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(54) Title: THREE-DIMENSIONAL HIERARCHICAL POROUS CARBON FOAMS FOR SUPERCAPACITORS

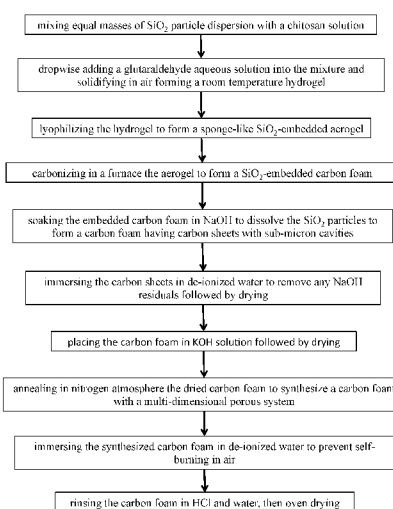


FIG. 5

(57) Abstract: A method of fabricating porous carbon foam includes mixing equal masses of SiO<sub>2</sub> particle dispersion with a chitosan solution, dropwise adding a glutaraldehyde aqueous solution into the mixture and solidifying it in air forming a room temperature hydrogel, lyophilizing the hydrogel to form a sponge-like SiO<sub>2</sub>-embedded aerogel, carbonizing in a furnace the aerogel to form a SiO<sub>2</sub>-embedded carbon foam, soaking the embedded carbon foam in NaOH to dissolve the SiO<sub>2</sub> particles to form a carbon foam having carbon sheets with sub-micron cavities, immersing the carbon sheets in de-ionized water to remove any NaOH residuals followed by drying, placing the carbon foam in KOH solution followed by drying, annealing in nitrogen atmosphere the dried carbon foam to synthesize a carbon foam with a multi-dimensional porous system, immersing the synthesized carbon foam in de-ionized water to prevent self-burning in air, and rinsing the carbon foam in HCl and water, then oven drying.



# THREE-DIMENSIONAL HIERARCHICAL POROUS CARBON FOAMS FOR SUPERCAPACITORS

## FIELD OF THE INVENTION

5 The present invention relates generally to chitosan derived carbon material. More particularly, the invention relates to a combination of template method and chemical activation to synthesize chitosan derived carbon foams with hierarchical porous structure and surface area of nearly 3000 m<sup>2</sup>/g.

## BACKGROUND OF THE INVENTION

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Enhancing charge storage capacity at ultrafast charging and discharging rates for electrical storage is an important topic of contemporary scientific research. High-capacity and low-cost energy storage systems are needed for technologies that include consumer electronics, and supercapacitors. The shortcomings of lithium-ion storage technologies include high  
15 costs and limited power density that restrict their applications.

What is needed is a three-dimensional hierarchical porous carbon foam that can maintain substantially higher capacitance at ultrafast charge and discharge rates than other conventional carbon materials that are used as supercapacitor electrodes.

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## SUMMARY OF THE INVENTION

To address the needs in the art, a method of fabricating chitosan-derived porous carbon foam is provided that includes mixing a SiO<sub>2</sub> particle dispersion with a chitosan solution, where the mass of the SiO<sub>2</sub> particle dispersion is equal to the mass of the chitosan polymer, dropwise adding a glutaraldehyde aqueous solution into the mixture of SiO<sub>2</sub> particle dispersion and chitosan, solidifying in air, the glutaraldehyde aqueous solution and the mixture of SiO<sub>2</sub> particle dispersion and chitosan forming a room temperature hydrogel, lyophilizing the room temperature hydrogel to form a sponge-like SiO<sub>2</sub>-embedded aerogel, carbonizing in a furnace the sponge-like SiO<sub>2</sub>-embedded aerogel to form a SiO<sub>2</sub>-embedded carbon foam, soaking the SiO<sub>2</sub>-embedded carbon foam in sodium hydroxide (NaOH) to dissolve the SiO<sub>2</sub> particles to form a carbon foam having carbon sheets with sub-micron cavities, immersing the carbon foam having carbon sheets with sub-micron cavities in de-ionized water to remove any NaOH residuals followed by drying, placing the carbon foam in potassium hydroxide (KOH) solution followed by drying, annealing in nitrogen atmosphere the dried carbon foam to synthesize a carbon foam with a multi-dimensional porous system, immersing the annealed carbon foam with a multi-dimensional porous system in de-ionized water to prevent self-burning in air, and rinsing the carbon foam with a multi-dimensional porous system in hydrochloric acid (HCl) and water, then oven drying.

According to one aspect of the invention, the carbon foam with a multi-dimensional and hierarchical porous system has pore sizes in a range from sub-nm to tens of μm.

In a further aspect of the invention, the carbon foam with a multi-dimensional porous system has a Brunauer–Emmett–Teller surface area of 2905 m<sup>2</sup> g<sup>-1</sup>.

According to one aspect of the invention, the synthesis process of the carbon foam with a multi-dimensional porous system does not involve toxic hydrocarbons.

5 In yet another aspect of the invention, the SiO<sub>2</sub> particle dispersion is formed using tetraethyl orthosilicate.

### BRIEF DESCRIPTION OF THE DRAWINGS

**FIGs. 1A-1B** show SEM images of the morphology of the as-prepared PCF, where  
10 **(1A)** shows the three-dimensional interconnected network of carbon sheets and **(1B)** shows a single piece of porous carbon sheet, with macro-pores of diameter around 2 μm uniformly dispersed on the carbon sheet, according to one embodiment of the invention.

**FIGs. 2A-2B** shown pore size characterizations, where **(2A)** shows the nitrogen  
15 adsorption-desorption isotherm collected for PCF at the liquid nitrogen temperature (77 K), and **(2B)** show the pore size distribution curve derived from Barrett-Joyner-Halenda theory using the isotherm shown in **(2A)**, according to one embodiment of the invention.

**FIGs. 3A-3B** show the morphology of as-prepared carbon foams with multiscale  
20 pores (CF-MP), where **(3A)** show a three-dimensional interconnected network of carbon sheets and **(3B)** shows a single piece of porous carbon sheet, where uniformly distributed macro-pores with diameters

around 200 nm were created after removal of silica nanospheres, according to one embodiment of the invention.

**FIGs. 4A-4B** show pore size characterizations, where **(4A)** shows the nitrogen adsorption-desorption isotherm collected for CF-MP at the liquid nitrogen temperature (77 K), and **(4B)** shows the pore size distribution curve derived from Barrett-Joyner-Halenda theory using the isotherm shown in **(4A)**, where the curve shows the presence of micro-pores and meso-pores in CF-MP, according to one embodiment of the invention.

**FIG. 5** shows a flow diagram of the fabrication method for the ultrahigh surface area CF-MP, according to one embodiment of the invention.

## DETAILED DESCRIPTION

The current invention provides a method to synthesize three-dimensional hierarchical porous carbon foam (PFC) with inherent nitrogen-doping and extremely large surface area (2905 m<sup>2</sup> g<sup>-1</sup>, measured by Bruanauer-Emmett-Teller test). The hierarchical porous carbon foam electrode delivers an outstanding specific capacitance of ~240 F g<sup>-1</sup> at an ultrahigh current density of 500 A g<sup>-1</sup>.

In one embodiment, a combination of using a template method and a chemical modification to increase the surface area of chitosan derived carbon material is provided. The as-prepared carbon material achieves a remarkable surface area of ~3000 m<sup>2</sup> g<sup>-1</sup>, which is the highest value reported for chitosan derived carbon materials.

In another aspect of the invention, the carbon structure is implemented as an electrode for a supercapacitor device. According to one embodiment, the invention achieves outstanding specific capacitances at ultrafast charging rates (e.g., ~240 F/g at ultrahigh current density of 500 A/g). These values are significantly better than the values obtained from any other  
5 chitosan derived carbon electrodes under same measurement conditions. These values are also better than the values of most (if not all) of the carbon materials measured at ultrahigh charging rates.

The invention is capable of providing a high capacitance at ultrafast charging and  
10 discharging rates. The three-dimensional hierarchical porous foams can maintain substantially higher capacitance at ultrafast charge and discharge rates than other conventional carbon materials that are used as supercapacitor electrodes.

The current invention uses chitosan as the major starting material. Chitosan is the second  
15 most abundant natural bio-polymer that is readily available in shrimp shells. The availability and sustainability of chitosan can greatly reduce the material cost of supercapacitors.

In general, a method of fabricating chitosan-derived porous carbon foam is provided that  
20 includes mixing a SiO<sub>2</sub> particle dispersion with a chitosan solution, where the mass of the SiO<sub>2</sub> particle dispersion is equal to the mass of the chitosan polymer, dropwise adding a glutaraldehyde aqueous solution into the mixture of SiO<sub>2</sub> particle dispersion and chitosan, solidifying in air, the glutaraldehyde aqueous solution and the mixture of SiO<sub>2</sub> particle dispersion and chitosan forming a room temperature hydrogel, lyophilizing the room

temperature hydrogel to form a sponge-like SiO<sub>2</sub>-embedded aerogel, carbonizing in a furnace the sponge-like SiO<sub>2</sub>-embedded aerogel to form a SiO<sub>2</sub>-embedded carbon foam, soaking the SiO<sub>2</sub>-embedded carbon foam in sodium hydroxide (NaOH) to dissolve the SiO<sub>2</sub> particles to form a carbon foam having carbon sheets with sub-micron cavities,  
5 immersing the carbon foam having carbon sheets with sub-micron cavities in de-ionized water to remove any NaOH residuals followed by drying, placing the carbon foam in potassium hydroxide (KOH) solution followed by drying, annealing in nitrogen atmosphere the dried carbon foam to synthesize a carbon foam with a multi-dimensional porous system, immersing the annealed carbon foam with a multi-dimensional porous system in de-ionized  
10 water to prevent self-burning in air, and rinsing the carbon foam with a multi-dimensional porous system in hydrochloric acid (HCl) and water, then oven drying.

In one exemplary experiment, chemical constituents were used that include chitosan (M.W. 100,000~300,000), acetic acid (glacial, 99.9 wt%), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), and  
15 glutaraldehyde aqueous solution (50 wt%). All chemicals were used without further purification.

According to one exemplary fabrication process, 1 mL of 10 wt% K<sub>2</sub>CO<sub>3</sub> aqueous solution was slowly added into 20 mL of 1 wt% chitosan solution (with 1 wt% acetic acid as  
20 solvent) under vigorous stirring. Then, 240 μL of 25 wt% glutaraldehyde aqueous solution was added dropwise into the solution. After adding glutaraldehyde solution, the mixed solution was immediately transferred into a plastic container (*e.g.*, a petri dish). The solution slowly solidified in the air and formed the hydrogel. The as-formed hydrogel was exposed in air for 1 day to age and then was frozen in a freezer. The frozen K<sub>2</sub>CO<sub>3</sub>-

embedded chitosan hydrogel was freeze-dried for 48 h to form the chitosan aerogel. Pyrolysis of the aerogel was carried out in a home-built tube furnace in nitrogen atmosphere at 800 °C for 2 hours to obtain PCF. The PCF was washed with 0.1 M hydrochloric acid solution and de-ionized water to remove any soluble residuals.

5

The scanning electron microscopy (SEM) images or **FIGs. 1A-1B** reveal the PCF possesses a three-dimensional porous structure. Macro-pores of diameter around 2  $\mu\text{m}$  are uniformly dispersed on each carbon sheet.

10 The porous structure of PCF was characterized by a nitrogen adsorption and desorption experiment. As shown in **FIG. 2A**, PCF exhibits combined characteristics of type I and type IV isotherms. The steep increase of adsorbed nitrogen volume at low relative pressure ( $P/P_0 < 0.1$ ) indicates the dominance of micro-pores in PCF. The hysteresis observed at  $P/P_0 > 0.4$  proves the existence of meso-pores (**FIG. 2B**). The surface area and pore  
15 volumes of PCF are summarized in **Table 1**. It clearly shows the presence of micro-pores and meso-pores in PCF.

**Table 1.** Textural properties of PCF

Sample	BET Surface Area, $S$ ( $\text{m}^2/\text{g}$ )	Total Pore Volume, $V_{\text{total}}$ ( $\text{cm}^3/\text{g}$ )	Micro-pore Volume, $V_{\text{micro}}$ ( $\text{cm}^3/\text{g}$ )	Meso-pore Volume, $V_{\text{meso}}$ ( $\text{cm}^3/\text{g}$ )	Ratio of $V_{\text{micro}}$ to $V_{\text{meso}}$
PCF	1013.0	0.576	0.461	0.154	2.994

Turning now to the preparation of hierarchical porous carbon foams from glutaraldehyde-crosslinked chitosan aerogel with silica spheres, in another exemplary experiment, chemical constituents were used that include chitosan (M.W. 100,000~300,000), acetic acid (glacial, 99.9%), tetraethyl orthosilicate (TEOS), potassium hydroxide (KOH),  
5 hydrochloric acid (HCl), absolute ethanol, and glutaraldehyde aqueous solution (50 vol%). All chemicals were used without further purifications.

In this exemplary fabrication process, SiO<sub>2</sub> spheres were prepared using the modified Stöber method. First, 100 mL of absolute ethanol, 15 mL of de-ionized water, and 5 mL of  
10 ammonia aqueous solution (25 wt%) were mixed in a 250-mL round-bottom flask. The mixture was stirred at 500 rpm and heated to 40 °C in a water bath. Second, 6.0 g of TEOS was quickly added into the mixture and kept the temperature at 40 °C for 6 h to let TEOS react with ammonia. After the reaction, the solution turned from clear to white. The white  
precipitation (SiO<sub>2</sub> spheres) was collected by centrifugation and rinsed with denatured  
15 alcohol (95 vol%) three times followed by de-ionized water until the pH value reached 7. The cleaned precipitation was re-dispersed in 20 mL de-ionized water prior to use.

In the preparation of silica embedded carbon foam (CF-SiO<sub>2</sub>), SiO<sub>2</sub> particle dispersion was slowly added into 18 g of 1.2 wt% chitosan solution (with 1 wt% acetic acid as solvent)  
20 under vigorous magnetic stirring. The mass of added SiO<sub>2</sub> particles was equal to the mass of chitosan powder. Then, 216 µL of 50 wt% glutaraldehyde aqueous solution was added into the mixture dropwise. Subsequently, the mixture was poured into a container, *e.g.*, a petri dish. The solution was gradually solidified in air and formed hydrogel under room temperature. The as-formed hydrogel was aged at room temperature for one day and then

lyophilized to obtain the spongy SiO<sub>2</sub>-embedded aerogel. This aerogel was then pyrolyzed in a tube furnace at 800 °C for 2 hours in nitrogen atmosphere to obtain the CF-SiO<sub>2</sub>.

Turning now to the preparation of carbon foam with templated walls (CF-TW), a piece of  
5 CF-SiO<sub>2</sub> was soaked into 2 M sodium hydroxide (NaOH) aqueous solution at 90 °C for 10 hours to completely dissolve the SiO<sub>2</sub> particles. The obtained CF-TW was immersed in de-ionized water overnight to remove any NaOH residuals followed by drying in an electric oven at 80 °C for 2 h.

10 For the preparation of carbon foam with multi-dimensional porous system (CF-MP), the aforementioned CF-TW was further reacted with potassium hydroxide (KOH) to create micro-pores. First, the CF-TW was put in 1.0 M KOH solution for 8 h and then dried in an electric oven at 80 °C for 2 hours. Second, the dried carbon foam was annealed in a tube furnace at 800 °C in nitrogen atmosphere for 1 hour to synthesize the CF-MP. After the  
15 annealing, the sample was quickly slid into a beaker of de-ionized water to prevent self-burning in the air. Finally, the obtained CF-MP was rinsed by 0.5 M HCl and ample amount of water to pH~7 and dried in the oven at 80 °C for 2 h.

For the characterization of the CF-MP, **FIGs. 3A-3B** show the morphology of as-prepared  
20 CF-MP. In **FIG. 3A**, the three-dimensional interconnected network of carbon sheets is shown, and in **FIG. 3B**, a single piece of porous carbon sheet is shown. Here, uniformly distributed pores with diameters around 200 nm were created after removal of silica nanospheres.

**FIG. 4A** shows the nitrogen adsorption-desorption isotherms of CF-MP. CF-MP exhibits combined characteristics of type I and type IV isotherms with steep increase of absorbed N<sub>2</sub> at low relative pressure ( $P/P_0 < 0.1$ ) and slightly steep adsorption at  $P/P_0 > 0.8$ , indicating the co-existence of micro-, meso-, and macropores. The textural properties of CF-MP are summarized in **Table 2**. The CF-MP has ultrahigh surface area of 2905.6 m<sup>2</sup>/g, much higher than conventional materials.

**FIG. 5** shows a flow diagram of the fabrication method for the ultrahigh surface area CF-MP, according to one embodiment of the invention.

**Table 2.** Textural properties of CF-MP

Sample	BET surface area, $S$ (m <sup>2</sup> ·g)	Total pore volume, $V_{total}^a$ (cm <sup>3</sup> ·g)	Micropore volume, $V_{micro}^b$ (cm <sup>3</sup> ·g)	$V_{non-micro}^c$ (cm <sup>3</sup> ·g)	Ratio of $V_{micro}$ to $V_{non-micro}$
CF-MP	2905.6	4.08	0.930	3.407	0.273

The present invention has now been described in accordance with several exemplary embodiments, which are intended to be illustrative in all aspects, rather than restrictive. Thus, the present invention is capable of many variations in detailed implementation, which may be derived from the description contained herein by a person of ordinary skill in the art. For example, developing 3D printed hierarchical porous carbon foam electrodes for supercapacitors and other devices, including batteries, catalysts and fuel cells.

All such variations are considered to be within the scope and spirit of the present invention as defined by the following claims and their legal equivalents.

## CLAIMS

What is claimed:

- 1) A method of fabricating chitosan-derived porous carbon foam, comprising;
  - a) mixing a SiO<sub>2</sub> particle dispersion with a chitosan solution, wherein the mass of  
5 said SiO<sub>2</sub> particle dispersion is equal to the mass of said chitosan solution;
  - b) dropwise adding a glutaraldehyde aqueous solution into said mixture of SiO<sub>2</sub>  
particle dispersion and chitosan;
  - c) solidifying in air, said glutaraldehyde aqueous solution and said mixture of SiO<sub>2</sub>  
particle dispersion and chitosan forming a room temperature hydrogel;
  - 10 d) lyophilizing said room temperature hydrogel to form a sponge-like SiO<sub>2</sub>-  
embedded aerogel;
  - e) carbonizing in a furnace said sponge-like SiO<sub>2</sub>-embedded aerogel to form a  
SiO<sub>2</sub>-embedded carbon foam;
  - f) soaking said SiO<sub>2</sub>-embedded carbon foam in sodium hydroxide (NaOH) to  
15 dissolve said SiO<sub>2</sub> particles to form a carbon foam comprising carbon sheets  
with sub-micron cavities;
  - g) immersing said carbon foam comprising carbon sheets with sub-micron cavities  
in de-ionized water to remove any NaOH residuals followed by drying;
  - h) placing said carbon foam in potassium hydroxide (KOH) solution followed by  
20 drying;
  - i) annealing in nitrogen atmosphere said dried carbon foam to synthesize a carbon  
foam with a multi-dimensional porous system;
  - j) immersing said annealed carbon foam with a multi-dimensional porous system  
in de-ionized water to prevent self-burning in air; and

k) rinsing said carbon foam with a multi-dimensional porous system in hydrochloric acid (HCl) and water, then oven drying.

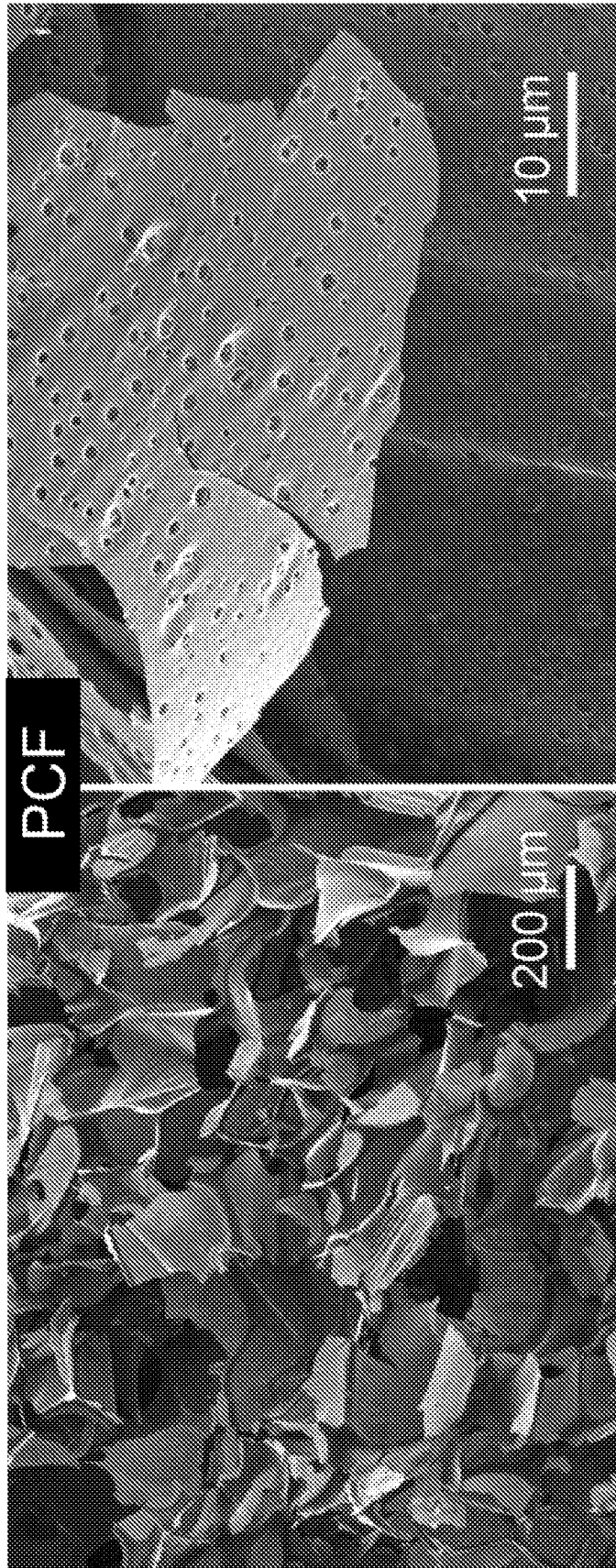
5 2) The method of fabricating chitosan-derived porous carbon foam of claim 1, wherein said carbon foam with a multi-dimensional porous system comprises pore sizes in a range from sub-nm to tens of  $\mu\text{m}$ .

10 3) The method of fabricating chitosan-derived porous carbon foam of claim 1, wherein said carbon foam with a multi-dimensional porous system has a Brunauer–Emmett–Teller surface area of  $2905 \text{ m}^2 \text{ g}^{-1}$ .

4) The method of fabricating chitosan-derived porous carbon foam of claim 1, wherein said carbon foam with a multi-dimensional porous system does not involve toxic hydrocarbons.

15

5) The method of fabricating chitosan-derived porous carbon foam of claim 1, wherein said  $\text{SiO}_2$  particle dispersion is formed using tetraethyl orthosilicate.



**FIG. 1B**

**FIG. 1A**

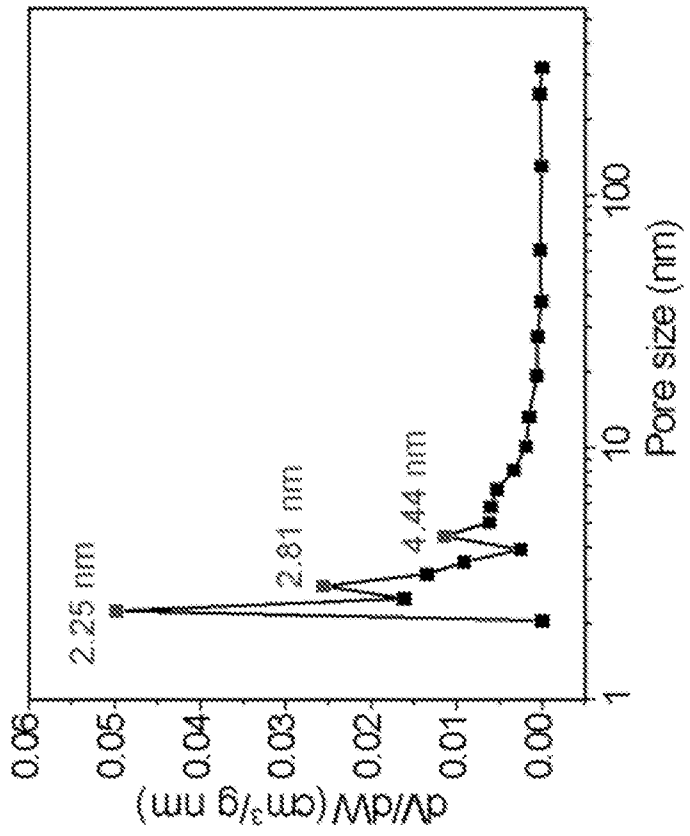


FIG. 2B

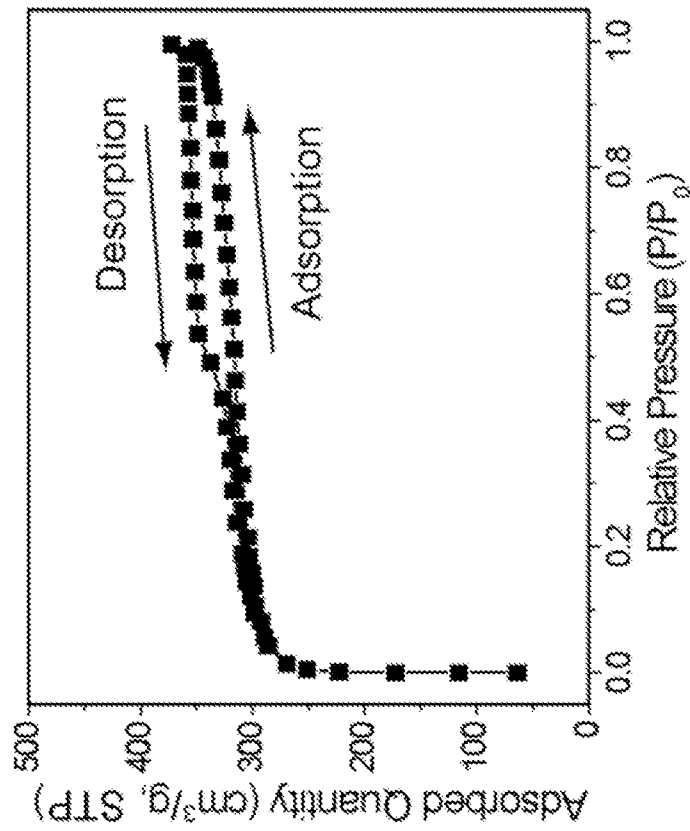
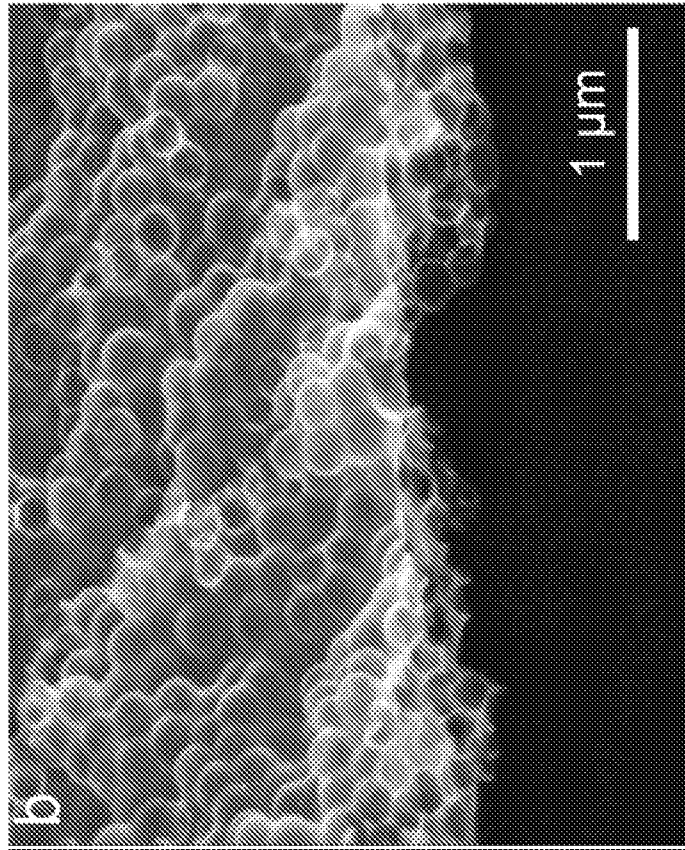
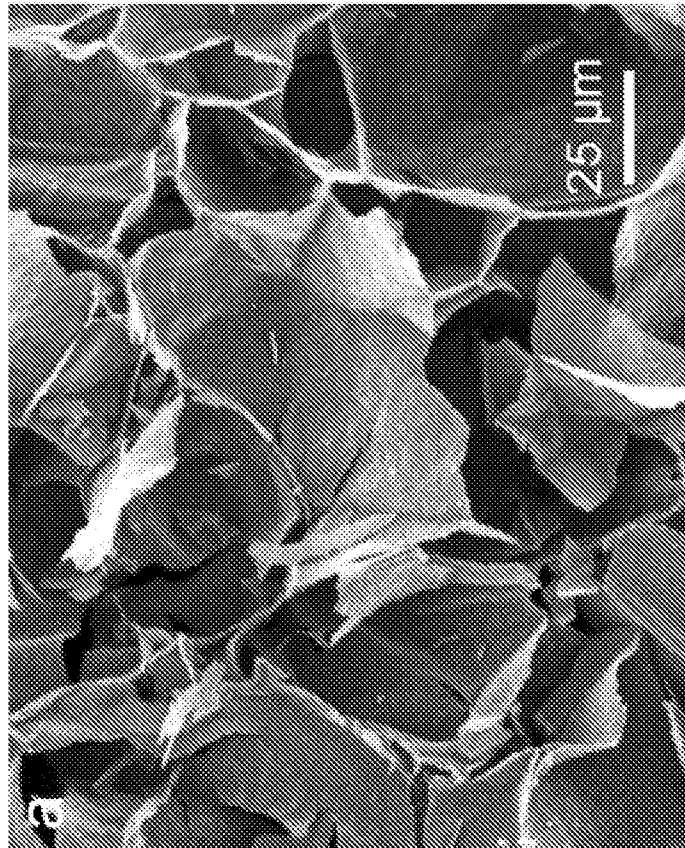


FIG. 2A



**FIG. 3B**



**FIG. 3A**

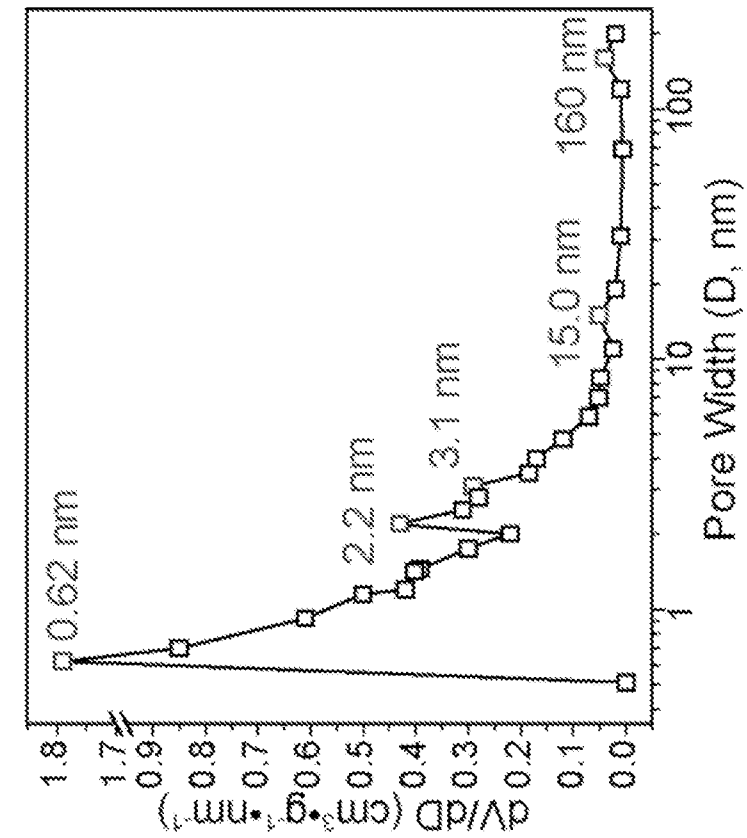


FIG. 4B

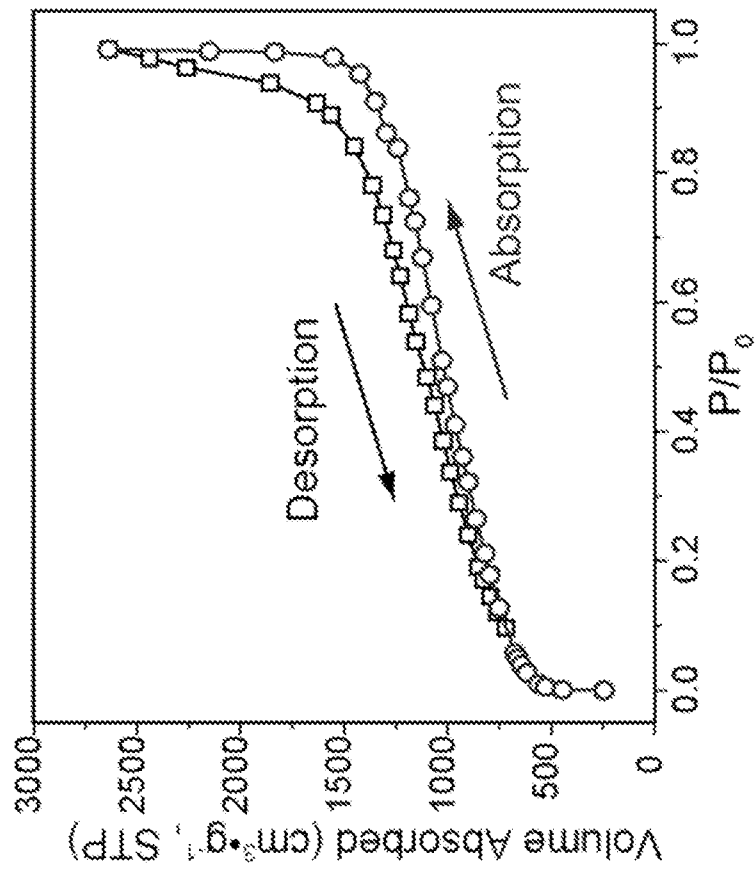
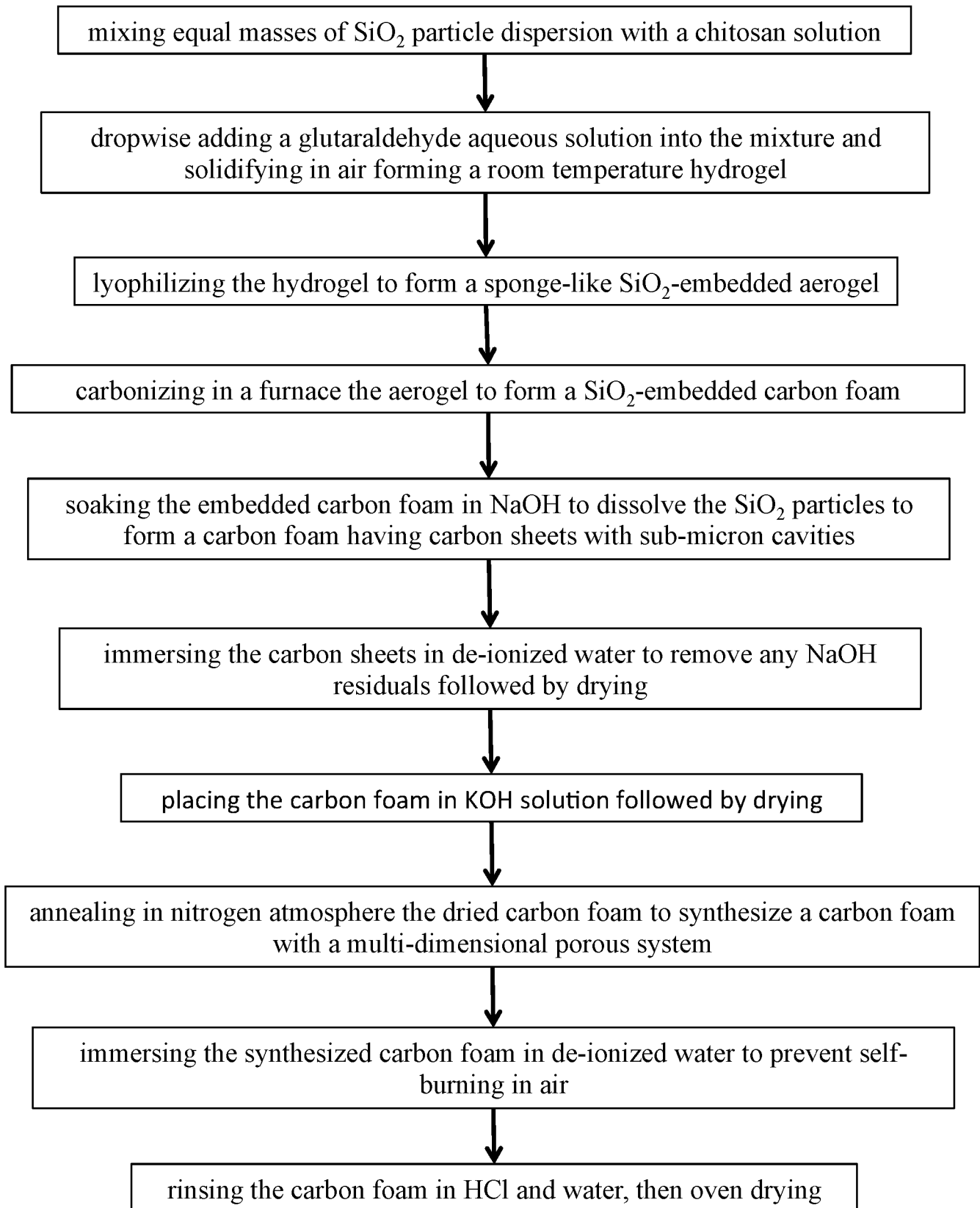


FIG. 4A

## Sheet 5 of 5

**FIG. 5**

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/22491

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(8) - C01B 31/00, C01B 31/02 (2017.01) CPC - C01B 31/0293, C01P 2006/12, C01P 2006/14, C01B 31/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) See Search History Document		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched See Search History Document		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) See Search History Document		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 1995001165 A1 (Nycomed Imaging) 13 January 1995 (13.01.1995) Entire document especially, pg 3, ln 32-34 and pg 27 ln 32 to pg 28, ln 3	1-5
A	US 4,873,218 A1 (Pekala) 10 October 1989 (10.10.1989) Entire document especially col 2, ln 40-43 and col 4, ln 34-53.	1-5
A	US 6,960,617 B2 (Omidian et al) 01 November 2005 (01.11.2005). Entire document, especially col 17, ln 31-36.	1-5
A	US 2009/0029147 A1 (Tang et al) 29 January 2009 (29.01.2009) Entire document, especially para 0036] and [0088].	1-5
A	US 4,263,268 A (Knox et al.) 21 April 1981 (21.04.1981) Entire document, especially col 2, ln 32-39 and col 4, ln 31-3.	1-5
A	US 2014/0134238 A1 (Reed et al.) 15 May 2014 (15.05.2014) Entire document, especially para [0084], [0138] and [0145].	1-5
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 08 May 2017		Date of mailing of the international search report <b>05 JUN 2017</b>
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300		Authorized officer: Lee W. Young  PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774