared carbon nanomembrane (Figure 3B). Fig. 3B is taken from M. Ai, S. Shishatskiy, J. Wind, X. Zhang, C. T. Nottbohm, N. Mellech, A. Winter, H. Vieker, J. Qiu, K.-J. Dietz, A. Götzhäuser, A. Beyer, *Carbon Nanomembranes (CNMs) Supported by Polymer: Mechanics and Gas Permeation*, Advanced Materials **26**, 3421 (2014). The cut-off kinetic diameter (gases with a smaller kinetic diameter can pass with high permeance, gases with larger kinetic diameter are hindered) is at around 2.8 Å also the lowest observed so far. This carbon nanomembrane is a starting point for tuning the gas separation characteristic for specific tasks by changing the structure of the precursor molecules to more complex shapes resulting in different packing densities of the self-assembled monolayers and different diameters of the intrinsic pores.
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Claims

1. A method for the manufacture of a carbon nanomembrane comprising:
preparing a metallised polymer substrate;
5 applying on the metallised polymer substrate a monolayer prepared from an aromatic molecule;
cross-linking the aromatic molecule to form a carbon nanomembrane;
protecting the carbon nanomembrane by a protective layer; and
removing the metallised polymer substrate.
10
2. The method of claims 1, further comprising placing of the carbon nanomembrane with the protective layer on a support layer.
3. The method of claim 2, further comprising removal of the protective layer.
15
4. The method of claim 1, 2 or 3, wherein the cross-linking is carried out by irradiation.
5. The method of any of the above claims, wherein the metallised polymer substrate is an aluminised polymer substrate.
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6. The method of anyone of the above claims, wherein the metallised polymer substrate is a metallised PET substrate.
7. The method of any one of the above claims, wherein the protective layer is made of PMMA.
25
8. The method of any one of the above claims wherein the protective layer is removed in acetone.
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9. The method of any one of claims 1 to 6, wherein the protective layer is created by electrospinning a porous polymer.
10. A membrane for gas separation or ultrafiltration comprising a carbon nanomembrane made by any one of the above claims.
35

FIGURES

Fig. 1

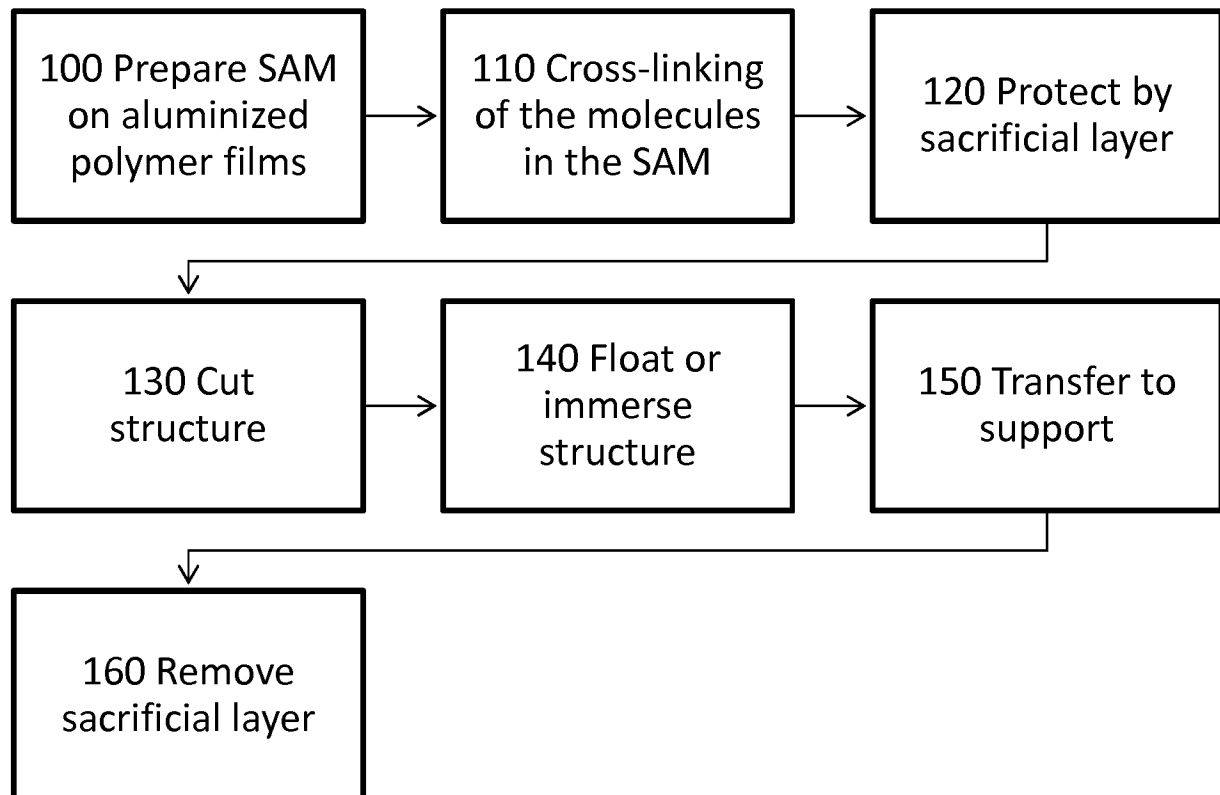


Fig. 2

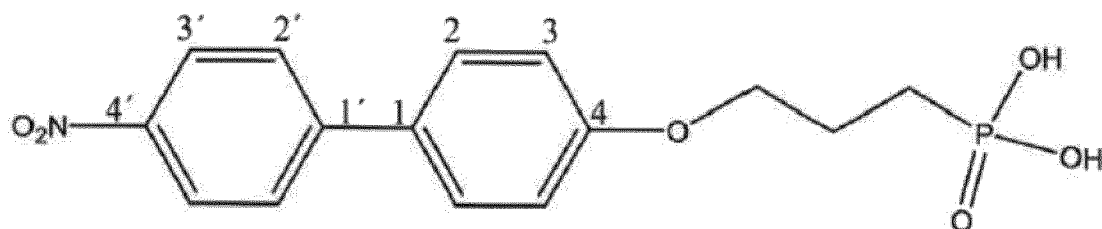


Fig. 3A

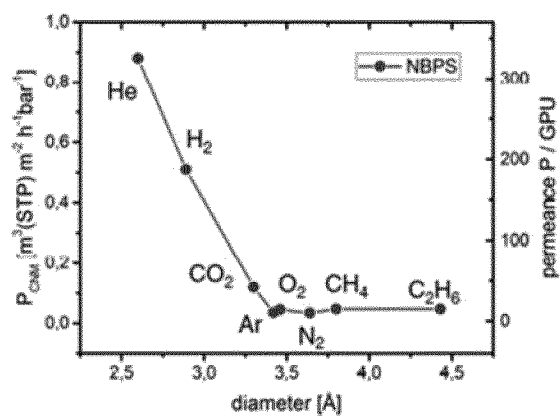
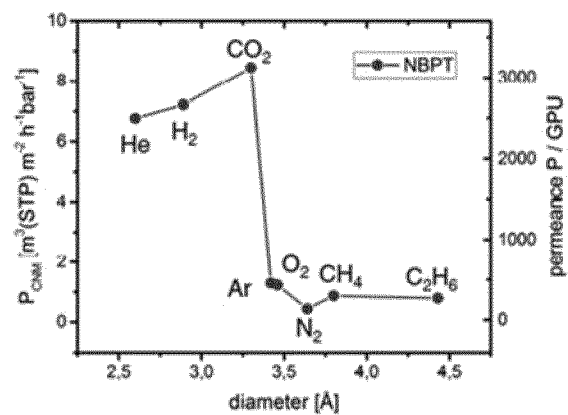
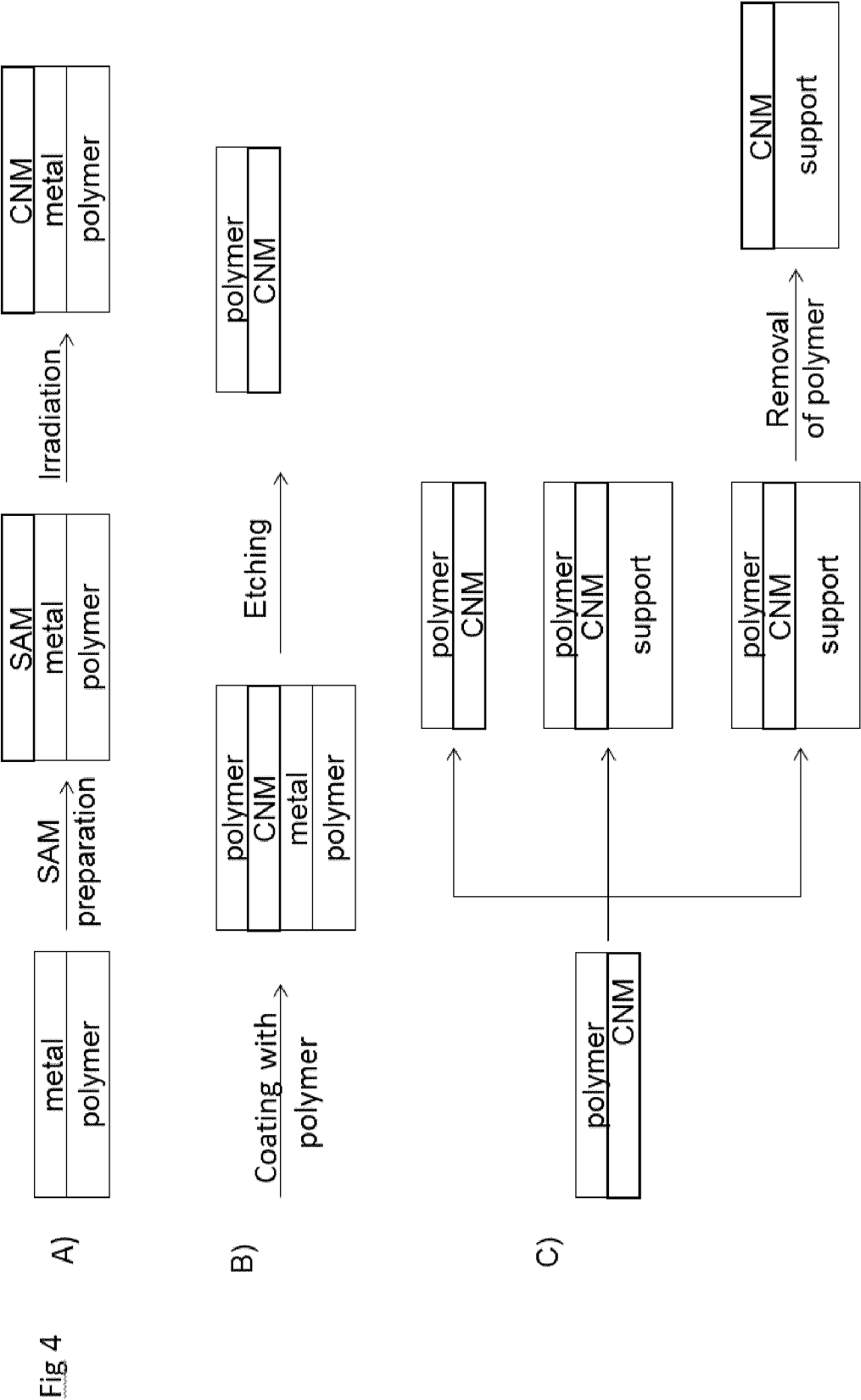


Fig. 3B





INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/076016

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D67/00 B01D69/10 B01D69/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>BEYER ANDRĂ CR ET AL: "Fabrication of metal patterns on freestanding graphenoid nanomembranes", JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART B, AVS / AIP, MELVILLE, NEW YORK, NY, US, vol. 28, no. 6, 11 November 2010 (2010-11-11), pages C6D5-C6D10, XP012144338, ISSN: 1071-1023, DOI: 10.1116/1.3511475 Title figure 1 abstract Section IIA; page C6D5 Section IIB; page C6D6 Section IIC; page C6D6</p> <p>-/--</p>	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

19 December 2016

Date of mailing of the international search report

20/01/2017

Name and mailing address of the ISA/

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Williams, Jennifer

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/076016

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>Section IIIA; page C6D6 Section IIIB; page C6D7</p> <p>-----</p>	
Y	<p>POLINA ANGELOVA ET AL: "A Universal Scheme to Convert Aromatic Molecular Monolayers into Functional Carbon Nanomembranes", ACS NANO, vol. 7, no. 8, 27 August 2013 (2013-08-27), pages 6489-6497, XP055236230, US ISSN: 1936-0851, DOI: 10.1021/nn402652f abstract page 6489 - column 1 page 6491 - column 1 experimental section; page 6496 page 6496 - column 2</p> <p>-----</p>	1-10
Y	<p>US 5 728 431 A (BERGBREITER DAVID E [US] ET AL) 17 March 1998 (1998-03-17) column 4, line 63 - line 65 column 3, line 61 - line 65 column 4, line 4 - line 8 claims 5,8</p> <p>-----</p>	1-10
Y	<p>US 6 468 657 B1 (HOU ZHIZHONG [US] ET AL) 22 October 2002 (2002-10-22) claims 1,3,5,23 abstract column 50, line 12 - line 23; example 1</p> <p>-----</p>	1-4,7-10
A	<p>US 6 764 758 B1 (GRUNZE MICHAEL [DE] ET AL) 20 July 2004 (2004-07-20) cited in the application the whole document</p> <p>-----</p>	1-10
A	<p>WO 2005/089415 A2 (UNIV CALIFORNIA [US]; UNIV WAYNE STATE [US]; LIU GANG-YU [US]; AMRO NA) 29 September 2005 (2005-09-29) the whole document</p> <p>-----</p>	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/076016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5728431	A	17-03-1998	NONE
US 6468657	B1	22-10-2002	US 6468657 B1 WO 0034033 A1
US 6764758	B1	20-07-2004	AT 416222 T AU 7771900 A DE 19945935 A1 EP 1222498 A2 US 6764758 B1 WO 0123962 A2
WO 2005089415	A2	29-09-2005	US 2005221081 A1 WO 2005089415 A2