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(54) **METHOD OF MANUFACTURING A THREE - DIMENSIONAL POROUS STRUCTURE OF PARYLENE**

VERFAHREN ZUR HERSTELLUNG EINER DREIDIMENSIONALEN PORÖSEN STRUKTUR VON PARYLEN

PROCEDE DE FABRICATION D'UNE STRUCTURE POREUSE DE PARYLÈNE TRIDIMENSIONNELLE

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URL:[http://onlinelibrary.wiley.com/store/10.1002/polb.1990.090280409/asset/090280409\\_ftp.pdf?v=1&t=jam9ixtt&s=996007c9e9dcbcb6781e01c5c1772563f6fc8c5c](http://onlinelibrary.wiley.com/store/10.1002/polb.1990.090280409/asset/090280409_ftp.pdf?v=1&t=jam9ixtt&s=996007c9e9dcbcb6781e01c5c1772563f6fc8c5c)**
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**Description**

## Field of the Invention

5 **[0001]** The present invention relates to a method of manufacturing a three-dimensional porous structure of parylene.

## Background of the Invention

10 **[0002]** The process of preparing the parylene film by chemical vapor deposition is a gas phase reaction, which can form a very dense and uniform coating under vacuum. The parylene film has some properties, such as good biocompatibility, biostability and excellent blood compatibility. Poly-p-xylylene has been approved by the US Food and Drug Administration, so has been utilized in many applications of relevant in vivo devices. Therefore, the porous materials made by this coating are not dangerous to human body.

15 **[0003]** The well-known vapor deposition polymer system of poly-para-xylylenes (PPXs) is used in the present invention. The deposition of PPXs occurs on a stationary substrate via adsorption of monomers (para-xylylenes) onto the surface, where the polymerization reaction initiates and the propagation continues by reaction of newly adsorbed monomers; equilibrium is eventually achieved between the rates of adsorption and desorption. The deposition of PPXs occurs, in most cases, irrespective of the substrate material and its shape, a cooled substrate facilitates deposition, and the deposition on a stationary surface creates a dense film of PPX. These characteristics are also found similar for other  
20 vapor deposition systems.

**[0004]** Porous materials with controlled mechanical and chemical properties are being developed for applications in separation systems, sensor systems, energy transfer and storage, heterogeneous catalysts, superhydrophobic surfaces, photonic devices, drug delivery, and biomedical scaffolds. These porous materials are currently constructed based on interventional processes, such as by templating, photolithography, soft lithography, gas foaming, and gas or flow mimicking geological processes, which are applied on a stationary material or a precursor. Alternative approaches include additive manufacturing, e.g., 3D printing, laser sintering, projection stereolithography, electrified jetting, the weaving technique, or direct writing, are used to build up porous materials in a layer-by-layer or stacking manner. Templating methods for manufacturing three-dimensional parylene porous structures are known from US2013/215197 or US2007/228606.  
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30 **[0005]** Current fabrication methods are limited by the large number of processing steps required the additional effort involved in removing the template, and the requirement of sophisticated computer programming and/or manual intervention to master the construction. Therefore, utilizing the simple principles to lower human costs by simple steps to form porous materials is challenging.

## 35 Summary of the Invention

**[0006]** This in mind, the present invention aims at providing a method of manufacturing a 3D porous structure which overcomes current fabrication methods are limited by the large number of processing steps required the additional effort involved in removing the template, and the requirement of sophisticated computer programming and/or manual intervention to master the construction. The key features of the present invention are that construction is based on the vanishing nature of a sublimating template that does not require an additional removal procedure and that a fine replica architecture is obtained in a single step by the conformality of the vapor deposition process and the direct guidance of the sublimating substrate. In addition, the pores are formed during the construction process and the porosity and sizes can be controlled by the sublimation behavior of the template (e.g., by varying the sublimation conditions according to the material's phase diagram or by selecting a different sublimation material).  
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45 **[0007]** These are achieved by a method of manufacturing a 3D porous structure according to claim 1.

**[0008]** The dependent claims pertain to corresponding further developments and improvements.

50 **[0009]** As will be seen more clearly from the detailed description following below, the claimed method of manufacturing a 3D porous structure comprising steps: providing a sacrificial solid template; performing a vapor deposition process such that a polymer monomer is deposited on the sacrificial solid template while the sacrificial solid template is conducted to a sublimation process; and consuming the sacrificial solid template to form a 3D porous structure.

## Brief Description of the Drawings

55 **[0010]** In the following, the invention is further illustrated by way of example, taking reference to the accompanying drawings. Thereof

FIG. 1 illustrates a method of manufacturing a 3D porous structure according to the present invention.

FIG. 2 illustrates steps of manufacturing a 3D porous structure according to the present invention.

FIG. 3 is an image of a 3D porous structure, the upper side of the image is a solid template image and the lower side of the image is an enlarged view of the porous structure.

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FIG. 4 is a scanning electron microscope (SEM) image of a 3D porous structure

FIG. 5 is a Fourier transform infrared spectrometer (FT-IR) spectrum of a 3D porous structure

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FIG. 6 to FIG.8 are SEM images of a 3D porous structure

FIG. 9 to FIG.10 are SEM images of a 3D porous structure

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FIG. 11 and FIG.12 are SEM image and three-dimensional computed tomography (micro-CT) image of a 3D porous structure produced by using the gradient sacrificial solid template.

FIG. 13 is a 3D conjugate-focus laser scanning microscopic image of a 3D porous structure

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FIG. 14 is a transmission electron microscope (TEM) image of a 3D porous structure

FIG. 15 is a TEM image of a 3D porous structure

#### Detailed Description

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**[0011]** To provide a better understanding of the presented invention, preferred embodiments will be made in detail.

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**[0012]** FIG. 1 illustrates a method of manufacturing a 3D porous structure according to the present invention. The method utilizes the two processes of sublimation 21 and vapor deposition 22, which simultaneously occur and dynamically compete, thereby forming a porous structure 1 in three dimensions. As shown in FIG. 1, the porous structure 1 is formed at the dynamic vapor-solid interface 2, wherein a deposition molecule 31 and a sacrificial sublimation solid template 32 exploit the same volumetric space; i.e., the vacated space from a sublimating solid template 32 is seamlessly filled by the deposition molecule 31 via vapor deposition.

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**[0013]** In contrast to the adsorption-limited mechanism of conventional PPX deposition onto a stationary substrate, in a method of the present invention, the sublimating ice rendered a dynamic substrate and the deposition of PPXs onto sublimating ice proceeded via a diffusion-limited mechanism in which the monomers diffused continuously to a newly formed surface of sublimating ice substrate. The adsorption on such surfaces was only temporary, allowing the polymerization reaction occurs in three dimensions. Macroscopically, the construction upon deposition is directed by the sublimation of a sacrificial template, whose surface/interface provides a temporary support before complete consumption of the template by sublimation. In addition, such a dependence also parallels a conformal mechanism of vapor deposition, which requires the adsorption of vapor precursors on the sublimating surface. These directive dependencies allow the resulting deposition to formulate a final architecture that replicates the sacrificial template.

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**[0014]** The 3D porous structures of the present disclosure are constructed via vapor deposition onto a sublimating solid template. Construction upon deposition of vapor-phase material occurs at a dynamic vapor-solid interface and is directed by the solid surface vanishing by sublimation. Characteristics of the pore structures are formed during the construction process as a result of the gas vapor and the space that is vacated by sublimation, thus enabling control of the porosity through regulation of the sublimation speed and/or the thermodynamic properties of the templates.

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**[0015]** FIG. 2 illustrates steps of manufacturing a 3D porous structure according to the present invention. As shown in FIG. 2, the method of the present invention includes the following steps:

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Step 400: providing a sacrificial solid template;

Step 402: performing a vapor deposition process such that a polymer monomer is deposited on the sacrificial solid template while the sacrificial solid template is conducted to a sublimation process; and

Step 404: consuming the sacrificial solid template to form a 3D porous structure.

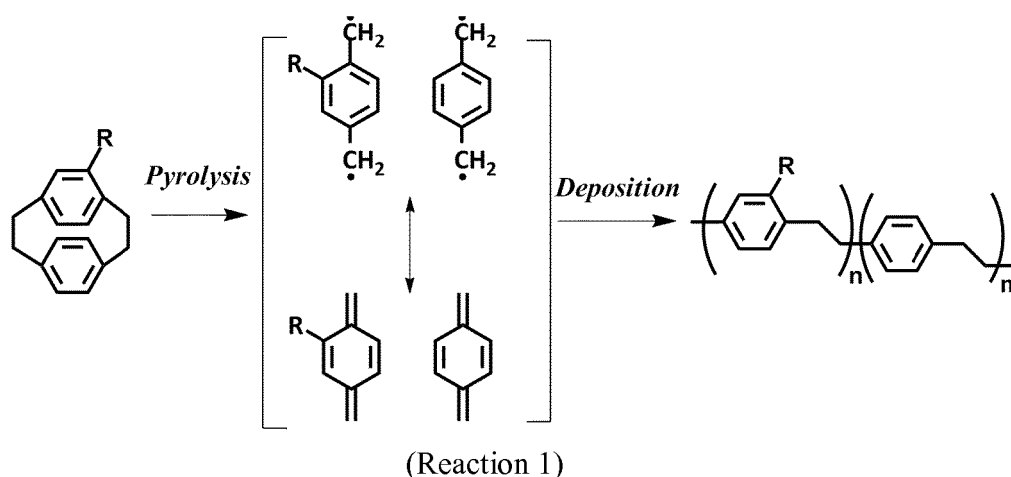
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**[0016]** The following describes each step.

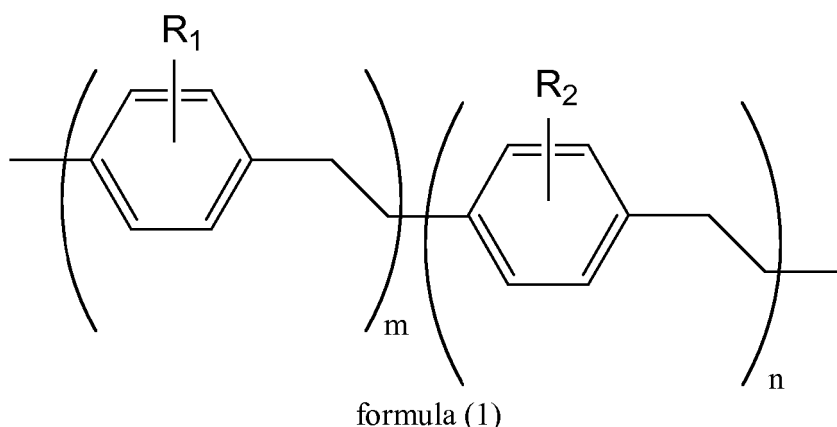
**[0017]** First, a sacrifice solid template is provided (step 400). The sacrificial solid template may be any substance or mixture in the form of a solid and may perform a sublimation reaction under a condition. In one embodiment, the sacrificial solid template is a water molecule. When the solid form (ice) of the water molecule is at 0.1 mbar, it can be sublimated from solid form (ice) to the water vapor at about more than -50°C. However, at the same pressure and temperature, the

gas phase monomer of PPX tends to polymerize and deposit. In one embodiment, the sacrificial solid template may also be formed by freezing the mixed solution having a different sublimation property. In one embodiment, the mixed solution may include two substances that are miscible, for example, water molecules and ethanol, but are not limited thereto. Alternatively, in another embodiment, the mixed solution may include two substances that are not miscible, for example, water molecules and hexane, but are not limited thereto. In one embodiment, the sacrificial solid template may contain a variety of target molecules in advance. In one embodiment of the present invention, the target molecule may include a fluorescent molecule, a biological factor and/or a nanoparticle. According to an embodiment of the present invention, the fluorescent molecule may be a fluorescein-labeled peptide (FITC-KKKRGD) or Alexa Fluor® 555 azide, but is not limited thereto. According to an embodiment of the present invention, the biological factor may be an organism including an homogeneous organism or a heterologous organism, for example, a fibroblast growth factor (FGF2) which is a newborn blood vessel. According to an embodiment of the present invention, the size of the nanoparticles is between 20 nm and 5  $\mu$ m. In one embodiment, the nanoparticles may be, for example, iron oxide ( $\text{Fe}_3\text{C}_4$ ), gold (Au) and / or silver (Ag), but are not limited thereto.

**[0018]** Next, a vapor deposition process is performed such that a polymer monomer is deposited on the sacrificial solid template while the sacrificial solid template is conducted to a sublimation process (step 402). Any polymer monomer that can perform the vapor deposition process provides a polymer having a low sticking coefficient, for example  $10^{-3}$  to  $10^{-5}$ , to ensure the conformality of the architecture and the uniformity of the pore structures. In the present invention, the PPX structure is formed by the vapor deposition process with a pyrolysis process shown in below reaction 1, from as paracyclophane as a monomer.



**[0019]** The paracyclophane can have various functional groups so as to form the functionalized PPX structure. The PPX structure may include the following structure with formula (1):

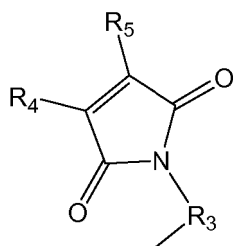


, wherein  $R_1$  and  $R_2$  is selected from a group consisting of hydrogen,  $-\text{C}(=\text{O})\text{H}$ ,  $-\text{C}(=\text{O})\text{CFH}_2$ ,  $-\text{C}(=\text{O})\text{CF}_3$ ,  $-\text{C}(=\text{O})\text{C}_2\text{F}_5$ ,  $-\text{C}(=\text{O})\text{C}_8\text{F}_{17}$ ,  $-\text{C}(=\text{O})\text{OH}$ ,  $-\text{C}(=\text{O})\text{Ph}$ ,  $-\text{C}=\text{CH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2\text{NH}_2$ ,  $-\text{NH}_2$ ,  $-\text{C}(=\text{O})\text{OCH}_3$ ,  $-\text{C}(=\text{O})\text{OC}_2\text{H}_5$ ,  $-\text{CH}_2\text{O-C}(=\text{O})\text{C}(\text{CH}_3)_2\text{Br}$ ,  $-\text{CH}_2\text{O-C}(=\text{O})\text{C}=\text{CH}$ , a chemical structure of formula (1-1), a chemical structure of formula

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(1-2) and a chemical structure of formula (1-3), and  $R_1$  and  $R_2$  are not simultaneous hydrogen, and  $m$  and  $n$  refer to an integral greater than 750,000:

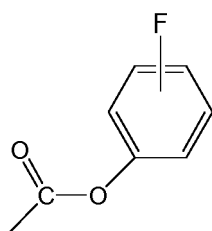
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formula (1-1)

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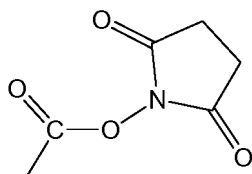
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formula (1-2)

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formula (1-3)

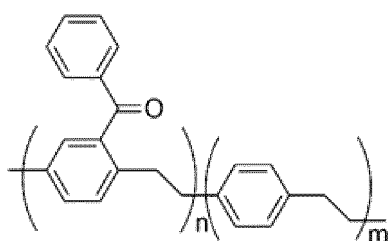
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, wherein in formula (1-1),  $R_3$  refer to  $-CH_2-$ ,  $-CH_2-CH_2-O-C(=O)-$ ,  $-CH_2-CH_2-NH-C(=O)-$ ,  $-C(=O)-$  or  $-O-CH_2-$ ; and  $R_4$  and  $R_5$  refer to hydrogen, methyl or chloride.

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**[0020]** The PPX structure may include the following structure:

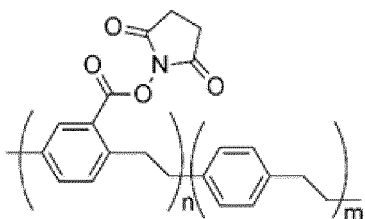
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formula (2-1)

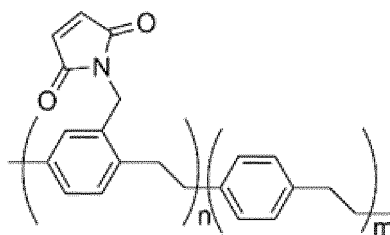
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formula (2-2)

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formula (2-3)

, wherein  $m$  and  $n$  refer to an integral greater than 750,000.

**[0021]** The PPX structure may be PPX-C (Parylene C).

**[0022]** The vapor deposition process depends on the polymer monomer used so as to select the most suitable deposition parameter. The preferred deposition temperature is the temperature required for the sublimation of the sacrificial solid template. In one embodiment of the present invention, the pressure of the chemical vapor deposition system is maintained at 0.1 mbar (mbar) with parylene. The compounds having a paracyclophane are pyrolyzed in the temperature range of 670 °C to 700 °C to obtain a polymer monomer. The sacrificial solid template is then placed on a stage and the polymer monomer is deposited on the sacrificial solid template with a stage temperature range of -20 °C to 60 °C.

**[0023]** Finally, after a sacrificial solid template is consumed, a 3D porous structure is formed (step 404). The porous structure of parylene has a plurality of pores and a porosity. The porosity refers to the volume of pores in the porous structure, that is, the ratio of the volume of all pores to the volume exhibited by the outermost contour of the porous structure. The porosity can be measured by a Mercury porosimeter, which is calculated using the relationship between the high surface tension of mercury and the pressure required to press into the pores, with the parameter below: at the pressure in the range of 0.1 to 50 psia and a measurement range of 360 to 3.6  $\mu\text{m}$ ; and at atmospheric pressure to 60000 psia and measurement range of 6 ~ 0.003  $\mu\text{m}$ .

**[0024]** Since the volume of the sublimed gas is proportional to the disappearance volume of the solid template, the porosity is associated with the sublimation rate, i.e., the higher sublimation rate causes a greater porosity. Therefore, the present method can obtain the porous structures having different porosities by adjusting any parameters that can affect the sublimation rate. The porosity is controlled by adjusting the temperature. For example, the water molecule is used as the sacrificial solid template, and the sublimation rate is varied by reducing or elevating the temperature to -15 °C or 25 °C while maintaining the system pressure at 0.1 mbar. In one embodiment of the present invention, the porosity is controlled by using a mixture solid template formed by mixing two or more kinds of substances having different sublimation heat. The rate of mass (or volume) transfer for sublimating the solid template is proportional to the temperature variation, following the mass transport equation I:

$$h(T_o - T_s) = \Delta H \left( \frac{dm}{dt} \right) = \Delta H \left( \frac{\rho dV}{dt} \right)$$

(equation I)

where  $h$  is the heat transfer coefficient of the system,  $T_o$  is the operating temperature,  $T_s$  is the temperature of sublimating the template,  $h$  is the heat transfer coefficient,  $\Delta H$  is the latent heat of sublimation,  $m$  is the mass of template,  $\rho$  is the density of template, and  $V$  is the volume of template.

**[0025]** The heat transfer coefficient  $h$  and the latent heat of sublimation  $\Delta H$  are consider constant during the fabrication

process when using the same solid template, and the differential term  $\left( \frac{dm}{dt} \right)$  describes the rate of solid template mass ( $m$ ) that is being sublimated and is equal to the product of density ( $\rho$ ) and volume ( $V$ ).

Example 1

**[0026]** The present embodiment is made of a special shape of ice as a solid sacrificial template, and the shape of the poly-p-xylylenes is replica architecture with the template because of the sticking coefficient of the parylene (about  $10^{-4}$ ), to ensure the conformality of the architecture and the uniformity of the pore structures. FIG. 3 is an image of a 3D porous structure the upper side of the image is a solid template image and the lower side of the image is an enlarged view of the porous structure. According to the present embodiment, using an ice model of a table (dimensions: 80 mm-diameter

and 50 mm-height) or a chair (dimensions: 30 mm-diameter and 35 mm-height) as the sacrificial solid template (the upper side image of FIG. 3) will form a porous structure of the table or the chair (the lower side image of FIG. 3). In an embodiment of the present invention, a cubic porous structure can be formed by using the cube ice model of  $400\ \mu\text{m} \times 400\ \mu\text{m} \times 400\ \mu\text{m}$  as the sacrificial solid template. In an embodiment of the present invention, a spherical porous structure can be formed by using a spherical ice model having a diameter of  $1,800\ \mu\text{m}$ . The above results demonstrate that the appearance of the porous structure can be designed according to the sacrificial solid template.

#### Example 2

**[0027]** The present invention may deposit other derivatives of parylene(PPX) on a sublimated sacrificial solid template. The derivative refers to parylene having various functional groups. The porous structure is formed by using a PPX having a special functional group. FIG. 4 is a scanning electron microscope (SEM) image of a 3D porous structure .

**[0028]** According to the second embodiment of the present invention, a parylene monomer with succinimidyl ester functionality is deposited on an ice solid template to form a functional parylene structure. As shown in FIG. 4, the parylene structure having a succinimidyl ester functionality formed has a porous structure. FIG. 5 is a Fourier transform infrared spectrometer (FT-IR) spectrum of a 3D porous structure in which the abscissa is a wavenumbers ( $\text{cm}^{-1}$ ) and the vertical axis is a reflectance (a. u.). As shown in FIG. 5, the chemical composition of the porous structure of the parylene derivative is measured, and the peak positions and intensities observed from the spectrum are consistent with those in the spectra of PPX derivative films prepared by conventional chemical vapor deposition methods. It was confirmed that the present invention successfully used the derivative of parylene to form a porous structure.

#### Example 3

**[0029]** Since the volume of the sublimed gas is proportional to the disappearance volume of the solid template, the higher sublimation rate cause greater porosity, while lower sublimation rates are reversed. According to the third embodiment of the present invention, the water molecule is used as the sacrificial solid template, and the sublimation rate is varied by reducing or elevating the temperature to  $-15\ ^\circ\text{C}$  or  $25\ ^\circ\text{C}$  while maintaining the system pressure at 0.1 mbar. Based on the equation I above, a sublimation volume increases by 6.3% when increasing the operating temperature from  $4\ ^\circ\text{C}$  to  $25\ ^\circ\text{C}$ ; and a 5.6% of decreased volume from  $4\ ^\circ\text{C}$  to  $-15\ ^\circ\text{C}$ . FIG. 6 to FIG.8 are SEM images of a 3D porous structure.

**[0030]** As shown in FIG. 6, a porous structure having a pore diameter of  $21\ \mu\text{m}$  and a porosity of 61% is formed by operating temperature of  $-15\ ^\circ\text{C}$ . As shown in FIG. 7, a porous structure having a pore diameter of  $40\ \mu\text{m}$  and a porosity of 69.1 % is formed by operating temperature of  $4\ ^\circ\text{C}$ . As shown in FIG. 8, a porous structure having a pore diameter of  $89\ \mu\text{m}$  and a porosity of 74.3% is formed by operating temperature of  $25\ ^\circ\text{C}$ . According to the results of FIGs. 6 to 8, it is shown that a smaller pore size is obtained at a lower sublimation rate (low temperature) and a larger pore size is obtained at a higher sublimation rate (high temperature). Furthermore, it can also be observed from the figures that a dense porous structure is formed at a lower sublimation rate and a branched porous structure is formed at a higher sublimation rate.

#### Example 4

**[0031]** The sacrificial solid template of the present invention can be prepared by mixing two or more kinds of substances, and the sublimation rate of the sacrificial solid template is adjusted based on the different sublimation properties of the substances. In the first case of the present embodiment, the two miscible substances are selected, and in the second case of the present embodiment, the two immiscible substances are selected, to thereby compare the porosity of the two cases.

**[0032]** In the first miscible embodiment, the two miscible substances may be water molecules and ethanol. According to an embodiment of the present invention, the water molecules (80%) and ethanol (20%) are mixed and the mixture solution is frozen in a cooling bath of liquid nitrogen to form a mixture solid template.

**[0033]** In the second immiscible embodiment, the two immiscible substances may be water molecules and hexane. According to an embodiment of the present invention, the water molecules (90%) and hexane (10%) are mixed and the mixture solution is frozen in a cooling bath of liquid nitrogen to form a mixture solid template.

**[0034]** FIG. 9 to FIG. 10 are SEM images of a 3D porous structure.

**[0035]** In the first miscible embodiment, as shown in FIG. 9, the porous structure of parylene is formed by using a mixture template composed of water molecules and ethanol at an operating temperature of  $4\ ^\circ\text{C}$ , and the pore size is  $64\ \mu\text{m}$  and the porosity is 82.5 %. Ethanol has a lower sublimation heat (higher sublimation rate) than the water molecules. Therefore, comparing with the porous structure formed by simply using water molecules as a sacrificial solid template at an operating temperature of  $4\ ^\circ\text{C}$ , a mixture template adding ethanol has a larger pore size and porosity. In addition,



since the water molecules are miscible with ethanol, the resulting porous structure has a similar pore size.

**[0036]** In the second immiscible embodiment, as shown in FIG. 10, the porous structure of parylene formed by using a mixture template composed of water molecules and hexane at an operating temperature of 4 °C, and the pore size is 36 μm and the porosity is 57.5%. Hexane has a higher sublimation heat (lower sublimation rate) than the water molecules. Therefore, comparing with the porous structure formed by simply using water molecules as a sacrificial solid template at an operating temperature of 4 °C, a mixture template adding hexane has a smaller pore size and porosity. In addition, since the water molecules are immiscible with hexane, the pore sizes correspond to independent systems from different sublimation rates, so the resulting porous structure has a graded pore size.

#### Example 5

**[0037]** The sacrificial solid template of the present invention may utilize a mixture template containing a gradient composition. This template provides a gradient of vapor pressure corresponding different sublimation rate, thereby forming a gradient porous structure has a plurality of pore sizes. The gradient composition in the present invention refer to the concentration of a substance in the mixture template varies in a particular direction.

**[0038]** The preparation of the gradient template is carried out by first flowing the ethanol into the water molecular system in a polypropylene centrifuge tube (10 mm inner diameter), wherein the concentration of ethanol increases with increasing height to generate a mixture system having a gradient composition, and a cooling bath of liquid nitrogen is used to freeze the flow mixture system approximately 5 seconds after the flow started and before it reached a fully developed state of a homogenous mixture system.

**[0039]** FIG.11 and FIG.12 are SEM image and three-dimensional computed tomography (micro-CT) image of a 3D porous structure produced by using the gradient sacrificial solid template.

**[0040]** The gradient porous structure formed by the present method includes a plurality of pore sizes which vary in a gradient. As shown in FIG. 11, the gradient porous structure formed by using the gradient mixture template, wherein the pore size increases with increasing the concentration of ethanol (above the image). The pore size changes in a gradient due to the higher vapor pressure of ethanol (faster sublimation rate), and hence the formation of larger pore size.

**[0041]** It is worth noted that the gradient porous structure is formed integrally. As shown in FIG. 12, the gradient porous structure is integrally formed by using the gradient mixture template and does not have a layered structure.

**[0042]** It should be understood that it is not necessary to use a gradient mixture template to create a gradient pore structure as long as the sublimation rate can be varied, for example, by applying a gradient operating temperature.

#### Example 6

**[0043]** The sacrificial solid template of the present invention may contain various target molecules in advance and the resulting porous structure also contains the target molecule. In the present example, the solution containing the target molecule was frozen by using a liquid nitrogen cooling bath to prepare a sacrificial solid template containing the target molecule. In the present example, the target molecule is a fluorescein-labeled peptide (FITC-KKKRGD) or Alexa Fluor® 555 azide. In other embodiments, the target molecules may be a biological factor and / or a nanoparticle.

**[0044]** FIG. 13 is a 3D conjugate-focus laser scanning microscopic image of a 3D porous structure.

**[0045]** In the embodiment containing the fluorescent molecule, as shown in FIG. 13, the upper row is the porous structure formed by using a sacrificial solid template containing a fluorescent label-containing FITC-KKKRGD as a target molecule, and the down row is the porous structure formed by using a sacrificial solid template containing a fluorescent label-containing Alexa Fluor® 555 azide as the target molecule. The results show that if a sacrificial solid template containing the target molecules is used, it will form a porous structure containing the target molecules.

**[0046]** During the sublimation and deposition process, the target molecules that separated from the sublimating solid template were followed by an "uptake process" by the deposited PPXs; this process was based on entrapment or adsorption affinity within the pores and/or on the PPXs' surfaces. Because of the continued sublimation and deposition process, or the separation and uptake process during the formation of the porous structure, the target molecules exhibit an isotropic and homogeneous distribution throughout the entire porous structure.

**[0047]** The use of a target molecules-containing sacrificial solid template provides a unique approach for the loading/localization of functional molecules into the porous materials and has overcome the challenge of diffusion inefficiency and inhomogeneity of the loaded materials.

#### Example 7

**[0048]** The porous structure of the present invention may be a nanoscale particles and may be combined with Example 6 of the present invention. The water molecules are sprayed on a superhydrophobic surface by using a nano-mist sprayer to form nanoscale water droplets, and then the nanoscale water droplets are frozen by using a liquid nitrogen cooling

bath to form a nanoscale sacrificial solid template.

[0049] FIG. 14 is a transmission electron microscope (TEM) image of a 3D porous structure. As shown in FIG. 14, a nanoscale porous structure is formed by using a nanoscale sacrificial solid template, wherein a size of the porous structure is between 20 nm and 5 cm.

[0050] In addition, the present embodiment may be combined with Example 6 of the present invention. In the present embodiment, the nanoscale sacrificial solid template may contain nanoparticles such as iron oxide ( $\text{Fe}_3\text{O}_4$ ), gold (Au), and/or silver (Ag).

[0051] FIG. 15 is a TEM image of a 3D porous structure.

[0052] The nanoscale porous structures containing the target molecules are formed by using a nanoscale sacrificial solid template respectively containing iron oxide (10-15 nm), gold (12 nm), and silver (20 nm) as a target molecule, as shown in FIG. 15, in which the dark-colored areas are the target molecule and the light-colored areas are 3D porous structure of parylene.

[0053] The present invention provides a novel method of manufacturing a 3D porous structure with overturning the conventional notion that vapor deposition must necessarily form a dense film on the substrate, and the 3D porous structure of the present invention still retains the chemical and structural advantages of the film. The present invention utilizes poly-p-xylyene to produce a porous structure of three-dimensional, diverse and different pore sizes with a porosity range from 55% to 85%. With also the knowledge of materials' sublimation thermodynamics, the technology for the vapor deposition of organic polymer, inorganics, and/or combined materials have been well documented.

## Claims

1. A method of manufacturing a three - dimensional porous structure, **characterised by:**

providing a sacrificial solid template;

subjecting a parylene monomer to a vapor deposition process while the sacrificial solid template simultaneously proceeds to a sublimation process such that at a dynamic vapor-solid interface, the sacrificial solid template is consumed and spaces vacated from the sacrificial solid template are filled by the parylene monomer to form the three - dimensional porous structure that has a plurality of pores.

2. The method of manufacturing a three - dimensional porous structure according to claim 1, **characterised in that** the three - dimensional porous structure formed when the sacrificial solid template is completely consumed has the same final architecture as that of the sacrificial solid template before being consumed.

3. The method of manufacturing a three - dimensional porous structure according to claim 1, **characterised in that** the parylene monomer has a functional group.

4. The method of manufacturing a three - dimensional porous structure according to claim 1, **characterised in that** the sacrificial solid template is ice.

5. The method of manufacturing a three - dimensional porous structure according to claim 1, **characterised in that** the sacrificial solid template is formed by mixing a first substance and a second substance, a sublimation heat of the first substance being different from the sublimation heat of the second substance.

6. The method of manufacturing a three - dimensional porous structure according to claim 5, **characterised in that** a concentration of the first substance or the second substance distributed in the sacrificial solid template varies in a particular direction.

7. The method of manufacturing a three - dimensional porous structure according to claim 6, **characterised in that** the three - dimensional porous structure is formed integrally.

8. The method of manufacturing a three - dimensional porous structure according to claim 6, **characterised in that** the of the pores of the three - dimensional porous structure have a pore diameter that increases with an increased concentration of one of the first and second substances which has a higher vapor pressure.

9. The method of manufacturing a three - dimensional porous structure according to claim 1, **characterised in that** the sacrificial solid template includes a plurality of target molecules, during the sublimation process of the sacrificial solid template, the target molecules are incorporated into the three - dimensional porous structure.

10. The method of manufacturing a three - dimensional porous structure according to claim 1, **characterised in that** the pores of the three - dimensional porous structure have a pore diameter that ranges from 21  $\mu\text{m}$  to 89  $\mu\text{m}$ .

5 **Patentansprüche**

1. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur, **gekennzeichnet durch:**

Bereitstellen einer festen Opferschablone;

Unterziehen eines Parylenmonomers einem Dampfabscheidungsprozess, während die feste Opferschablone gleichzeitig einem Sublimationsprozess unterzogen wird, so dass an einer dynamischen Dampf-Feststoff-Grenzfläche die feste Opferschablone verbraucht wird und die von der festen Opferschablone frei gewordenen Räume durch das Parylenmonomer gefüllt werden, um die dreidimensionale poröse Struktur zu bilden, die eine Vielzahl von Poren aufweist.

2. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 1, **dadurch gekennzeichnet, dass** die dreidimensionale poröse Struktur, die gebildet wird, wenn die feste Opferschablone vollständig verbraucht ist, dieselbe endgültige Architektur aufweist wie die der festen Opferschablone vor deren Verbrauch.

3. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 1, **dadurch gekennzeichnet, dass** das Parylenmonomer eine funktionelle Gruppe aufweist.

4. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 1, **dadurch gekennzeichnet, dass** die feste Opferschablone aus Eis besteht.

5. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 1, **dadurch gekennzeichnet, dass** die feste Opferschablone durch Mischen einer ersten Substanz und einer zweiten Substanz gebildet wird, wobei die Sublimationswärme der ersten Substanz von der Sublimationswärme der zweiten Substanz verschieden ist.

6. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 5, **dadurch gekennzeichnet, dass** eine Konzentration der ersten Substanz oder der zweiten Substanz, die in der festen Opferschablone verteilt ist, in einer bestimmten Richtung variiert.

7. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 6, **dadurch gekennzeichnet, dass** die dreidimensionale poröse Struktur einstückig ausgebildet wird.

8. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 6, **dadurch gekennzeichnet, dass** die Poren der dreidimensionalen porösen Struktur einen Porendurchmesser aufweisen, der mit zunehmender Konzentration einer der ersten und zweiten Substanzen, die einen höheren Dampfdruck aufweist, zunimmt.

9. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 1, **dadurch gekennzeichnet, dass** die feste Opferschablone mehrere Zielmoleküle enthält und dass während des Sublimationsprozesses der festen Opferschablone die Zielmoleküle in die dreidimensionale poröse Struktur eingebaut werden.

10. Verfahren zur Herstellung einer dreidimensionalen porösen Struktur nach Anspruch 1, **dadurch gekennzeichnet, dass** die Poren der dreidimensionalen porösen Struktur einen Porendurchmesser im Bereich von 21  $\mu\text{m}$  bis 89  $\mu\text{m}$  aufweisen.

**Revendications**

1. Procédé de fabrication d'une structure poreuse tridimensionnelle, **caractérisée par:**

fournir un gabarit solide sacrificiel;

soumettre un monomère de parylène à un processus de dépôt en phase vapeur tandis que le gabarit solide sacrificiel est soumis simultanément à un processus de sublimation de sorte qu'à une interface vapeur-solide dynamique, le gabarit solide sacrificiel est consommé et les espaces libérés par le gabarit solide sacrificiel sont

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remplis par le monomère de parylène pour former la structure poreuse tridimensionnelle qui présente une pluralité de pores.

- 5
2. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 1, **caractérisé en ce que** la structure poreuse tridimensionnelle formée lorsque le gabarit solide sacrificiel est complètement consommé a la même architecture finale que celle du gabarit solide sacrificiel avant d'être consommé.
- 10
3. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 1, **caractérisé en ce que** le monomère de parylène possède un groupe fonctionnel.
- 15
4. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 1, **caractérisé en ce que** le gabarit solide sacrificiel est de la glace.
- 20
5. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 1, **caractérisé en ce que** le gabarit solide sacrificiel est formé par le mélange d'une première substance et d'une seconde substance, la chaleur de sublimation de la première substance étant différente de la chaleur de sublimation de la seconde substance.
- 25
6. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 5, **caractérisé en ce qu'**une concentration de la première substance ou de la seconde substance distribuée dans le gabarit solide sacrificiel varie dans une direction particulière.
- 30
7. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 6, **caractérisé en ce que** la structure poreuse tridimensionnelle est formée intégralement.
- 35
8. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 6, **caractérisé en ce que** les pores de la structure poreuse tridimensionnelle ont un diamètre de pore qui augmente avec une concentration accrue de l'une de la première et de la deuxième substance qui a une pression de vapeur plus élevée.
- 40
9. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 1, **caractérisée en ce que** le gabarit solide sacrificiel comprend une pluralité de molécules cibles, et au cours du processus de sublimation du gabarit solide sacrificiel, les molécules cibles sont incorporées dans la structure poreuse tridimensionnelle.
- 45
10. Procédé de fabrication d'une structure poreuse tridimensionnelle selon la revendication 1, **caractérisée en ce que** les pores de la structure poreuse tridimensionnelle ont un diamètre de pore compris entre 21  $\mu\text{m}$  et 89  $\mu\text{m}$ .
- 50
- 55

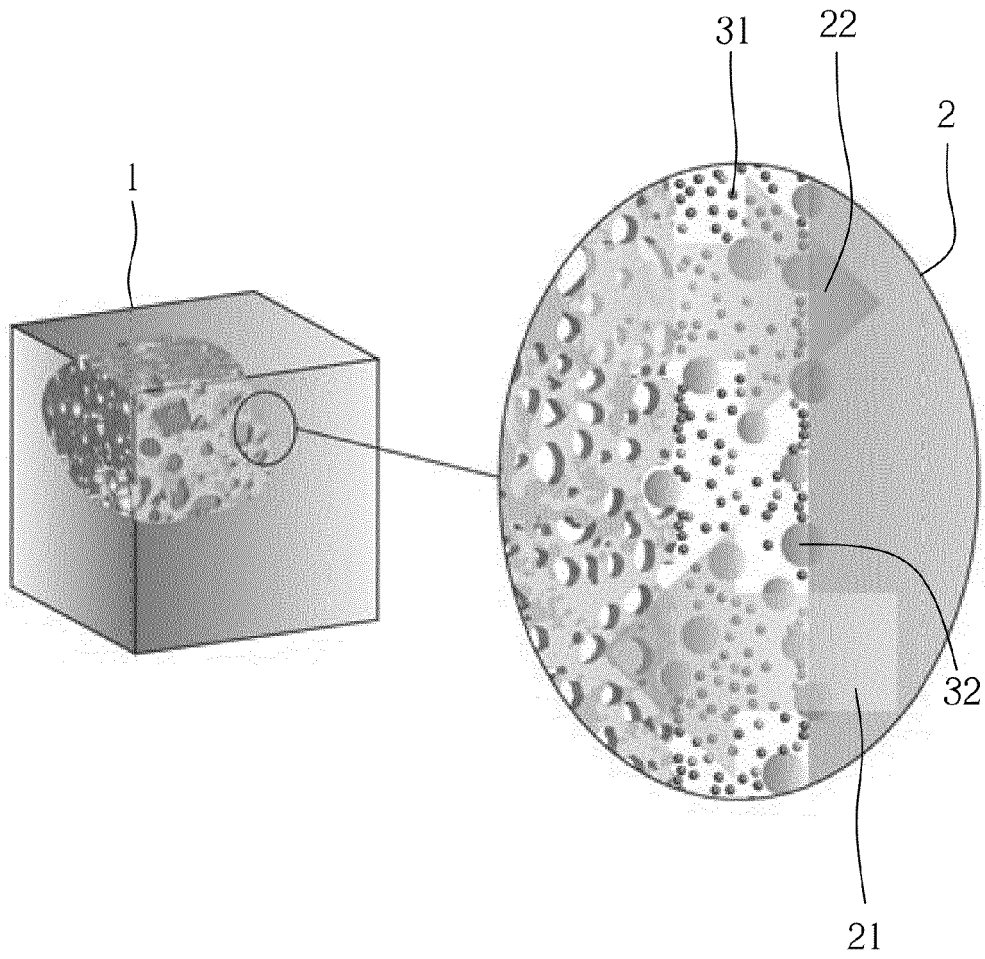


FIG. 1

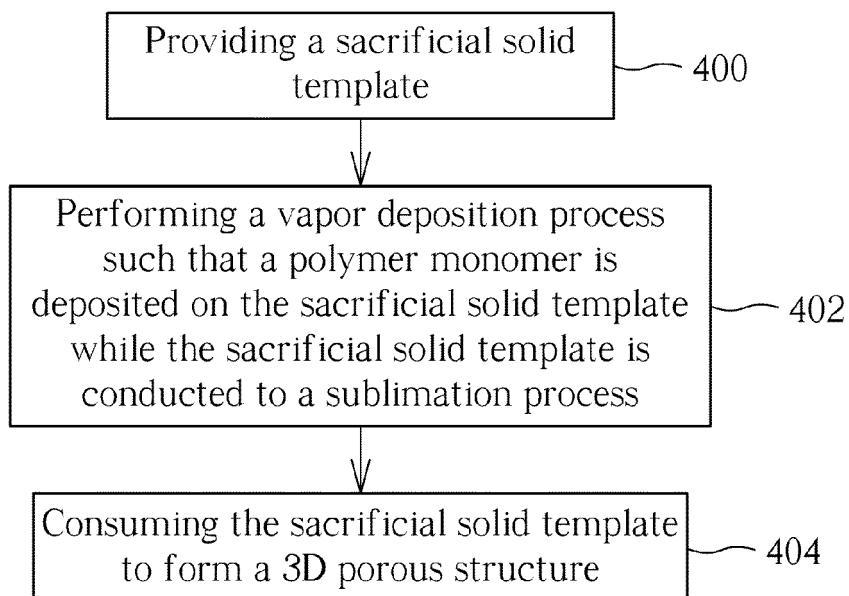


FIG. 2

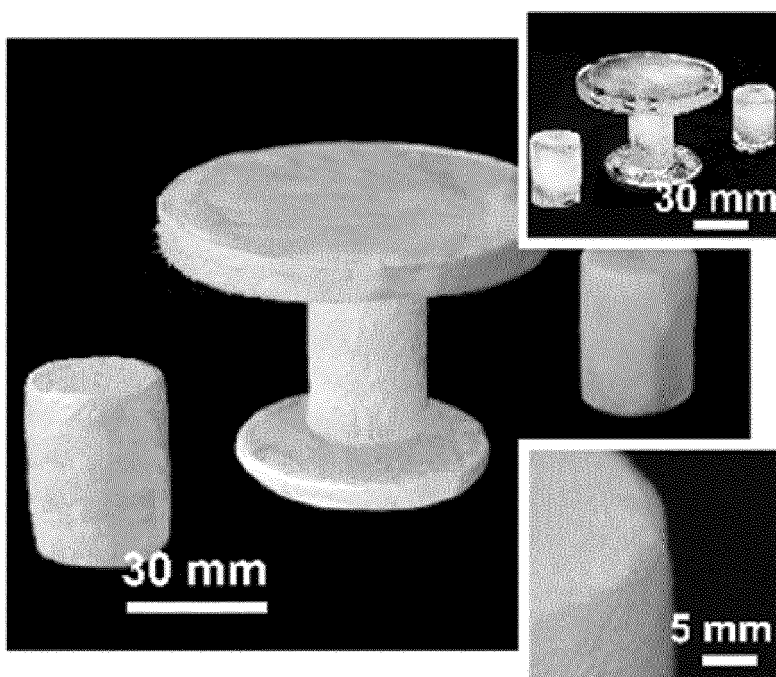


FIG. 3

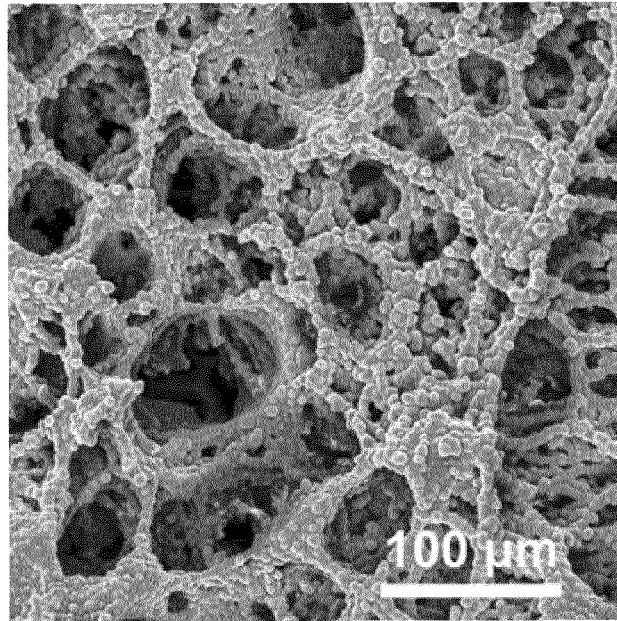


FIG. 4

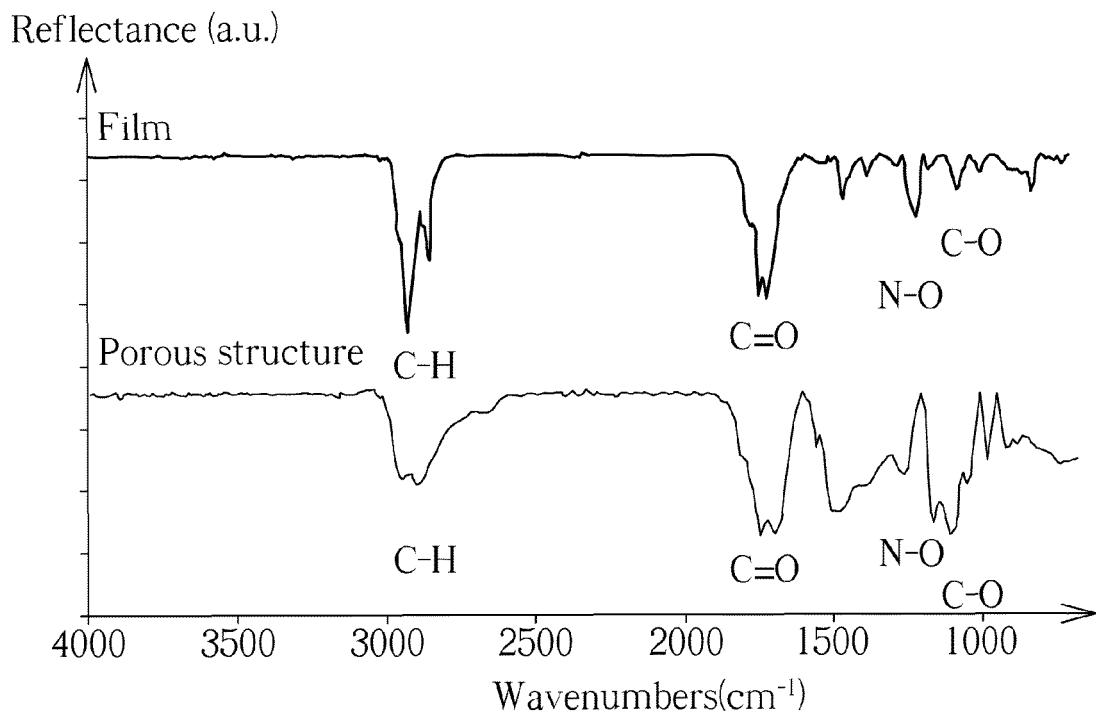


FIG. 5

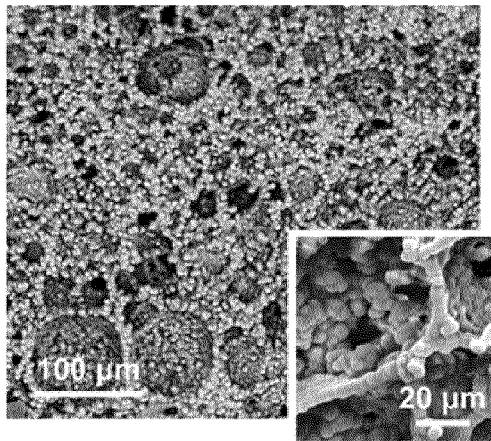


FIG. 6

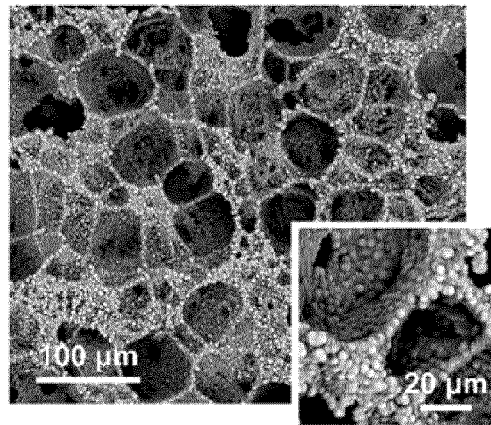


FIG. 7

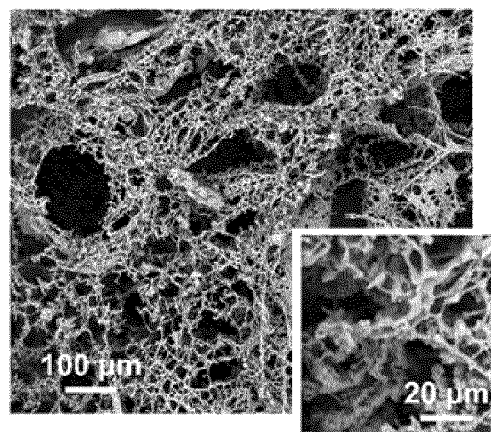


FIG. 8



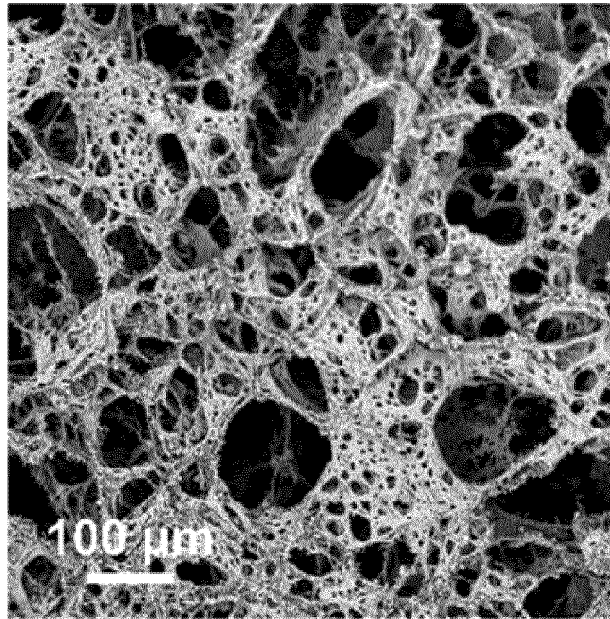


FIG. 9

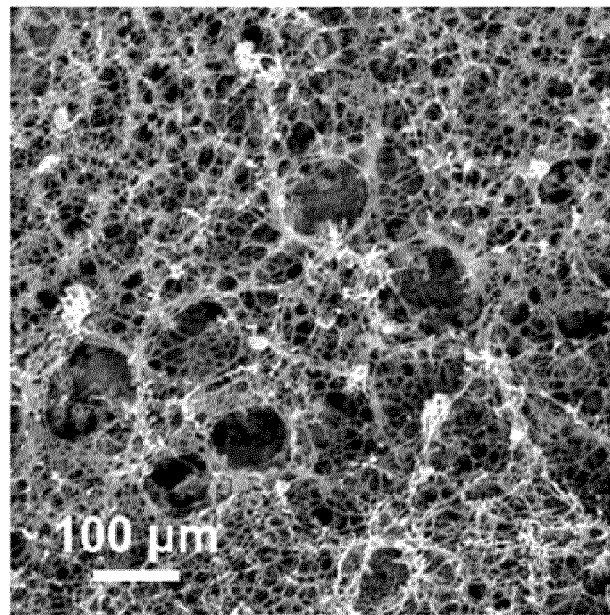


FIG. 10

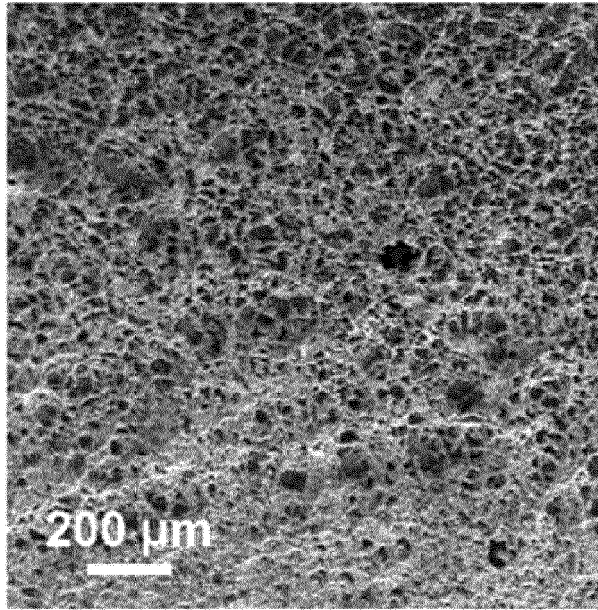


FIG. 11

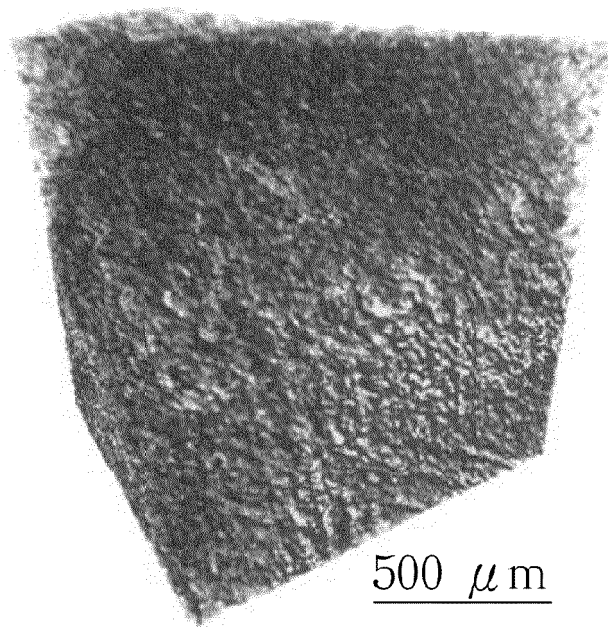


FIG. 12

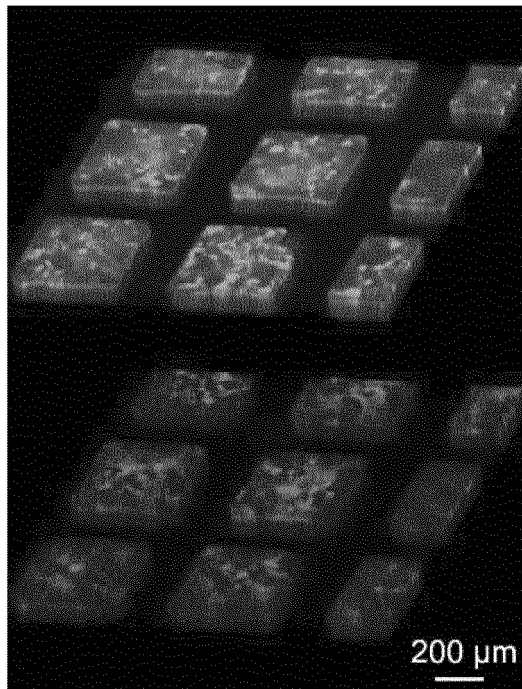


FIG. 13

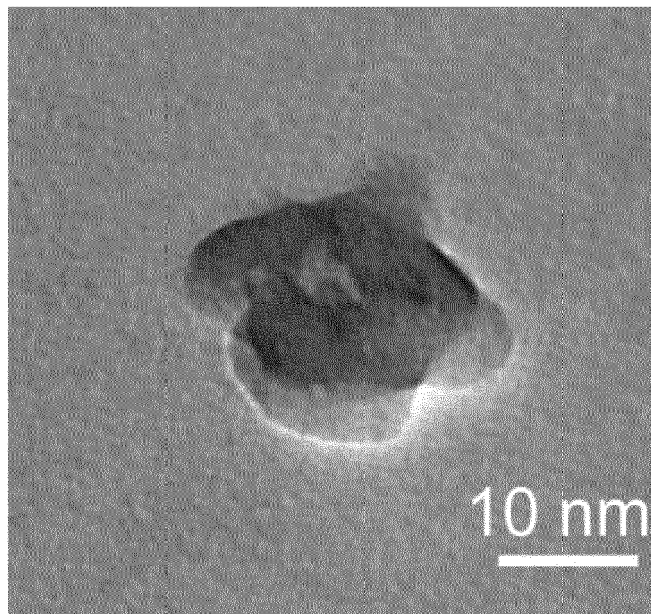
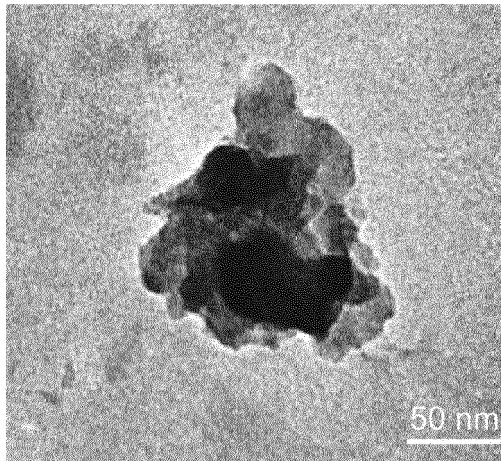
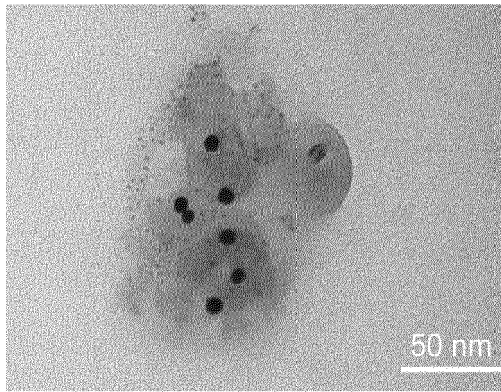


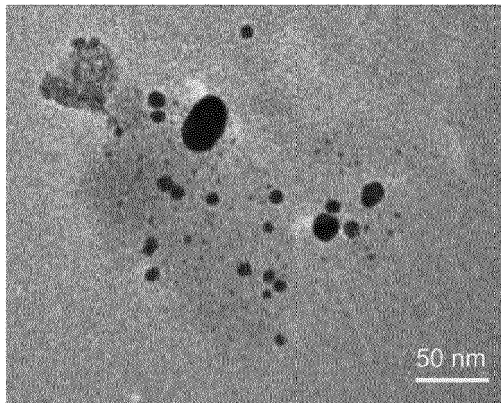
FIG. 14



$\text{Fe}_3\text{O}_4$



Au



Ag

FIG. 15

**REFERENCES CITED IN THE DESCRIPTION**

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